COAL SURFACE STRUCTURE AND THERMODYNAMICS

By
John W. Larsen
Patrick C. Wernett
Amy S. Glass
Deanne Quay
James Roberts

May 1994

Work Performed Under Contract No. AC22-89PC89757

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Lehigh University
Bethlehem, Pennsylvania

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the U.S. Department of Commerce, Technology Administration, National Technical Information Service, Springfield, VA 22161, (703) 487-4650.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DE-AC22-89PC89757

COAL SURFACE STRUCTURE AND THERMODYNAMICS

John W. Larsen, Patrick C. Wernett, Amy S. Glass
Deanne Quay, James Roberts

May 1994

Lehigh University
Department of Chemistry
6 E. Packer Avenue
Bethlehem, Pennsylvania 18015

Final Report prepared for the United States Department of Energy
Under Contract No. DE-AC22-89PC89757

Final

C. M. Bao

Back-up
6/1/94

EXECUTIVE SUMMARY

Molecules first encounter the coal surface. They are adsorbed and may proceed to diffuse into the solid coal. The rates of many coal reactions are limited by the diffusion of the reagent into the coal. To understand coal reactivity, it is necessary to understand the coal surface; how large it is and its structure. Because coals are porous, much of the surface may not be accessible to all molecules. Understanding coal reactivity is one reason for studying the surface of coals.

Another reason is coal cleaning processes. The separation of organic coal from mineral matter depends significantly on the different surface interactions of the materials. To understand and to optimize these processes, a basic understanding of the structure and interactions of coal and mineral matter surfaces is necessary.

For these reasons, we undertook a systematic fundamental investigation of coal surfaces. Using low angle X-ray scattering, we showed that the surfaces of Argonne Premium Coals were fractal. By comparing these surface areas with those measured by static hydrocarbon adsorptions (BET), it became clear that the hydrocarbons were diffusing into solid coal in order to reach the pore surfaces. Coals do not possess interconnected pore networks, but have isolated pores reachable only by diffusion through the bulk solid. This is a new structural model for coal pores. This model is confirmed by the absence of any discontinuous size effects of small molecule adsorption thermodynamics measured by inverse gas chromatography (IGC).

Inverse gas chromatography was developed as a means for measuring adsorption heats on coals. It is capable of discriminating between the adsorption on and the diffusion into the coal which immediately follows adsorption. The interactions of non-polar molecules are, as expected, directly proportional to their molecular polarizabilities. They are not specific. The interactions of bases with coal surfaces is simple. The enthalpy of interaction is the sum of the polarizability interaction and the heat of hydrogen bonding to phenol. Amphoteric molecules have more complex interactions.

This work has produced a new structure model for coal pores and surfaces together with a new method for measuring adsorption thermodynamics on coal surfaces. Data obtained include the fractal dimensionality of these surfaces of all of the Argonne Premium coals, the largest existing set of adsorption enthalpies on coals, and a large set of diffusion rates.

ABSTRACT

Coals surfaces were studied using static surface adsorption measurements, low angle X-ray scattering (LAXS), inverse gas chromatography (IGC) and a new ^{13}C NMR relaxation technique.

A comparison of surface areas determined by hydrocarbon gas adsorption and LAXS led to the twin conclusions that the hydrocarbons had to diffuse through the solid to reach isolated pores and that the coal pores do not form interconnected networks, but are largely isolated. This conclusion was confirmed when IGC data for small hydrocarbons showed no discontinuities in their size dependence as usually observed with porous solids. IGC is capable of providing adsorption thermodynamics of gases on coal surfaces. The interactions of non-polar molecules and coal surfaces are directly proportioned to the gas molecular polarizability. For bases, the adsorption enthalpy is equal to the polarizability interaction plus the heat of hydrogen bond formation with phenol. Amphoteric molecules have more complex interactions. Mineral matter can have highly specific effects on surface interactions, but with most of the molecules studied is not an important factor.

INTRODUCTION

This extensive investigation into the structure and thermodynamics of coal surfaces was carried out by five individuals and the DOE supported work was supplemented by collaborative studies carried out at the Exxon beam port on the Brookhaven synchrotron. Three fundamentally different approaches were used: static adsorption and diffusion measurements, inverse gas chromatography (IGC), and surface NMR. Because the techniques are so different, this report has been divided into three sections, each capable of standing independently.

The first section contains the work of Dr. Patrick Wernett. It is a study of the static adsorption of hydrocarbons on coal surfaces and of their diffusion into coals. It is supplemented by low angle X-ray scattering (LAXS) measurements carried out at Brookhaven by Dr. Peter Hall and Dr. Wernett and by ^{129}Xe NMR studies of coal micropores. The principal conclusions of this work is that coals do not contain an interconnected pore network, but that the pores are largely isolated from each other and reachable only by diffusion through the solid. This conclusion was confirmed by the IGC measurements which provided no evidence for diffusion into a pore network. IGC has been developed into a convenient tool for measuring adsorption thermodynamics on coals. Not surprisingly, adsorption enthalpies of non-polar molecules on coals correlate with their molecular polarizability. For organic bases, their interactions are exactly the sum of polarizability interactions and the heat of hydrogen bonding to an isolated phenolic hydroxyl. The adsorption thermodynamics of amphoteric

compounds is not easily dissected into components.

The last section describes our attempts to develop an NMR technique for determining the surface structure of coals. It involved depositing a relaxation agent on the coal surface and obtaining by spectral subtraction that part of the ^{13}C NMR spectrum which disappears due to the nearby presence of the relaxation agent. This work is still in progress and we believe the technique will work. This work was carried out by Deanna Quay and Professor Jim Roberts.

Back-up
Blank

PART 1

Surface Adsorption and Diffusion Studies

Book 1/2
2/2/2

I. Macromolecular Structure of Coals

A. Macroscopic Coal Composition

Coals are highly complex amorphous solids consisting of organic and inorganic components. The organic phase of coals is a mixture of three groups of optically homogeneous organic materials called macerals. These coal macerals groups are Vitrinites, Liptinites, and Inertinites. Macerals in coals are analogous to minerals in rocks. Vitrinite macerals are derived from coalified woody and cortical tissues. Liptinites are derived from resinous and waxy plant materials. Inertinites are believed to be charred remains of plant tissues.^{1,2} Common coal maceral types are listed in Table 1. The major maceral component of bituminous coals are Vitrinites, typically 70-80% of the coal.²

The major inorganic component of coals is mineral matter which is mostly a combination of quartz, pyrite, and calcite with minor amounts of gypsum and analcime.³ Ash is the altered solid mineral matter remaining after complete coal combustion. The major ash components in coals are

Maceral Group	Coal Maceral	Maceral Description
Vitrinite	Telinite	Optically observable cellular structure
	Collinite	No optically observable cellular structure
Liptinites	Sporinite	Fossil remains of spore and pollen walls
	Cutinite	Cuticles of leaves and plant stems
	Resinite	Fossil remains of plant resins and waxes
	Alginite	Remains of algal colonies
	Subernite	Cork cell walls
Inertinites	Fusinite	Carbonified plant cell walls retaining cellular structure
	Micronite	Structureless remains of highly decayed plant materials

Table 1. Organic Maceral Components of Coals^{1,2}

Al_2O_3 , SiO_2 , and Fe_2O_3 .

B. Structural Model of a Bituminous Coal

A number of individuals have composed structural models for bituminous coals.⁴⁻⁸ A comparison of them is beyond the scope of this thesis. The most recent, and preferred, model will be described and used throughout this thesis. All of the generally accepted models are more similar than different.

Shin has constructed a model of a vitrinite-rich bituminous coal to describe its liquefaction behavior (Figure 1).⁸ No single coal model exists that can accurately describe coal reactivity under all experimental conditions. Despite this, coal models are useful depictions of the functional groups present and the types of associative forces holding coals together.

Shin based his coal structure model on the distribution of aromatic and aliphatic groups obtained from ^1H and ^{13}C NMR spectroscopy and H/C ratios from elemental analysis. The distribution of oxygen functional groups was determined from reactivity studies conducted by Liotta⁹, Cronauer¹⁰, and Blom¹¹. Organo-sulfur and nitrogen distributions were determined from products of

Figure 1. Structural Model of a Vitrinite-Rich Bituminous Coal.⁸

mild coal liquefaction reactions.¹²

Shin's coal model is by no means a quantitative structural model for these types of bituminous coals. The identity of the aliphatic groups linking the various aromatic groups was based on coal reactivity studies under liquefaction conditions. Coal-coal intermolecular rearrangements are expected to occur under liquefaction conditions.⁸ For this reason these aliphatic links may not accurately represent the arrangement of aromatic and hydroaromatic groups in unreacted coals.

In spite of its problems, Shin's structural model for a vitrinite-rich bituminous coal is useful to demonstrate the arrangement of aromatic and polynuclear aromatic (PNA) functionalities in coals.

C. Macromolecular Structure of Coals

Van Krevelen was the first to suggest that coals are best described as three-dimensional cross-linked macromolecules, although he never used the term "macromolecule" to describe coal. Van Krevelen suggested coal is polymeric based on the following set of observations. Similar to cross-linked polymers, coals swell when exposed to most organic solvents rather than

dissolve. Certain solvents are capable of extracting some soluble material from coals but are incapable of causing complete coal dissolution. Infrared analysis from solvolysis studies show that coal residues and extracts are similar to each other and the untreated coals. Hydrogenolysis of coals increase the amount of extractable material from coals and these extracts have the same chemical character and distribution of functional groups as the extracts from untreated coals. IR analysis show similarities between coals subjected to high vacuum pyrolysis and untreated coals. Van Krevelen concludes from these observations that coals behave like large molecules being cleaved. Based on these studies, van Krevelen stated:

"... It may be concluded that there are many indications suggesting that coal has a polymeric structure; although none of these indications furnishes sufficient evidence by itself, their combination may be taken as conclusive."¹

Further evidence supporting the polymeric nature of coals is that coals are viscoelastic.¹³ Coals deform when subjected to a stress, having a viscosity that approaches Bakelite (a cross-linked polymer once used to make billiard balls). Molecules which are not covalently cross-linked will flow when subjected to a prolonged stress. This

deformation is permanent when the stress is removed. Coal's ability to return to its original dimensions after a stress causing deformation is removed is typical of a cross-linked macromolecular solid.

In summary, an overwhelming amount of evidence supports a three-dimensionally cross-linked structure of coals. A macromolecular structure for coals is based on coal's behavior under a wide variety of different experimental conditions.

D. The Coalification Process

The term "rank" is used to describe the degree of metamorphism a coal has undergone. Coals begin as lignites and end as anthracites. This process is known as coalification.² Coal rank may be based on the fixed carbon content and caloric value of the coal. Van Krevelen described the coalification process as a three-dimensional poly-condensation reaction of coal "monomers" to give a cross-linked macromolecular structure.¹ Larsen *et al.* have shown this view of the coalification process to be incorrect.¹⁴ Larsen determined molecular weight distributions of pyridine extracts from six coals ranging from 82.5% C to 90.7% C (dry mineral matter free basis

(dmmf)) obtained from the Pennsylvania State University Coal Bank (PSOC). The molecular weight distributions of the coal-pyridine extracts were determined using a gel permeation chromatograph equipped with a mass sensitive detector and also by vapor pressure osmometry. If the coalification process is a condensation polymerization reaction, the extractable material from coals would consist of monomer units not yet incorporated into the insoluble macromolecular coal structure. The concentration of pyridine soluble monomers should decrease as the molecular weight of the monomers increases. Larsen observed the exact opposite behavior. Larsen suggested that coalification is a depolymerization process. The extractable coal portion consists of macromolecular degradation products and macromolecules not yet incorporated into the insoluble coal structure.

X-ray scattering studies by Hirsch suggest that coals consist of small aromatic and heteroaromatic clusters.¹⁵ Cluster refers to aromatic and polynuclear aromatic systems cross-linked by attractive forces ranging from London dispersion forces to chemical bonds. NMR spectroscopy¹⁶, X-ray diffraction techniques¹⁷, and FT-IR spectroscopy¹⁸ confirm that, as coals metamorphosize to higher ranks, aromaticity in coals generally increases while oxygen

concentration decreases. Pugmire determined aromatic and aliphatic carbon distributions in coals as a function of rank using cross-polarization magic angle spinning (CP/MAS) NMR spectroscopy (see Figure 2).¹⁶ Although aromaticity generally increases with coal rank, the size of the polynuclear aromatic (PNA) clusters of the coals examined in this study remains almost constant for coals 76.0% C to 85.5% C (dmmf basis) as shown in Figure 3.

E. Coals as Glassy Materials

Brenner characterized the physical state of vitrinite thin sections from an Illinois No. 6 coal by transmission optical microscopy.¹⁹ The coal thin sections examined were either untreated, pyridine swollen, or chemically derivatized by methylation of the hydroxyl groups in the coal. Each coal thin section was examined under two orthogonally oriented polarized light sources. If the arrangement of molecules in the sample is totally random, the sample is said to be isotropic. Polarized light at orthogonal angles will have the same velocity through an isotropic material and the sample will appear totally black. If the molecules in a sample are not randomly oriented, the material is anisotropic and a birefringence

Argonne Coal	%C ^a
North Dakota (Beulah Zap) lignite	74.1
Wyodak-Anderson	76.0
Blind Canyon	81.3
Illinois No. 6	80.7
Pittsburgh No. 8	85.0
Stockton (Lewiston-Stockton)	85.5
Upper Freeport	88.1
Pocahontas No. 3	91.8

a. %C on a dry mineral matter free basis (dmmf).

Figure 2. Aromatic and Aliphatic Carbon Distribution of the Argonne Coals Determined by CP/MAS NMR Spectroscopy.¹⁶

Figure 3. Average Number of Aromatic Carbons Per Cluster of the Argonne Coals Determined by CP/MAS NMR Spectroscopy.¹⁶

pattern will be observed. Birefringence is the difference in the refractive index of a sample between the two orthogonal directions of the polarized light. Two perpendicularly oriented polarized light sources entering an anisotropic material in phase will leave the sample out of phase. An anisotropic material will not appear totally black and the transmitted light pattern can be viewed optically.

Brenner observed a birefringence pattern from the untreated Illinois No. 6 coal thin section. The refractive index of polarized light was found to be greater perpendicular than parallel to the bedding plane of the untreated coal (termed negative axial anisotropy).²⁰ The bedding plane is an orientational reference for coals which is the direction normal to the gravitational force during coalification. When pressure was applied to the untreated thin section, the axial anisotropy gradually changed to a radial birefringence pattern. The radial birefringence was identified by rotating the coal thin section parallel to the direction of both polarized light sources. The birefringence pattern appeared to remain fixed in space during rotation of the sample. This is characteristic of radial symmetry perpendicular to the direction of polarized light. The radial anisotropy remains even after the stress

is removed. The retention of the stress-induced anisotropy indicates that the untreated coal is a plastic at room temperature. Plastic materials retain a permanent deformation when stressed, unlike rubbery materials which rapidly recover their original conformation when a stress causing deformation is removed.

An untreated coal thin section was exposed to a few drops of pyridine at room temperature. Pyridine is a good hydrogen bond acceptor capable of breaking most if not all coal-coal hydrogen bonds.^{21,22} Within a few minutes, the coal sample appeared completely black under the cross polarizers indicating the coal sample was isotropic. When pressure was exerted on the pyridine swollen thin section, a radial birefringence pattern was induced. When the pressure was removed from the pyridine swollen sample, the thin section again appeared black, indicating relaxation of the induced optical anisotropy. The ability of the thin section of the pyridine swollen coal to revert back to an isotropic state when the stress which induced optical anisotropy was removed is behavior typical of a rubber. If the pyridine swollen coal sample is dried under pressure, the pressure induced radial anisotropy remains even after the stress is removed. The pyridine dried coal is a plastic material since the stress induced anisotropy

remains after removal of the stress.

Brenner O-methylated the hydroxyl groups in the thin section of the Illinois No. 6 coal using methyl iodide as the alkylating agent and tetrabutylammonium hydroxide as a neutralizing agent. IR analysis of the coal thin sections was performed to confirm that O-alkylation occurred. Brenner alkylated the coal to eliminate its hydrogen bonding capabilities. The O-methylation resulted in the loss of the natural axial anisotropy observed for the untreated coal sample. The O-alkylated thin section appeared completely black under the cross polarizers. When pressure was applied to the O-methylated coal, a radially symmetric birefringence pattern was slowly induced. When the stress was removed, the induced anisotropy remained. The O-methylated coal is a plastic at room temperature, since the stress caused a permanently induced birefringence pattern even after the stress was removed.

From these studies, Brenner suggested that the untreated and O-methylated coals are both plastic materials at room temperature. The untreated coal becomes rubbery when immersed in pyridine at room temperature. Removal of coal hydrogen bonds by chemically derivatizing the coal or swelling the coal in pyridine (a good hydrogen bond acceptor solvent) relaxes the initial anisotropy of the

untreated coal sample. Based on this study, Brenner suggested that hydrogen bonding may be responsible for the anisotropy of the untreated coal.

Peppas determined the glass transition temperature (T_g) of a variety of untreated and pyridine swollen coals by differential scanning calorimetry.²³ The T_g is the temperature at which polymers transform from a glassy (hindered macromolecular motion) to a rubbery (increasing macromolecular chain mobility) state. Peppas monitored the change in heat capacity at constant pressure (ΔC_p) as a function of temperature for coals varying from 69% to 94% C (dmmf). Coal T_g 's were found to generally increase with increasing carbon content. The untreated coals were found to have T_g 's varying from 580K for a 69.9% C coal to 632K for a 94.2% C coal. The coals exposed to pyridine vapor for up to 30 days (total pyridine uptake varied from 4.2% to 81.9% by weight) all had much lower T_g 's, ranging from 395K to 516K. The experiments of Peppas and Brenner both suggest that coals are glassy macromolecular systems at room temperature. Pyridine is capable of lowering the glass transition temperature of coals. Brenner suggests that a pyridine swollen coal has a T_g below room temperature, while Peppas suggests the T_g of pyridine swollen coals is much higher (122 - 243 °C).

Painter recently offered an explanation for the discrepancy of the T_g of pyridine swollen coals.²⁴ Painter calculated T_g 's of coals based on Couchman's method:

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (1)$$

where T_g is the glass transition temperature of the polymer-solvent system, the subscripts (1) and (2) refer to the pure solvent and pure polymer respectively, w is the weight fraction of each component, ΔC_p is the change in heat capacity, and T_g is the glass transition temperature of the pure components.²⁵ The ΔC_p values for coal and pyridine were estimated from the Simha-Boyer relationship²⁶:

$$T_g \Delta C_p = 115.5 \text{ J/g} \quad (2)$$

Painter suggested that the coal-pyridine system may be separated into two swollen phases in equilibrium with the pure solvent. This would give two distinct T_g 's, one due to the swollen coal and one due to the solvent (pyridine) containing dissolved coal.

F. Volumetric Swelling of Coals

Volumetric solvent swelling experiments have been extensively applied to characterize the macromolecular structure of coals. Volumetric swelling experiments measure the expansion of coals exposed to solvents applying the following relationship:

$$Q_v = \frac{H_2}{H_1} \quad (3)$$

where Q_v is the volumetric swelling ratio, H_1 is the initial height of the coal in a cylindrical tube after centrifugation, and H_2 is the height of the coal exposed to a solvent after centrifugation.

Before the interactions between coals and swelling solvents can be discussed, a brief understanding of the solvent solubility parameter is necessary. The Hildenbrand solubility parameter (δ) of a pure liquid is the square root of the cohesive energy density (CED) of the liquid:

$$\sqrt{\text{CED}} = \delta = \sqrt{\frac{E}{V_m}} \quad (4)$$

where E and V_m are the molar cohesive energy (energy of

evaporation) and molar volume of the liquid respectively.²⁷ The CED is the amount of energy required to disrupt all of the intermolecular interactions in one mole of a pure liquid.²⁸ Theoretically, different solvents having the same solubility parameter would be completely miscible in one another, in other words, like-dissolves-like. Regular solution theory assumes random mixing of the solvent pair.

G. Importance of Hydrogen Bonding in Bituminous Coals

Larsen monitored volumetric coal swelling using a series of nonpolar solvents incapable of interacting with hydrogen bonds in coal as a function of the solvent δ .²⁹ Figure 4 demonstrates the swelling of an Illinois No. 6 coal (79.8% C, on a dry ash free basis (daf)) by nonpolar solvents for the untreated coal, its pyridine extracted residue, the O-methylated, and O-acetylated coal. The volumetric swelling is low for the untreated Illinois No. 6 coal by the nonpolar solvents. Q_v values range from 1.0 to 1.2, corresponding to 0 to 20% volumetric coal expansion. This indicates a lack of specific interactions between this coal and these nonpolar solvents. An increase in coal swelling by the nonpolar solvents reveals O-acetylated > O-methylated > pyridine extracted >> the untreated Illinois

Figure 4. Swelling ratio ($Q_{v,dry}$) for an Illinois No. 6 coal (78.9% C, daf) (■), the pyridine-extracted coal (●), the oxygen-methylated unextracted coal (○), and the pyridine extracted oxygen-acetylated coal (▲) as a function of the Hildebrand solubility parameter (δ) of the swelling solvent. The swelling solvents are: (1) n-pentane; (2) n-heptane; (3) methylcyclohexane; (4) cyclohexane; (5) o-xylene; (6) toluene; (7) benzene; (8) tetralin; (9) naphthalene; (10) carbon disulfide; (11) biphenyl.²⁹

No. 6 coal. A similar trend was observed for a Bruceton coal (83.1% C, daf) examined in this study. The coals were extracted with pyridine and the coal residues were vacuum dried. Approximately 3% of the pyridine could not be removed from both coal residues measured by the weight increase after extraction and vacuum drying. This amount of residual pyridine corresponds to 12% of the hydroxyl group concentration in the Illinois No. 6 coal. The nonpolar hydrocarbon solvents, having a δ between 9 and 10 (cal/cm³)^{1/2}, swell the pyridine extracted Illinois No. 6 coal residue to a volume three times greater than the untreated coal. The presence of residual pyridine (3% by weight) in the extracted coal residue may be responsible for the increase in swelling by the nonpolar solvents compared to the untreated Illinois No. 6 coal. The presence of the small amount of residual pyridine in the Illinois No. 6 residue caused an increase in swelling of 10% by chlorobenzene compared to an untreated Illinois No. 6 coal. The 10% increase in swelling of the pyridine extracted coal residue by chlorobenzene is much less than the 130% increase in maximum swelling observed for the pyridine extracted residue of the Illinois No. 6 coal by the nonpolar solvents. The enhanced swelling by the nonpolar solvents for the pyridine extracted coal residue cannot be attributed to the small residual pyridine in the

coal residue. The enhanced swelling of the pyridine extracted coal residue is most likely due to the destruction of coal-coal hydrogen bonds during pyridine swelling of this coal.

When the hydrogen bonding capability of the coals was removed by O-acetylating or O-methylating the coals, maximum coal swelling was observed (Figure 4). The O-alkylation procedures used to derivatize the coals does not break any C-C or C-O σ -bonds.³⁰ The increase in coal swelling by the nonpolar solvents of the derivatized and pyridine extracted coal residues was attributed to the destruction of hydrogen bond cross-links in these coals.

Hall monitored the swelling of 8 British coals (ranging from 50% C to 95% C, dmmf) by a series of substituted pyridines.³¹ He was concerned with the importance of solvent basicity. Pyridine and substituted pyridines were used in this study because they provide a wide range of basicities while having the same molecular geometry. This eliminates steric effects and yields a direct correlation between coal swelling and solvent basicity. Table 2 shows the substituted pyridines and tetramethylene-imine used in this study and their corresponding pK_b values. The volumetric swelling of the bituminous coals as a function of solvent basicity is shown

Solvent	pK_b	Molar Volume
Tetramethylene- imine	2.7	84.1
2-Methylpyridine	8.0	98.8
Pyridine	8.6	80.9
3-Chloropyridine	11.5	95.1
2-Chloropyridine	13.5	94.1
2-Fluoropyridine	14.4	86.1

Table 2. Swelling Solvents and Their pK_b Values.³¹

in Figure 5. Bituminous coals contain several heteroatom functionalities capable of forming coal-coal intermolecular hydrogen bonds (see Figure 1) which have a distribution of hydrogen bond strengths. Hall effectively titrated hydrogen bond strengths in these coals by varying swelling solvent basicity. As solvent basicity was increased from a pK_b of 14.4 to 8.6, a greater number of coal-coal hydrogen bonds were being broken as indicated by an increase in swelling, shown in Figure 5. There is no increase in coal swelling by solvents having a pK_b below 9. Solvents having a pK_b below 9 apparently are sufficiently basic to disrupt the strongest coal-coal intermolecular hydrogen bonds, swelling the coals to their maximum extent. Hall found no correlation between coal swelling and solvent basicity for the higher rank coals ($> 89\%$ C, dmmf) examined in this study (Figure 6). This may be due to a low population of hydrogen bond cross-links in higher rank coals. This will be discussed in more detail shortly.

Larsen and Baskar have directly studied hydrogen bonding between a Rawhide coal (69.3% C, daf) and a series of solvents using diffuse reflectance Fourier transform infrared spectroscopy (DRIFT).²² Larsen and Baskar monitored the change in the O-H stretching frequency of the Rawhide coal exposed to solvent vapors as a function of

Coal Identity:

(▲) Rawdon Coal (76.3% C, dmmf); (●) Cresswell Coal (84.5% C, dmmf); (■) Gelding Coal 81.6% C, dmmf); (□) Belle Ayre Coal (50.0% C, dmmf).

Figure 5. Variation of the Coal Swelling Ratio (Q_v) with Solvent Basicity (pK_b).³¹

note: The Authors did not specify how the points in the graph were fit by the lines. No mention was made of how lines drawn between points.

Coal Identity:

(•) Taff Merthyr Coal (92.4% C, dmmf);

(■) Nantgarw Coal (89.2% C, dmmf).

Figure 6. Variation of the Coal Swelling Ratio (Q_v) with Solvent Basicity (pK_b).³¹

solvent basicity. Figure 7 shows the DRIFT spectrum of the Rawhide coal (5.8% by weight) in a KBr pellet, the coal exposed to d_5 -pyridine vapor for 16 hours, and the difference spectrum between the pyridine exposed and untreated Rawhide coal. The pyridine exposed rawhide coal shows a loss of intensity at 3550 cm^{-3} . This was due to the loss of free and weak hydrogen-bond hydroxyl groups in the coal which are replaced by coal hydrogen-bonding to the pyridine. The DRIFT difference spectrum shows a broad O-H stretch centered at 2850 cm^{-3} . This 700 cm^{-3} shift of the coal O-H stretch upon exposure to pyridine is typical of IR shifts observed when pyridine bonds to hydroxyl groups on silica surfaces.³²

A correlation between solvent base strength and the shift in O-H stretching frequency of the Rawhide coal is shown in Figure 8. No change in the coal O-H stretching frequency was observed when benzene, a solvent incapable of forming hydrogen bonds, was adsorbed by the coal. The DRIFT coal O-H frequency shift parallels solvent basicity (Figure 8). This indicates stronger coal-solvent hydrogen bonding as a function of stronger solvent base strength. This is expected behavior.

Observations, by optical microscopy of coal swelling by Brenner (previously discussed), the swelling experiments

Figure 7. Diffuse Reflectance Fourier Transform Infrared (DRIFT) Spectra of an Untreated Rawhide (69.3% C, daf) Coal ^(a); the Rawhide Coal Exposed to Pyridine Vapor for 16 Hours ^(b); and the Difference Spectrum of b - a ^(c).²²

Figure 8. Plot of the DRIFT Wavenumber Shift (cm^{-1}) of the O-H Stretching Frequency of a Rawhide Coal (69.3% C, daf) versus the Base Strength (pK_a) of the Absorbed Solvent.²²

of Larsen and by Hall, and the direct observation of solvent-coal hydrogen bonding by DRIFT spectroscopy performed by Larsen and Baskar demonstrate that hydrogen bonding is an important contributor of cross-links for coals having carbon contents below 87% C, dmmf.

H. Importance of Stacking Interactions in High Rank Coals

The importance of hydrogen bond cross-links in coals decreases as coal rank increases. This must occur because the hydroxyl group concentration decreases with increasing coal rank.^{16,33} Several types of evidence suggest that "stacking interactions" between PNA's in coal become important structural contributors as coal rank increases. Stacking interactions are instantaneous dipole-induced-dipole interactions which occur between all molecules. Stacking interactions can produce strong associative forces in PNA systems. The attractive forces of stacking interactions generally increase with increasing PNA size as molecular polarizability increases.³⁴ This through space interaction between PNA systems is highly distance dependent. Attractive stacking interactions are generally proportional to r^{-6} , where r is the distance between

Coal	% Carbon (daf)	Hydroxyl Content (equivalents/100 C)
PSOC-726	87.5	2.5
PSOC-1100	88.1	---
PSOC-619	88.5	0.7
PSOC-134	86.1	---
PSOC-1197	88.5	0.5
PSOC-127	88.9	---

Table 3. Carbon and Hydroxyl Group Content of the Pennsylvania State University Coals (PSOC) Used by Stock and Mallya.³⁶

interacting PNA clusters.³⁵

Stock and Mallya examined the importance of non-covalent bond interactions in 6 high rank coals (shown in Table 3).³⁶ Stock O-methylated and O-butylated the coals using a mild alkylation reaction described by Liotta.³⁷ The purpose of O-alkylating these coals was to disrupt stacking interactions by forcing the interacting coal PNA clusters apart by inserting alkyl groups into the coals. Stock used pyridine extractability as a probe to determine the effectiveness of disrupting coal stacking interactions by O-alkylation. Coal-solvent interactions which are as strong or stronger than coal-coal associative forces result in coal molecules dissolved in the extracting solvent. Comparing the pyridine extractability of the untreated and alkylated coals will demonstrate the effectiveness with which the alkylation reaction disrupts associative forces in coals.

Table 4 shows the pyridine extractability of the untreated coals, the coals subjected to all reagents involved in the alkylation reactions except the alkylating agent (the control experiment), the pyridine extractability of the butylated coals, and the pyridine extractability of the methylated coals. The control experiment showed an insignificant change in the pyridine extractability for two

Pyridine Extractability (%C, daf)

Coal	Control			
	Raw Coal	Experiment	O-butylated	O-methylated
PSOC-726	46	40	76	46
PSOC-1100	33	--	65	--
PSOC-619	20	25	53	24
PSOC-134	20	--	67	--
PSOC-1197	5	17	10	8
PSOC-127	28	--	38	--

Table 4. Pyridine Extractability of 6 High Rank Coals and Their Alkylated Products.³⁶

of the three coals examined. The pyridine extractability of the PSOC-1197 was slightly greater for the control experiment, but this coal appears to be anomalous compared to the other five coals examined in this study. O-methylation did not significantly increase the pyridine extractability of the coals. The O-butylation does greatly increase the pyridine extractability of all the coals except the PSOC-1197 (Table 4). Elemental analysis and ^{13}C NMR spectroscopy were used to verify that the coal alkylation reactions occurred virtually exclusively on oxygen. The number of added alkyl groups was found to be equal or slightly less than the number of hydroxyl groups in the untreated coals.

O-methylation and O-butylation of the coals are equally effective in disrupting the hydrogen bond interactions in coals. The pyridine extractability of the O-butyated coals is much greater than the pyridine extractability of O-methylated or the untreated coals. The increase on pyridine extractability of the O-butyated coals is most likely due to the disruption of non-covalent, non-hydrogen bonding coal interactions since the O-methylation of the coals did not significantly increase the pyridine extractability of the coals compared to the pyridine extractability of the untreated coals. The steric

requirement of the bulky butyl group is responsible in forcing interacting PNA clusters apart. Based on the marked increase in pyridine extractability due to O-butylation compared to O-methylation and untreated coals, stacking interactions in high rank coals are important coal associative forces.

Quinga and Larsen have demonstrated the importance of stacking interactions in high rank coals.³⁴ Larsen modified 6 coals ranging from 83.1% C to 92.1% C (dmmf) by a Diels-Alder reaction with maleic anhydride. Their rationale for creating maleic anhydride-coal adducts was to disrupt the PNA stacking interactions between coal clusters. This is accomplished in two ways: 1) Stacking interactions can be reduced by geometrically forcing interacting PNA systems apart since these stacking interactions greatly decrease with increasing separation and (2) reducing the size of PNA systems in coal reduces the associative forces between aromatic clusters.

The effectiveness of the maleic anhydride reaction at disrupting stacking interactions in coals was determined by comparing the pyridine extractability of untreated coals and coal-maleic anhydride adducts. It is crucial that the maleic anhydride reaction not cleave any σ bonds in the coals because coal-coal covalent bond cleavage and the

disruption of coal-coal stacking interactions will both increase coal's pyridine extractability. The maleic anhydride-coal reactions were performed under mild experimental conditions (coal + maleic anhydride in chlorobenzene at 110°C) which were not expected to break covalent coal-coal bonds.

The pyridine extractability of the untreated coals is compared to the pyridine extractability of the maleic anhydride treated coals in Table 5. No difference in the pyridine extractability of the untreated coals and their maleic anhydride adducts was found for coals < 90% C (dmmf) (Table 5). Coals > 90% C (dmmf) show a marked increase in pyridine extractability for the maleic anhydride treated coals in comparison to the untreated coals. This increase in extractability can be attributed to the disruption of stacking interactions in higher rank coals. Larsen's data do not reveal the extent of stacking interactions in high rank coals but confirms their presence.

The studies by Stock and by Larsen both indicate the importance of stacking interactions as associative forces in high rank coals (> 90% C, dmmf).^{36,34} Neither of these two studies indicate that stacking interactions are not present in lower rank coals; they simply confirm the importance of stacking interactions as associative forces

Coal	% C (dmmf)	Coal		Coal Adduct	
		% Residue	% Extract	% Residue	% Extract
Bruceton	83.1	72	30	71	30
PSOC-1309	84.3	73	33	72	32
PSOC-721	88.3	72	31	70	33
PSOC-1133	90.7	99	2.6	82	20
PSOC-648	92.1	99	3.6	83	21
101:no.0004 ^a	88.9	64	40	--	--
101:no.0005 ^a	88.9	64	40	--	--
101:no.00010 ^a	88.9	--	--	64	39
101:no.00012 ^a	88.9	--	--	56	40

a. Argonne Premium Coal Sample.

Table 5. Pyridine Extraction of Coals and Their Maleic Anhydride Adducts.³⁴

in high rank coals.

Backup
Blank

II. Pore Structure of Coals

A. Coal Pore Models

The characterization of the pore structure of coals is crucial for understanding coal reactivity. A reagent must first encounter the coal surface before any reaction involving solid coal can occur. How much of the coal surface is accessible to a molecule and the interactions occurring on contact with the coal surface are important parameters in predicting coal reactivity.

Bond has proposed a pore structure model for coals illustrated in Figure 9.³⁸ This model views coals as having an extensive system of slit-like cavities interconnected by narrow capillary constrictions. Bond claims the capillary constrictions, or bottle-necked pores, in coals consist of a bi-modal distribution of widths ranging from 10-20 Å and 15-30 Å in diameter. The coal pore model shown in Figure 9 is claimed to be based on heat of wetting, adsorption, and apparent density studies of four coals using organic adsorbates having a wide range of molecular sizes, shapes, and chemical properties. Bond never published the experimental details that lead him to the proposed coal pore model shown in Figure 9.

Figure 9. Bottle-Necked Pore Model of Coal Porosity.³⁸

Despite the lack of experimental evidence, this pore model has been widely accepted as a valid depiction of coal pores.³⁹⁻⁴³

An alternative to Bond's model for the pore structure of coals is shown in Figure 10. In this closed pore model, coals are considered glassy polymers, having no interconnected pore network. This closed pore model depicts pores in coals as isolated "bubbles". We have proposed a closed pore model for coals to rationalize the gas adsorption data which will be discussed in great detail shortly.

B. BET Gas Adsorption Theory

The Brunauer, Emmett, and Teller (BET) gas adsorption theory was formulated to describe physical gas-solid adsorption processes.⁴⁴ The BET equation is fit to a gas-solid adsorption isotherm. An adsorption isotherm is determined by monitoring the quantity of a gas adsorbed (the adsorbate) on a pre-evacuated solid (the adsorbent) as a function of the adsorbate gas pressure. The BET equation in linear form is:

Figure 10. Closed Pore Model of Coal Porosity. Coal Pores Are Considered to Be Isolated "Bubbles" Having No Extensive Interconnected Pore Network.

$$\frac{P_e}{V(P^0 - P_e)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P_e}{P^0} \quad (5)$$

where P_e and P^0 represent the equilibrium pressure and the saturated vapor pressure of the adsorbate gas respectively, C is the BET constant, V is the volume of the gas adsorbed at relative pressure $\frac{P_e}{P^0}$, and V_m is the monolayer capacity. The BET C constant is the "net" heat of adsorption defined as:

$$C = e^{\frac{(E_1 - E_L)}{RT}} \quad (6)$$

where E_1 is the heat of adsorption of the first adsorbed layer and E_L is the heat of liquefaction of the adsorbate.^{42,44} The BET theory is useful in determining the number of adsorbate molecules required for monolayer coverage of a surface even though monomolecular surface coverage is never achieved.⁴⁵ The surface area of a solid is the product of the effective cross-sectional area of the adsorbate molecule and the monolayer capacity.

The application of BET theory to determine surface areas of solids involves the following assumptions: a) lateral interactions between adsorbate molecules are ignored; (b) the heat of adsorption of the second and higher adsorbed layers on the surface is equal to the heat

of liquefaction of the adsorbate molecules; and (c) all adsorption sites on the adsorbent surface are energetically identical. No real surface can be considered energetically homogeneous. It is reasonable to expect at low relative pressures, adsorbent sites of higher energy will be the first occupied by the adsorbate molecules. As the relative pressure of the adsorbate gas increases, lower energetic sites on the solid's surface become occupied by the adsorbate gas up to the completion of a monolayer.⁴⁵ The adsorption potential of the gas-solid system generally decreases as the relative pressure of the adsorbate increases. Lateral interactions between neighboring adsorbate molecules will increase as the surface becomes more completely covered. The increase in lateral adsorbate interactions and the decrease in adsorption potential with increasing adsorbate gas pressure tend to cancel each other and yield a nearly constant overall adsorption energy up to the completion of a monolayer (Figure 11).⁴⁵ The assumption that the heat of adsorption of the second and greater adsorbed layers is equal to the heat of liquefaction is certainly not valid at high relative pressures where multilayer gas adsorption is expected. For this reason, the BET equation is applied at low relative pressures, typically between $0.35 \leq \frac{P_e}{P_0} \leq 0.05$ presumably where extensive multilayer adsorption is not expected.⁴⁵

Figure 11. Variation in the Energy of Adsorption and Lateral Interaction Potential as a Function of Increasing Adsorbate Concentration. C is the Sum of the Energy of Adsorption and Lateral Interaction Potential.⁴⁵

C. Surface Area of Coals

Many different adsorbate molecules (ie. methane, argon, xenon, nitrogen, carbon dioxide, hydrogen, etc.) have been used to determine the surface area of coals.^{42,46-48} The determination of coal surface areas is dependent on many factors such as: adsorption temperature; coal rank; adsorbate shape; the adsorbate size; and adsorbate/adsorbent interactions.⁴⁹ The dependence of coal surface areas on the adsorbate probe is exemplified by the difference in coal nitrogen and carbon dioxide surface areas.

Nitrogen surface areas of coals are typically much less than coal surface areas determined by CO₂ adsorption, even though the N₂ molecule has smaller molecular dimensions than CO₂.⁵⁰ Walker *et al.* have correlated CO₂ and N₂ surface areas of a wide variety of coals as a function of coal rank (Figure 12).⁵¹ Although considerable scatter is found, the coal N₂ surface areas, measured at 77K, are much less than the corresponding CO₂ coal surface areas, measured at 195K to 298K. It has been suggested that all of the coal micropores are not accessible to the N₂ molecule at 77K due to an activated diffusion process

Figure 12. Variation of the Nitrogen and Carbon Dioxide Coal Surface Areas as a Function of Coal Rank (o, •, N₂ Coal Surface Areas; ■, CO₂ Coal Surface Areas).⁵¹

and/or coal pore shrinkage at lower temperatures.^{49,52,53}

To ascertain the "true" surface areas of coals, comparisons between gas adsorption techniques and physical probes such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) have been performed. X-ray scattering techniques for measuring surface areas have a great advantage over classical gas adsorption techniques since X-rays are not restricted by the aperture size of a pore. SAXS measures the total porosity of coals including pores which may be closed to various adsorbate gases.⁵⁴ X-rays are either absorbed by the sample, pass through the sample unaffected, or are scattered by the sample. X-rays are scattered due to differences in electron densities in different regions of a sample. The intensity of the scattered X-ray beam $I(h)$ is directly dependent on the total surface area of the sample at relatively high angles and is obtained by the Porod method:

$$I(h) = \frac{2\pi(\Delta\rho)^2 S}{h^4} \quad (7)$$

where:

$$h = \frac{4\pi}{\lambda} \sin \frac{\epsilon}{2}$$

λ is the wavelength of the X-ray beam, ϵ is the relative

scattering intensity, $\Delta\rho$ is the electron density difference between the electron cloud scattering the incident X-ray beam and the matrix, and S is the surface area of the solid.^{55,56}

Spitzer and Ulicky have reported comparisons between coal surface obtained by SAXS and CO_2 gas adsorption for two American coals (Table 6).⁵⁷ The close agreement between the surface areas measured by CO_2 adsorption and SAXS for these coals suggesting adsorption of CO_2 provides accurate coal surface areas. Disagreement between CO_2 and SAXS surface areas of two brown coals (60 to 70% C) has been reported and is shown in Table 6.⁵⁸

In a similar study, Gethner determined the surface area of an Illinois No. 6 coal (78% C, dmmf) using small angle neutron scattering (SANS) techniques (Table 6).⁵⁹ Gethner determined the surface area of the Illinois No. 6 coal to be $195 \pm 27 \text{ m}^2/\text{g}$ by SANS. This value agrees with the surface area obtained by Spitzer and Ulicky of $160 \text{ m}^2/\text{g}$ for a similar Illinois No. 6 coal determined by CO_2 gas adsorption. The SAXS studies of coal surface areas by Spitzer and Ulicky and the SANS study by Gethner suggest CO_2 gas adsorption provides accurate surface areas of coals. The problem that needs to be resolved is why N_2 coal surface areas are so much less than corresponding CO_2 coal

surface areas.

D. Swelling of Coals by CO_2

The solubility of CO_2 in coals may be the reason that the coal surface areas measured with CO_2 are much greater than the surface areas measured with N_2 . Reucroft and Patel dilatometrically studied three coals exposed to He, N_2 , CO_2 , and Xe gases.⁶⁰ The three coals examined were a Webster bituminous coal, Sample 1, (83.8% C, daf), a Hopkins subbituminous coal, Sample 2, (78.3% C, daf), and a Carlisle lignite coal, Sample 3, (65.8% C, daf). Pencil-shaped coal samples (about 1 cm long x .4 cm wide) were evacuated in a dilatometer and exposed to about one atmosphere of the adsorbate gas at room temperature. The length of the coal sample was determined in the dilatometer prior to evacuation, after evacuation, and upon exposure of the sample to 20 psig of each gas. Dimensional changes were recorded only in the "long" direction of the coal sample which coincided with dimensional changes in the direction perpendicular to the coal bedding plane. Two different samples of each coal were examined to check for reproducibility.

Coal	% C (daf)	SANS	Surface Area (m ² /g)		CO ₂ Adsorption
			SAXS		
St. Nicholas ^a	92.5	---	275		234
Illinois No. 6 ^a	78.3	---	179		160
Illinois No. 6 ^b	78	195±27	---		---
Brown Coals ^c :			Pore Shapes:		
			<u>Oblate</u>	<u>Prolate</u>	
Dark Lithotype		---	91	1130	298
Light Lithotype		---	72	828	216

a. Data from reference 57.

No coal pore shape assumptions given.

b. Data from reference 59.

c. Data from reference 58.

No elemental analysis of the brown coals was given.

Table 6. Comparison of CO₂ Gas Adsorption Surface Areas of Coals with Corresponding Coal Surface Areas Determined by Small Angle X-ray Scattering (SAXS) or Small Angle Neutron Scattering Techniques (SANS).

Initial evacuation of the three coals studied caused a decrease in sample length ranging from $-.14\%$ to -2.0% contraction. Reucroft and Patel attributed this initial coal sample shrinkage to water loss in coal pores during sample evacuation. Exposure of the coal samples to He or N_2 did not result in the expansion of the coals to their original length. CO_2 exposure produced an increase in length of 0.36% to 1.31% expansion based on the original sample height prior to evacuation. Xe was also found to increase the length of the coals, but to a lesser extent than CO_2 (ranging from 0.004% to 0.22% expansion). Based on the amount of coal swelling by CO_2 , Reucroft and Patel have estimated that coal surface areas determined from CO_2 adsorption may be overestimated by 7% to 15% due to CO_2 imbibition (Table 7). This small amount of CO_2 imbibition in coals is not great enough to explain why CO_2 coal surface areas are generally two orders of magnitude greater than corresponding N_2 coal surface areas.

Walker et al. dilatrometrically measured the expansion of 18 coals ranging from 70.4% C to 92.4% C (dmmf) as a function of CO_2 pressure at ambient temperature.⁶¹ Powdered coal samples (-20 mesh) were placed in the micro-dilatometer and a probe rod that could freely move up and down was placed on top of the coal sample. The probe rod

Sample No.	%C (daf)	CO ₂ Surface Area (m ² /g)	Estimated Swelling	Measured ^a Swelling
			Volume (%)	Volume (%)
1	83.8	150	5.4	0.36 (6.7%)
2	78.3	150	5.4	0.60 (11.1%)
3	65.8	250	9.0	1.31 (14.5%)

a. Expressed as a percentage of estimated coal swelling by CO₂ in parentheses.

Table 7. Estimated Contribution of Coal Swelling by CO₂ to Measured CO₂ Coal Surface Areas.⁶⁰

of the micro-dilatometer was connected to a thermal analyzer. Any movements in the probe rod due to the expansion of the coal were recorded by the thermal analyzer. Table 8 summarizes the dependence of coal swelling (% expansion) as a function of CO_2 pressure for 6 typical coals. As a point of reference, a CO_2 gas pressure of 5 MPa represents a relative vapor pressure of 0.8 at ambient temperatures. An increase in coal swelling by CO_2 with increasing gas pressure was found for each coal studied (Table 8). Most surface area measurements using CO_2 adsorption are determined at pressures below 0.1 MPa where the maximum of CO_2 swelling observed by Walker *et al.* was less than 0.5% expansion. Based on the small amount of CO_2 imbibition below 0.1 MPa, Walker asserts that CO_2 adsorption does measure the total surface areas of coals.

Stacy and Jones attempted to measure CO_2 swelling of 3 brown coals ranging from 69.1% C to 70.3% C (dmmf) using a mercury intrusion technique.⁶² The density of a known mass of coal was determined by mercury intrusion before and after exposure to CO_2 gas. Stacy and Jones found no difference in coal density before and after CO_2 exposure. They concluded from this study that CO_2 does not swell these coals. Based on the small amount of CO_2

CO ₂ Pressure (MPa)	PSOC Coal Expansion (%) Upon CO ₂ Exposure ^a					
	1197 (91.0%C)	1201 (89.3%C)	1166 (84.4%C)	1170 (85.7%C)	248 (75.4%)	246 (71.5%C)
0.68	0.59	0.78	0.64	0.90	0.86	1.03
1.4	0.78	0.98	0.83	0.98	1.05	1.38
2.0	0.86	1.18	0.94	1.80	1.24	2.07
2.7	0.98	1.29	1.40	1.92	2.06	2.41
3.4	1.06	1.84	1.51	1.92	2.22	3.10
4.1	1.18	1.88	1.73	1.96	2.60	3.17
4.8	1.57	1.92	1.85	2.00	3.11	3.79

a. % C expressed on a dry mineral matter free basis.

Table 8. Percent Expansion of the Pennsylvania State Coal
Samples (PSOC) Coals Exposed to Increasing CO₂ Gas
Pressure.⁶¹

swelling found by Walker,⁶¹ it is likely that the mercury intrusion technique is not sensitive enough to measure the small amount of CO₂ imbibition in these coals. The authors acknowledge that this mercury intrusion technique may be insensitive to small CO₂ swelling of these coals.⁶²

The difference in coal surface areas determined by CO₂ and N₂ gas adsorption techniques is most likely an indirect effect of the solubility difference of these two molecules in coals. The slight solubility of CO₂ in coals allows CO₂ to diffuse rapidly through the solid coal and penetrate into pores which are inaccessible to insoluble molecules.

Another possibility is that surface areas of coals are not being measured by gas adsorption techniques. Rather, the solubility of the molecules in the coals is being measured. In other words, it may be a bulk property and not a surface property being probed. This argument is controverted by the close agreement of coal CO₂ surface areas and those obtained by SAXS and SANS experiments.^{57,59} Gas adsorption techniques using CO₂ as the adsorbate are expected to give accurate total surface areas of coals. To understand how the solubility of CO₂ in coals influences the measured coal surface areas, an examination of diffusion mechanisms and diffusion rates of gases through coals and glassy polymers is necessary.

III. Diffusion of Molecules Through Coals and Glassy Polymers

A. Diffusion Mechanisms

Diffusion of gas and liquid molecules through polymer systems has been extensively studied and good reviews are available.⁶³⁻⁶⁵ Many different mechanisms are responsible for penetrant sorption by a polymer. These sorption mechanisms include a rapid adsorption on the exposed surface of the polymer; migration of the penetrant into pre-existing holes in the polymer; and swelling of a polymer by a penetrant resulting in an increase in the distance between polymer molecules.^{66,67}

Simple diffusion of a penetrant into pre-existing holes of a polymer can be described by Fick's Laws of diffusion.^{63,65} Fickian, or Case I, diffusion into spherical particles can be expressed as the integer series:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 K_F t) \quad (8)$$

where:

$$K_F = 4\pi^2 D/d^2$$

and K_F is the Fickian rate constant, M_t and M_∞ are the mass of penetrant sorption by the polymer at time t and infinity respectively, n is the series of integers, D is the diffusional coefficient, and d is the diameter of the spherical polymer particles.⁶⁸ Equation 8 is a model approximating Fickian diffusion of a penetrant through spherical particles. Equation 8 is only valid for an initial uniform penetrant concentration through spherical solid particles having a constant penetrant surface concentration and a constant diffusivity through the spherical particles.⁶⁸ Ideal Fickian behavior is characterized by an initial penetrant uptake that is linearly dependent on the square root of time (where Equation 8 is valid) reaching a maximum value when the concentration of the penetrant is uniform throughout the polymer (see Figure 13).

Case II diffusion is observed when the sorption rate of a penetrant is governed by relaxation of the polymer network. The penetrant plasticizes, or solvates, the polymer which increases the distance between polymer molecules.⁶⁶ In Case II diffusion, the penetrant creates "holes" in the polymer in contrast to Fickian diffusion where the penetrant migrates into pre-existing holes in the polymer network. Since viscoelastic properties of polymers

Figure 13. Vinylchloride Monomer (VCM) Uptake by Polyvinylchloride at 23° C and a VCM Relative Pressure = 0 → 0.0037. VCM Uptake Obeys Ideal Fickian Diffusional Behavior (o, Experimental; Solid Line is the Experimental Data Fit to Equation 8).⁶⁸

are described by a distribution of relaxation times, the expression for relaxation controlled penetrant sorption (Case II) in spherical particles is given by the following distribution:

$$M_t = \sum_i M_{\infty,i} [1 - \exp(-k_i t)] \quad (9)$$

where M_t is the mass of the penetrant sorbed at time t , k_i represents individual relaxation rate constants, and $M_{\infty,i}$ represents the equilibrium sorption of the i 'th relaxation process.⁶⁶ Case II governed sorption of organic vapor penetrants by polymers can be described by the additive combination of two major relaxation processes (termed dual mode sorption⁶⁹) which are a contribution from a Henry's law solubility of the penetrant for the polymer and Langmuir adsorption.⁶⁵ Case II diffusional behavior is characterized by an initial penetrant uptake that is proportional to time, rather than the square root of time, and is commonly observed in polymer systems below their glass transition temperatures.⁵⁰ Super Case II is an upper limit to Case II diffusion characterized by an increase in penetrant mobility with time usually indicative of solvent crazing of a polymer.⁷⁰

B. Anomalous Diffusion in Polymer Systems

The transport of organic vapors and liquids through glassy polymers is often a combination of both Fickian diffusion and relaxation controlled (Case II) diffusion.^{66,71} When both Fickian and Case II diffusion describe the penetration of an adsorbate through a solid, the combined diffusion processes are termed anomalous diffusion. Berens and Hopfenberg were the first to characterize anomalous diffusion in examining the sorption of vinylchloride monomer (VCM) in polyvinylchloride (PVC).⁶⁸ Anomalous transport of a penetrant into a polymer system is considered as the linear superposition of the two independent diffusional processes (Fickian + Case II) and is given by the combination of Equations 8 and 9:

$$M_t = M_\infty \left(1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 K_F t) \right) + \left(\sum_i M_{\infty,i} [1 - \exp(-k_i t)] \right) \quad (10)$$

The rate of Fickian diffusion in a spherical substrate is inversely proportional to the square of the diameter of the adsorbent sphere (see Equation 8). The rate of the Case II

diffusional coefficients (K_i) is independent of the adsorbent particle size. Berens and Hopfenberg were able to separate the Fickian component of diffusion from Case II relaxation by using small spherical polymer particles having diameters $< 184 \mu\text{m}$ in diameter.^{66,72} Figure 14 describes the sorption of vinylchloride monomer (VCM) in $0.44 \mu\text{m}$ diameter polyvinylchloride (PVC).⁶⁶ The sorption of VCM in the PVC spheres is characterized by an initial rapid Fickian dominated diffusion process that attains equilibrium within a few minutes followed by a slow relaxation controlled approach to equilibrium. The solid line in Figure 14 represents an empirical fit of the experimental data (x) with equation 10 having a K_F of $3.8 \times 10^{-3} \text{ sec}^{-1}$ and two characteristic relaxation rate constants K_1 and K_2 of 1×10^{-4} and $5 \times 10^{-5} \text{ sec}^{-1}$ respectively (characteristic of dual sorption mode diffusion).⁶⁵ Equation 10 has been shown to be a valid means of interpreting anomalous diffusion for the sorption of a variety of organic molecules in glassy polymers.^{65,72,73}

C. Diffusion Rates of Molecules Through Glassy Polymers

The overall rate of diffusion of molecules through

Figure 14. Vinylchloride Monomer (VCM) Uptake by Polyvinylchloride at 30° C and a Relative Pressure of 0.5 → 0.10 (x, Experimental; Solid Line = Experimental Data Fit to Equation 10 with a $K_F = 3.8 \times 10^{-3} \text{ sec}^{-1}$; $K_1 = 1 \times 10^{-4} \text{ sec}^{-1}$; and $K_2 = 5 \times 10^{-5} \text{ sec}^{-1}$). *bb*

glassy polymers has been shown to be highly dependent on the size and shape of the penetrating molecule.^{63,64,74} Berens and Hopfenberg have correlated the diffusivity rates of a wide variety of molecules of various shapes in glassy polymer spheres of polyvinylchloride (PVC); polystyrene (PS); and polymethyl-methacrylate (PMMA).⁷⁴ The sorption of the organic penetrants studied by Berens and Hopfenberg in the polymer powders were found to exhibit anomalous diffusion. To permit a direct comparison of penetrant diffusivity with penetrant diameter, only the diffusivities due to the initial Fickian diffusional component were compared. The diffusivities of the penetrants were determined applying the following solution to Fick's Law of diffusion for spherical geometry:

$$D = 7.66 \times 10^{-3} d^2/t_{.5} \quad (11)$$

Where $t_{.5}$ represents the time when $\frac{M_t}{M_\infty} = 0.5$

D is the diffusivity of the penetrant (having typical units of cm^2/sec), d is the diameter of the adsorbent sphere, M_t is the mass of penetrant sorbed at time t , M_∞ is the equilibrium mass of penetrant sorbed, and $t_{.5}$ is the Fickian half time of total penetrant sorption.⁷⁵

A typical plot of M_t vs. $\sqrt{\text{time}}$ for n-butane adsorption

on 7.1 μm PS spheres is shown in Figure 15. The solid line indicates the Fickian diffusion component used to calculate the diffusivity of n-butane in PS using Equation 11. The diffusivities of penetrant molecules in PS shown in Figure 16 were determined in the same manner. The closed circles in Figure 16 represent molecular diameters of penetrants calculated using the Lennard-Jones force constants from published gas viscosity measurements ($d_{\text{L-J}}$).⁷⁶ The open circles in Figure 16 represent molecular diameters of penetrants calculated from the liquid densities of the penetrants given by:

$$d_{\rho} = \left(\frac{M}{\rho N} \right)^{\frac{1}{3}} \quad (12)$$

where d_{ρ} is the molecular diameter of the penetrant having a density of ρ and N is Avagadro's number. The correlation line in Figure 16 was based on the D of the spherical penetrants (He, Ne, Ar, CH_4 , SF_6 , CCl_4 , and neo-pentane) in the PS spheres. A definite positive deviation from the line drawn in Figure 16 is observed for the normal alkane penetrants (the most linear of the penetrants studied). The D of n-hexane is 3 orders of magnitude greater than predicted for spherical molecule having the same d_{ρ} . The diffusivities of the anisomeric molecules are apparently

Figure 15. Mass of n-butane Uptake as a Function of Time (M_t) by 7.1 μm Polystyrene (PS) Spheres at 30° C and a Relative Pressure of 0 $\rightarrow$ 0.02 (o, Experimental; Solid Line is the Initial Experimental Data Fit to Equation 8 for Fickian Diffusion into Uniform PS Spheres).⁷⁴

Figure 16. Gas and Vapor Fickian Diffusivities in Polystyrene (PS) Spheres at 30° C as a Function of the Penetrant Mean Diameter. Correlation Line Drawn for the Spherical Penetrant Molecules. 74

governed by a dimension smaller than their mean diameters. Berens and Hopfenberg believe that the diffusion of the linear alkanes through the polymer sample is along their "long" axis and hence they diffuse through the polymer more quickly than predicted by a spherical molecule having an equivalent d_p .⁷⁴

The overall size of the molecule has the largest effect on the diffusion rate of the penetrant through the glassy PS sample. The diffusivity of He ($d_{L-J} = .26$ nm) is over 11 orders of magnitude faster than neo-pentane ($d_p = .58$ nm) through the PS sample. This extremely steep dependence of penetrant size on diffusivity was also observed for the PMMA and PVC polymer powders examined in this study and has been observed and reported for a large number of penetrant/polymer systems.^{64,74,77}

The rates of penetrant uptakes by glassy polymers which obey Case II kinetics show a steep dependence of penetrant diffusivity through the polymer on the size of the penetrant. Hopfenberg *et al.*, examined the sorption rate of a linear series of alkanes (n-pentane, n-hexane, and n-heptane) and isopentane through a thin polystyrene film at 30° C.⁷⁸ The uptake of the alkanes by the polystyrene exhibited Case II behavior. Figure 17 compares the penetrant uptake of the alkanes by the polystyrene film as

Figure 17. Penetrant Size Dependence on the Uptake by a Polystyrene Film. The Uptake of the Alkanes by the PS Film Obey Case II Diffusional Behavior (Equation 9).⁷⁸

a function of time. As the size of the penetrant increases, the rate of the penetrant uptake by the polystyrene greatly decreases.

The rate of penetrant uptake by a glassy polymer is highly dependent on the size of the penetrant whether the penetrant diffusion through a glassy polymer is characterized by Fickian or Case II kinetics.

D. Diffusion of Penetrants Through Coals

Evidence from the literature has been presented in this thesis demonstrating the major organic phase of coals is best described as a glassy macromolecule.^{19,23} It is not surprising that the sorption of organic penetrants in coals is analogous to the sorption of organic vapors in synthetic polymers.^{50,67,71} A major difference between coals and synthetic polymers is that coals contain extractable organic materials which are not incorporated into the coal macromolecular network. When solvent vapor is brought in contact with coals, the solvent can:

- a) adsorb onto the outer coal surface and accessible pore walls
- b) diffuse into the solid coal by means of a Fickian, anomalous, Case II, or Super Case II diffusion

mechanism

- c) condense in small capillary coal pores
- d) chemically interact with the coal by dissolving into a portion of the coal which the penetrant is soluble.⁷⁹

If coals contain extractable materials which are soluble in an adsorbate penetrant, an extraction induced penetrant condensation will be one of the mechanisms responsible for the coal particles gaining weight upon exposure to the penetrant.⁶⁷ Duda⁶⁷ and Peppas^{70,80} studied the diffusional transport of organic molecules through pyridine extracted coal residues. Their rationale for using pyridine extracted coal residues and not untreated coals to study penetrant transport mechanisms through coals was to separate the weight gain of coals exposed to a penetrant due to diffusion into the coal from the weight gain of coal resulting from an extraction induced condensation of the penetrant in coals.

The assumption that diffusion mechanisms of penetrants through pyridine extracted coal residues are directly comparable to untreated whole coals may be invalid. Maceil et al. have recently compared solid state ^{13}C cross polarization (CP) magic angle spinning (MAS) NMR spectra of 7 untreated coals (ranging from 59.4% C to 87.4% C (daf)),

with their corresponding pyridine extracts and residues.⁸¹ Composite ^{13}C NMR spectra based on the sum of the pyridine extracted coal residues and extracts were scaled in proportion to the amounts of pyridine-coal extraction products isolated. The composite ^{13}C NMR residue + extract coal spectra were compared to the corresponding ^{13}C NMR spectra of the untreated coals. Maciel found that:

"Composite (^{13}C NMR) spectra prepared as weighted averages of the (pyridine) extracts and residue spectra differ substantially for some coals from the spectra of the corresponding original coals; this implies that either some structural conversions occur during pyridine extraction, or more likely, some structural features are selectively lost during (product) isolation procedures."⁸¹

Based on Maciel's comparative ^{13}C NMR study of untreated coals with their pyridine extracted residues and extracts, caution should be exercised in directly correlating penetrant diffusion data through pyridine extracted coal residues with untreated coals.

Hsieh and Duda studied the sorption of organic vapors in untreated and pyridine extracted residues of a Kentucky Hazard No. 9 bituminous coal (71.0% C, daf).⁶⁷ One gram of an untreated coal sample was exposed to DMSO in a desiccator at 25°C and saturated solvent vapor (solvent activity of 1). The coal sample was periodically removed

Figure 19. Tetralin Uptake by a Kentucky Bituminous Coal (71.0% C, daf) at 110° C and a Solvent Relative Pressure of 0.44 (o Untreated Coal; • The Pyridine Extracted Residue of the Coal Particles).

untreated coal is most likely due to an extraction induced solvent condensation in the coals in addition to solvent diffusion into the coal. Removal of the pyridine soluble coal molecules, by pyridine extraction, may eliminate an extraction induced condensation of tetralin in the Kentucky coal. Tetralin soluble molecules in the untreated coal are most likely responsible for the difference in the time dependence of solvent uptake by the Hazard coal between the untreated and pyridine extracted coal residue (Figure 19).

The uptake of toluene by the pyridine extracted residue of the Kentucky coal as a function of time is shown in Figure 20. An initial rapid, almost instantaneous, uptake of toluene by the coal residue was observed due to adsorption of the toluene on the outer surface of the coal and coal pore walls. The toluene uptake by the coal residue was found to increase with time long after an anticipated Fickian equilibrium would have been reached. The absorption of toluene by the coal residue was best modeled by a coupled diffusion-relaxation process (anomalous diffusion) similar to the Berens and Hopfenberg model described by Equation 10. The solid line in Figure 20 correlates the toluene uptake as a function of time for the Kentucky coal residue with the diffusion-relaxation model of Long and Richman.⁸² The Long and Richman model is

Figure 20. Toluene Uptake by a Pyridine Extracted Coal Residue of a Kentucky Bituminous Coal (71.0% C, daf). The Solid Line is the Correlation of the Experimental Uptake Data (o) with a Fickian + Relaxation Coupled Diffusion Model⁸¹ Similar to Equation 10.⁷⁹

very similar to the Berens and Hopfenberg model of diffusion-relaxation controlled penetrant uptake by a solid (Equation 10) which Hseih and Duda claim describes the uptake of toluene by the coal residue equally as well. The uptake of toluene by the Kentucky coal as a function of time exhibits anomalous diffusion based on the good correlation of the toluene uptake with a coupled relaxation-diffusion model.

A convenient method for determining diffusional mechanisms of penetrant sorption in coals and polymers utilizes the difference in the time dependence between pure Fickian diffusion (penetrant uptake is proportional to the square root of time) and pure Case II (penetrant uptake is directly proportional to time). The Berens and Hopfenberg model of diffusion (Equation 10) considers anomalous diffusion as the linear superposition of Fickian and Case II diffusion.⁶⁶ The individual contributions of Fickian and Case II diffusion to anomalous transport of a penetrant through a solid can be quantified by determining the diffusion exponent (n) of the penetrant/solid system. The diffusional exponent can be determined by analyzing the sorption of a penetrant through a solid by the following equation:

$$\frac{M_t}{M_\infty} = kt^n \quad (13)$$

where M is the mass of penetrant sorbed at time t and infinity, k is a constant which depends on the penetrant/sorbent interactions, and n is the diffusional exponent which indicates the diffusional mechanism(s) of penetrant uptake by an adsorbent.⁶⁵ The slope of $\ln M_t$ or $\ln M_t/M_\infty$ vs. $\ln t$ is equal to the diffusional exponent (n). Equation 13 is only valid during the initial portion of the sorption analysis, before the Fickian component of diffusion reaches equilibrium. Peppas has correlated n with diffusional mechanisms based on the geometrical shape of the adsorbent (Table 9).⁷⁰

Peppas studied diffusion mechanisms of pyridine sorption in pyridine extracted coal residues from a variety of coals.⁷⁰ Figure 21 shows typical sorption behavior found by Peppas for a PSOC (Pennsylvania State University coal sample) 853 coal (80.1% C, dmmf). The coal residues studied by Peppas all had average particle diameters between 600-850 μm . Table 10 shows the correlation of the diffusional exponent (n) with the sorption of pyridine in the pyridine extracted residues of the coals studied by Peppas. The diffusional exponent n indicates an apparent anomalous diffusional mechanism for the transport of

Diffusion Exponent (n)		
Thin Section	Spheres	Diffusional Mechanism
<hr/>		
0.5	0.43	Fickian Diffusion
$0.5 < n < 1.0$	$0.43 < n < 0.85$	Anomalous Diffusion
1.0	0.85	Case II Relaxation
$n > 1.0$	$n > 0.85$	Super Case II

Table 9. Analysis of Diffusional Behavior of Penetrants Through Solids as a Function of the Geometry of the Solid. The Diffusion Exponent (n) is Determined from Equation 13.⁷⁰

Figure 21. Pyridine Uptake by Pyridine Extracted PSOC-853 (80.1% C, dmmf) Coal Particles (600-850 μm) at 25° C as a Function of Time. 69 70

PSOC	% C	Diffusional ^a	Linear
Coal No.	(dmmf)	Exponent (n)	Correlation Coefficient
418	70.0	0.65	0.993
791	72.2	0.56	0.999
247	75.5	0.65	0.999
312	78.4	0.92	0.993
853	80.1	0.84	0.999
402	82.5	0.75	0.999
989	88.2	0.85	0.854

a. The diffusional exponent was determined from the first 60% of the total pyridine uptake by the PSOC coals ($0 < \frac{M_t}{M_{\infty}} < 0.6$, where M is the mass of pyridine uptake by the PSOC coals at time t and at equilibrium.)

Table 10. Analysis of Pyridine Uptake by PSOC Pyridine
Extracted Coal Residues to Determine the Diffusional
Exponent (n) by Equation 13.⁷⁰

pyridine in the PSOC coal residues for all the coals studied.

Peppas attempted to correct his sorption data to account for the amount of pyridine adsorbed or condensed in the coal pores. He determined pore volumes for the coal residues using mercury porosimetry studies. Pore volumes of particles can be determined by forcing mercury into pores of known geometry by:

$$p = -2\gamma \cos \theta / r \quad (14)$$

where p is the pressure required to force mercury into a cylindrical pore of radius (r), γ is the surface tension of the mercury, and θ is the contact angle between the mercury and a cylindrical pore wall.⁴² Mercury porosimetry is believed to determine only the macropore volume of coals (pores $> 500 \text{ \AA}$ diameter).⁴⁹ Mercury porosimetry has been recently strongly criticized and probably gives no reliable information about coal pore structure.⁸³

Peppas subtracted the amount of pyridine that would occupy the macroporous coal volume, based on Hg porosimetry studies, from the total pyridine sorption in the coal residues. The resulting "corrected" diffusional exponents were much higher than those determined by not correcting

PSOC Coal No.	%C (dmmf)	Diffusional ^a Exponent (n)	Pyridine Diffusion rate (m ² /s)
791 (UN)	72.3	0.56	2.24×10^{-8}
791 (COR)	72.3	1.11	1.86×10^{-8}
312 (UN)	78.4	0.92	8.6×10^{-8}
312 (COR)	78.4	0.92	8.6×10^{-8}
402 (UN)	82.5	0.75	11.2×10^{-8}
402 (COR)	82.5	1.07	5.6×10^{-8}
989 (UN)	88.2	0.85	5.6×10^{-8}
989 (COR)	88.2	0.95	2.24×10^{-8}

a. The diffusional exponent (n) was calculated based on the first 60% of the final pyridine uptake by the pyridine PSOC coal residues based on Equation 13.

Table 11. The Determination of the Diffusional Exponent of Pyridine Uptake by Pyridine Extracted PSOC Coal Residues Before (UN) and After (COR) Correction for the Macropore Coal Volumes.⁷⁰

for the macroporosity of the coal residue (Table 11). Peppas concluded from the pore volume corrected data that the sorption of pyridine in the pyridine extracted residue samples is governed by a relaxation controlled (Case II) diffusional transport mechanism irrespective of the rank of the coals studied.

Peppas and Duda's sorption studies on pyridine extracted coal residues indicate that non-Fickian diffusional mechanisms govern the penetration of molecules through the coal residues. These sorption modes, anomalous or Case II, are similar to the sorption curves observed for the penetration of organic vapors through glassy polymers below their glass transition temperatures.

IV. Fractal Dimensionality of Coal Surfaces

A. Description of a Fractal Surface

The surface area of a solid measured by molecular adsorption techniques is highly dependent on the roughness of the surface. The amount of a probe molecule adsorbed on a convoluted surface depends on the size of the adsorbate molecule and the degree of surface roughness of the adsorbent. The surface area dependence on the size of the

adsorbate probe is shown graphically in Figure 22.⁸³ The convoluted surface (in Figure 22) is covered by two spherical molecular probes of different diameters. The smaller molecules are able to follow the rough surface much more effectively than the larger molecular spheres. If the surface area is calculated by counting the number of molecules adhering to the surface and multiplying by the molecular area of each probe, the smaller molecules will report a larger total area than the larger molecules. The degree of surface roughness can be characterized by a numerical value known as the dimensionality (D) of the surface.⁸⁴⁻⁸⁶

A perfectly smooth flat surface by definition will have a dimensionality of 2. The measured surface area will be independent of the size of the adsorbate molecule used to measure it. As a surface becomes more and more convoluted, its dimensionality will approach 3. The dimensionality of a surface can never equal or exceed 3 since then the surface is so highly convoluted it has become a solid. If a surface is fractal, it will satisfy the criterion of scaling self-similarity expressed as:

$$n \propto r^{-D} \quad (15)$$

Figure 22. Visualization of Equation 15 for the Adsorption of Two Spherical Adsorbates (Having Different Radii) on a Convoluted Fractal Surface. The Total Area of the Surface Grows Faster Than $n \propto r^{-2.55}$ 74

where n is the number of molecules of size r required to cover the fractal surface. In the case of a perfectly smooth surface, $n \propto r^{-2}$. The shape of a fractal surface must be the same regardless of the size or resolving power of the probe used to measure it.

B. The Determination of the Fractal Dimensionality of a Surface

Gas adsorption and X-ray scattering techniques have both been successfully used to determine the dimensionality (D) of fractal surfaces.⁸⁷⁻⁸⁹ The application of gas adsorption techniques, such as the BET theory, for determining the dimensionality of a fractal surface involves careful choice of adsorbate probes. Typically, a series of adsorbates are chosen which have the same general shape, interact in the same way with the adsorbent surface, and vary in size. Figure 23 shows the determination of the dimensionality of an activated charcoal using a series of straight chain hydrocarbons, N_2 , and iso-butane.⁹⁰ The relationship between the BET gas adsorption data and the dimensionality of a surface (D) is given by:

$$n \propto \sigma^{-D/2} \quad (16)$$

Figure 23. Log of the Number of Moles Adsorbate Required for Monolayer Surface Coverage ($\log n$) of an Activated Charcoal as a Function of the Adsorbate Cross-Sectional Area (σ). σ in $\text{\AA}^2$.

where n is the number of moles adsorbate having a cross-sectional area σ required for monolayer coverage. The dimensionality of the surface is determined by plotting $\log n$ versus $\log \sigma$ (n is directly obtainable from the BET theory). For the activated charcoal in Figure 23, a dimensionality of 2.78 was determined by this method. The linearity of the log-log plot indicates that the surface meets the fractal criterion of scaling self-similarity.

Bale successfully applied SAXS techniques to determine the fractal dimensionality of a Beulah Zap lignite.⁸⁹ Bale found a power law dependence on the X-ray scattering intensity as a function of the scattering angle from the lignite coal. The dimensionality of a surface can be determined by SAXS or SANS applying Erdelyi's theorem for asymptotic expansion of a Fourier integral:

$$I(q) \propto q^{-(6-D)} \quad (17)$$

$$\text{where} \quad I(q) = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

λ is the X-ray wavelength and θ is the scattering angle.⁹¹ A fractal surface must satisfy the power law relationship of self-similarity given by equation 15. $\log I(q)$ vs. $\log q$ will yield a straight line for X-rays scattering off a

fractal surface having a slope of D-6 (equation 17). The relationship expressed by equation 17 assumes a uniform electron density for the sample. This assumption is only valid for X-rays or neutron scattering at small angles (no greater than a few degrees) where the scattering cannot resolve atomic structures.⁹²

The dependence of the X-ray scattering intensity on the scattering angle for a Beulah Zap lignite is shown in Figure 24. The power law (expressed by equation 17) holds for over 7 orders of magnitude of scattering intensity. Bale determined the slope of the plot in Figure 24 to be -3.44 ± 0.03 which corresponds to a fractal dimensionality of $(6 - 3.44 \pm 0.03)$ or 2.56 ± 0.03 . Bale has demonstrated that the scattering of X-rays, at small angles, from this coal sample is governed by a fractal coal surface.⁸⁹

Figure 24. X-ray Scattering Intensity as a Function of the X-ray Scattering Angle for a Beulah Zap Lignite. 89

V. ^{129}Xe NMR Spectroscopy

A. The Xenon Atom as a Molecular Probe

^{129}Xe NMR spectroscopy has been successfully applied to determine cavity size, channel dimensions, crystallinity, and structural defects in zeolites.⁹³⁻⁹⁷ ^{129}Xe NMR spectroscopy has also been applied to understand non-specific solvent-solute interactions by dissolving Xe gas in organic solvents, proteins, and biological membranes.^{98,99} The Xenon atom is an excellent probe of certain properties of microporous solids and nonspecific solvent-solute interactions in liquids for a number of reasons. Xenon is a monoatomic atom and highly nonreactive. The ^{129}Xe isotope has a natural abundance of 26.44% and an NMR sensitivity of 0.02 relative to an equal number of protons at constant magnetic field strength. For most ^{129}Xe NMR experiments, isotopically enriched ^{129}Xe is not required. The ^{129}Xe isotope has a nuclear spin of $\frac{1}{2}$ so its NMR spectra are not complicated by quadrupole splitting patterns.¹⁰⁰ The xenon atom has a spherically symmetric electron cloud. Any distortion that disrupts the symmetry of xenon's electron cloud can be observed by monitoring the ^{129}Xe NMR chemical shift.¹⁰¹

B. Xe Dissolved in Liquids

Stengle *et al.*, dissolved Xe gas in a variety of organic solvents to correlate the ^{129}Xe NMR chemical shift with non-specific (van der Waals) solvent-solute interactions.⁹⁸ The magnetic shielding of a molecule dissolved in a solvent is due to the bulk magnetic susceptibility of the sample and the nuclear screening resulting from solvent-solute interactions. The NMR chemical shift arising from solvent-solute interactions is termed a medium shift. Interactions responsible for a medium shift can be classified as specific or nonspecific. Specific solvent-solute interactions involve definable molecular structures (ie. hydrogen bonding), while nonspecific interactions involve molecular aggregates resulting from intermolecular van der Waals attractive and repulsive forces. Xe dissolved in most solvents is involved only in nonspecific solvent-solute interactions. The medium shift of any non-specific interacting solute-solvent system (σ_m) is given by:

$$\sigma_m = \sigma_a + \sigma_E + \sigma_W + \sigma_{\text{rep}} \quad (18)$$

where σ_a is the nuclear shielding from the magnetic

anisotropy of the solvent molecules, σ_E is the nuclear shielding resulting from electric fields generated by any permanent dipole moments of the solute or solvent, σ_W is the shielding from the dispersive part of the van der Waals interactions between solvent and solute, and σ_{rep} is the repulsive part of the van der Waals interactions.¹⁰¹ For nonpolar solutes dissolved in nonpolar, magnetically isotropic solvents, the σ_m is equal to the van der Waals terms in equation 18, σ_W and σ_{rep} . When Xe gas is the solute, medium effects on the ^{129}Xe NMR chemical shift have been found to be very large ($\sim 10^2$ ppm).⁹⁹ Solvent-solute systems exhibiting this large a medium effect indicates the dominance of the van der Waal terms in equation 18, and to a first approximation the other terms can be ignored.⁹⁹

Stengle applied the reaction field concept of Onsager¹⁰² to correlate ^{129}Xe NMR chemical shifts of Xe-solvent systems with σ_m .⁹⁸ The reaction field model of Onsager views the solvent as a continuum having a uniform dielectric constant. A reaction field is an induced electric field about a solute caused by spontaneous dipole moments in the solute. The reaction field of the solvent induced by the solute affects the magnetic shielding of the solute nucleus.¹⁰¹ The reaction field model predicts a correlation between the σ_W of the medium shift and a

function of the refractive index of the solvent. The contribution of the van der Waals dispersion term to the gas-liquid NMR medium shifts for nonpolar solvents can be correlated to the solvent refractive index applying McRae's formula:

$$\sigma_m = C(n_2^2 - 1) / (2n_2^2 + 1) \quad (19)$$

where σ_m is the observed medium shift, C is a constant which depends on the solute, and n_2 is the refractive index of the solvent.¹⁰³

Stengle prepared Xe-solvent solutions by shaking Xe gas with various hydrocarbon solvents (listed in Table 12) in a syringe. The hydrocarbon solutions containing the Xe were transferred from the syringe to an NMR sample tube and the ^{129}Xe NMR spectrum of each solution was determined.

The NMR medium shifts of the ^{129}Xe isotope dissolved in the saturated hydrocarbon solvents are shown in Figure 25 (the solvent designation numbers on the plot are from Table 12). The ^{129}Xe medium shift for the homologous series of straight chain and cyclic aliphatic solvents appears to correlate well with the reaction field model based on the linearity observed between σ_m vs. the solvent refractive index function (given by Equation 19); but the

Solvent			
Number	Solvent	n_D^a	$-\sigma_m^b$
1	n-pentane	1.3558	154.1
2	n-hexane	1.3731	160.9
3	n-heptane	1.3853	166.0
4	n-octane	1.3954	169.9
5	n-nonane	1.4031	173.0
6	n-decane	1.4096	175.4
7	n-dodecane	1.4198	179.4
8	n-tetradecane	1.4271	182.4
9	n-hexadecane	1.4327	184.5
10	2,2-dimethylbutane	1.3674	174.7
11	2,3-dimethylbutane	1.3733	169.2
12	2-methylpentane	1.3697	167.4
13	3-methylpentane	1.3752	165.1
14	2-methylheptane	1.3934	175.9
15	2,5-dimethylhexane	1.3910	181.7
16	2,2,4-trimethylpentane	1.3891	190.5
17	cyclohexane	1.4244	163.7
18	cycloheptane	1.4432	171.4
19	cyclooctane	1.4568	176.2
20	cyclodecane	1.4689	182.9

a. Refractive index measured at 25°C on the actual solvents used for the ^{129}Xe NMR experiments.

b. ^{129}Xe NMR chemical shifts in ppm from the Xe gas extrapolated to zero Xe concentration.

Table 12. Medium Shifts of ^{129}Xe NMR of Xe Gas Dissolved in Saturated Hydrocarbon Solvents.⁹⁹

Figure 25. ^{129}Xe NMR Chemical Shift ($-\sigma_m$) of Xe Gas Dissolved in Saturated Hydrocarbon Solvents at 25°C (Corrected for Bulk Susceptibility) as a Function of the Solvent's Refractive Index (n). The Numbers on the Plot Correspond to the Solvent Numbers Listed in Table 12.⁹⁸

intercepts of both plots did not pass through the origin as the equation predicts. The observed positive Y-intercepts of σ_m vs. the solvent refractive index for Xe dissolved in the linear and cyclic hydrocarbon solvents are most likely due to the contribution of the van der Waals repulsive term to the measured medium shift. The van der Waals repulsive term (σ_{rep}) is essentially constant for any homologous series of hydrocarbons having equal branching but increases as the branching of the hydrocarbons increases.⁹⁸

The ^{129}Xe NMR medium shifts of Xe dissolved in the branched hydrocarbon solvents showed considerable scatter when plotted against the refractive index term of the solvent. The different contributions of the van der Waals repulsive term to the measured ^{129}Xe medium shift are most likely responsible for the observed scatter found for Xe dissolved in the branched hydrocarbons (Figure 25).

Stengle, using ^{129}Xe NMR spectroscopy, has shown that the reaction field model is valid for predicting nonspecific medium effects only within a limited series of related solvents. The model was found to be poor for predicting σ_M for hydrocarbon solvents having different geometries.

C. Xe as a Molecular Probe for Microporous Solids

^{129}Xe NMR spectroscopy is a useful probe for determining micropore ($< 20 \text{ \AA}$) size and surface characteristics of solids. Jameson *et al.* have found a linear dependence on the ^{129}Xe NMR chemical shift on Xe gas density up to 100 amagats¹⁰⁴ xenon gas pressure.¹⁰⁵ Jameson *et al.* concluded that for pure Xe gas below densities of 100 amagats, the molecular interactions affecting the ^{129}Xe NMR chemical shift are solely binary (ie. Xe-Xe collisions). Xe gas pressures greater than 100 amagats resulted in a non-linear dependence of the ^{129}Xe NMR chemical shift with Xe gas pressures resulting from two and three body collisions affecting the ^{129}Xe NMR chemical shift. Frassaird has extended the work of Jameson *et al.* to show that the NMR chemical shift of ^{129}Xe atom in any system is the sum of the perturbations experienced by the Xe atom. The observed chemical shift of ^{129}Xe in a zeolite (δ) is given by:

$$\delta = \delta_S + \delta_E + \delta_N + \int_0^{\rho_{\text{Xe}}} \delta(\text{Xe-Xe}) d\rho_{\text{Xe}} \quad (20)$$

where δ_S is due to the collision frequency between xenon

atoms and a solid surface. δ_E is due to the change in chemical shielding of the Xe atom in the presence of an electric field and is described by Jameson *et al.* by second-order perturbation theory.¹⁰⁶ Fraissard demonstrated δ_E is a negligible contribution to the observed ^{129}Xe NMR chemical shift for monovalent cationic zeolites.¹⁰⁰ δ_N is due to nonspecific solvation effects resulting from Xe adsorption on the solid sample. This term becomes important if Xe atoms have a long residence time (on the NMR time scale) on specific sites of the solid. The last term in equation 19 is the increase in the ^{129}Xe NMR chemical shift due to Xe-Xe collisions which is directly dependent on Xe gas density (ρ_{Xe}).¹⁰⁷

Fraissard *et al.* studied the influence of electric fields created by cations in zeolites on the ^{129}Xe NMR chemical shift.¹⁰⁰ Figure 26 shows the variation of the ^{129}Xe NMR chemical shift as a function of Xe gas pressure for Xe adsorbed in six faujasite zeolites (NaY or HY). The subscript of the NaY zeolites in Figure 26 represents the ratio of the number of Si atoms to Al atoms in the faujasite structure. The concentration of Na^+ ions in the Y-zeolites is directly proportional to the Si/Al ratio of the zeolite since the Na^+ are associated with the Al atoms.⁹⁶

Figure 26. ^{129}Xe NMR Chemical Shift and Resonance Linewidths of Xe Gas Adsorbed in NaY and HY Zeolites as a Function of Xe Gas Pressure (the Corresponding Numbers Indicate the Si/Al Ratio of the Y-Zeolites).¹⁰⁰

Figure 26 demonstrates that the ^{129}Xe NMR chemical shift extrapolated to zero Xe concentration is nearly independent of the concentration of Na^+ ions in these zeolites and independent of the nature of the cation (H^+ or Na^+). Fraissard concluded that the electric field created by Na^+ or H^+ ions in the Y-zeolites has a negligible affect on the measured ^{129}Xe NMR chemical shift. A short residence on the NMR time scale of the Xe atom adsorbed on the zeolite pore wall may be responsible for the ^{129}Xe chemical shift invariance on the concentration or identity of the zeolite cation (H^+ or Na^+). The increase δ with increasing Xe gas pressure for these zeolites is solely due to Xe-Xe collisions since δ_s is independent of Xe concentration.

The NMR line widths of ^{129}Xe adsorbed in the NaY and HY zeolites are also shown in Figure 26 as a function of Xe gas pressure. Intuitively, one would expect the line width to increase with increasing Xe gas pressure due to an increase in Xe-Xe collisions. The exact opposite is observed. The linewidths of Xe adsorbed in the NaY zeolites are independent of Xe gas concentration and the linewidth of Xe adsorbed in the HY zeolite decreases with increasing gas pressure. Fraissard calculated the second moments due to local magnetic fields at the Xe nucleus when

Xe is either adsorbed on a zeolite cage wall (cation) or collides with another Xe atom.¹⁰⁰ The calculations indicate that if the motion of the Xe atoms is slow on the NMR time scale, then significant line broadening is expected. At ambient temperatures, the motion of the Xe atom adsorbed in the Y-zeolites must be fast enough to narrow the NMR signal. Lowering the experimental temperature, which decreases the motion of the Xe atoms in the zeolites, resulted in broadening of the ^{129}Xe NMR signals confirming Fraissard's hypothesis.

The pressure dependence of the ^{129}Xe NMR chemical shift of Xe adsorbed in a CaY zeolite is shown in Figure 27. The non-linear dependence of Xe gas pressure on the ^{129}Xe NMR chemical shift (Figure 27) is not fully understood, but Fraissard offers a possible explanation.¹⁰⁸ The heat of adsorption of Xe on the CaY, NaY, and HY zeolites as calculated from the Xe-zeolite adsorption isotherms is given in Table 13. The Xe atom may have a longer residence time on the Ca^{2+} exchanged zeolite compared to the NaY or HY zeolites as indicated from the measured heats of adsorption of Xe on these zeolites (Table 13). At very low Xe gas pressures, the probability of a Xe-Xe collision is small and the observed chemical shift is a function of $\delta_s + \delta_E$. At low Xe gas concentrations, the

Figure 27. ^{129}Xe NMR Chemical Shift of Xe Gas Adsorbed in a CaY Zeolite as a Function of the Number of Xe Atoms per Zeolite Cavity. . . / 00

Zeolite Sample	Xe Heat of Adsorption (KJ/mole)
NaY ^a	18.4
HY	14.6-16.7
CaY ^b	30.1

a. Si to Al ratio of 54.2

b. 71% of the Na⁺ in the NaY zeolite has been
Ca²⁺ exchanged.

Table 13. The Heat of Adsorption of Xe on Y-Zeolites
as Calculated from the Xe Adsorption Isotherms.¹⁰⁸

electric field created by the Ca^{2+} may strongly affect the ^{129}Xe NMR chemical shift due to Xe adsorbed on or near Ca^{2+} ions. As the concentration of Xe gas increases, the observed δ decreases due to a rapid exchange between Xe atoms adsorbed on the Ca^{2+} surface and Xe adsorbed on other sites of the zeolite cavity. As the concentration of Xe gas increases further, Xe-Xe collisions become important contributors to the observed ^{129}Xe NMR chemical shift and the dependence of the δ on Xe gas concentration is similar to the NaY zeolite case (Figure 26). The slope of the $\text{Xe}_{(\text{g})}$ pressure dependence on the ^{129}Xe NMR chemical shift is qualitatively related to the void volume of the pore containing the Xe atom(s). For any given number of Xe atoms in a sample, the number of Xe-Xe atom collisions will depend on the volume of the pore.

Extrapolation of the ^{129}Xe NMR chemical shift to zero Xe concentration (δ_Z), where the probability of a Xe-Xe atom collision is zero, is directly related to the pore void volume, if δ_E and δ_N (from Equation 20) are negligible. The δ_Z is directly related to the collision frequency of the Xe atom with the pore walls. The smaller the pore, the greater the collision frequency between the Xe atom and pore walls. As the collision frequency increases, the average distortion to the symmetrical Xe

electron cloud increases per unit time resulting in an increase in the measured ^{129}Xe NMR chemical shift.

Xe gas adsorbed in a sample consisting of a mixture of microporous solids differing in structure will show an individual ^{129}Xe NMR resonance for each component in the mixture. Fraissard prepared a mixture of a 58 weight % NaY zeolite with 42% CaA. Irrespective of the Xe gas pressure, Fraissard always observed two well resolved resonances in the ^{129}Xe NMR spectrum (Figure 28).¹⁰⁹ For the Xe-zeolite samples shown in Figure 28, a correlation was found between the intensities of the ^{129}Xe NMR resonance and the composition of the mixture to within $\pm 1\%$ when comparing the NaY intensity with a standard NaY sample of known Xe gas concentration.

D. Determination of the Average Micropore Diameter of Zeolites by ^{129}Xe NMR Spectroscopy

The ^{129}Xe NMR chemical shift extrapolated to zero Xe concentration (δ_Z) is dependent on the pore dimensions of the solid in which the Xe atom is adsorbed.⁹³ Fraissard et al. have successfully correlated δ_Z at ambient temperatures with the mean diameter of the pore in which the Xe atom is entrapped.¹⁰⁹ The mean free path of a Xe atom adsorbed in

Figure 28. ^{129}Xe NMR Chemical Shift of Xe Gas Adsorbed in a 58 Weight % NaY + 42 weight % CaA Zeolite Mixture (at a Xe gas Equilibrium Pressure of 400 torr). 8897

a zeolite cage of known dimensions was determined by computer simulation. The computer simulation involved measuring the mean distance a Xe atom would travel between successive collisions in a zeolite pore. The simulation program began by placing Xe atom at an arbitrary location on a pore wall of a zeolite cavity of known geometry and dimensions. A sub-program was employed to allow the Xe atom to leave the pore wall in a random direction (but non-tangential to the surface) with a random velocity. The mean free path of the Xe atom was determined by averaging the distance traveled by the Xe atom between successive collisions. For all the zeolite structures studied in these simulation programs, the mean free path of the Xe atom in the zeolite pores remained constant after no more than 100 simulated collisions.

Fraissard calculated the mean free path of a Xe atom adsorbed in zeolites whose pores could be approximated by simple geometrical shapes. The direct calculation of the mean free path of a Xe atom was used if the zeolite cavity could be approximated by spherical or cylindrical geometries. An example is a faujasite cavity whose supercage can be approximated by a sphere ($6.5 \text{ \AA}$ radius) having four cylindrical openings (radius $3.9 \text{ \AA}$) at 109° from each other. The mean free path of the Xe atom in the

faujasite cavity was calculated based on the geometry of the spherical supercage and the cylindrical windows from the following:

$$i = D_c - D_{Xe} \quad (21)$$

for an infinite cylinder where i is the mean free path of the Xe atom, D_c is the diameter of the cylinder, and D_{Xe} is the van der Waals diameter of the Xe atom = 4.4 Å. In the case of a Xe atom entrapped in a spherical pore:

$$i = \frac{1}{2} (D_s - D_{Xe}) \quad (22)$$

where D_s is the diameter of the spherical cavity. Table 14 compares the mean free path of the Xe atom in a variety of zeolites determined by the computer simulation program (termed method I) with i obtained from calculations using equations 21 and 22.¹⁰⁹ Good agreement is found between these two methods where comparison is possible.

Figure 29 shows a correlation of the mean free path of a Xe atom adsorbed in zeolite cavities (pores) with the δ_z for Xe adsorbed in each zeolite. When Xe is adsorbed in a cavity whose dimensions approach the molecular diameter of the Xe atom (4.4 Å), the mean free path of the Xe atom in

Zeolite	$i \text{ (Å)}^a$	$i \text{ (Å)}^b$
	Method I	Method II
Cylinder		$D_c - 4.4$
Sphere		$\frac{1}{2}(D_s - 4.4)$
Mordenite Z Channel	<u>2.45</u>	<u>2.50</u>
Mordenite L Channel	<u>3.10</u>	
Faujasite	<u>5.6</u>	
A	<u>3.7</u>	<u>3.5</u>
Ferrierite Cavity		(1.3 - 3.3)
Ferrierite Channel		<u>0.5</u>
Rho Sphere		(2.0 - 2.5)
Rho Prism		<u>0.1</u>

a. Method I is the mean free path of a Xe atom in the zeolite cavity by use of computer simulation.

b. Method II is the mean free path of a Xe atom in the zeolite cavity determined from the ^{129}Xe NMR chemical shift extrapolated to $[\text{Xe}] = 0$ (determined from Figure 29).

— are exact values of the mean free path of a Xe atom in the zeolite, the void zeolite cavity space being well defined.

== is an approximate value

() are values difficult to calculate due to an irregular zeolite structure and so a range is given.

Table 14. The Mean Free Path of a Xe Atom Trapped in Various Zeolites Calculated From the Zeolite Structures.¹⁰⁹

this pore approaches zero. This is observed for Xe adsorbed in a rho prism zeolite which has a $3.9 \times 5.1 \text{ \AA}$ base with a $3.2 \text{ \AA}$ height. The ^{129}Xe NMR chemical shift is largest for this rho zeolite ($\delta_Z = 230 \text{ ppm}$) resulting from a rapid collision frequency on the NMR time scale between the Xe atom and the zeolite pore wall. The other extreme case is where the mean free path of a Xe atom in a solid approaches ∞ where the ^{129}Xe NMR chemical shift is indistinguishable from Xe not adsorbed in a pore. In practice, when Xe is entrapped in pores $> 20 \text{ \AA}$ in diameter, the collision frequency of a Xe atom with the pore wall is not frequent enough on the NMR time scale at and below room temperature to cause an NMR detectable perturbation to the ^{129}Xe nucleus. The ^{129}Xe NMR chemical shift remains constant (neglecting Xe-Xe collisions) for Xe entrapped in any pore $> 20 \text{ \AA}$ in diameter. This NMR technique is capable of determining unknown micropore diameters of solids ($20 \text{ \AA} > \text{pore diameter} > 4.4 \text{ \AA}$) by correlating the δ_Z of the solid obtained at ambient temperatures with the mean free path of the Xe atom from Figure 29.

Fraissard *et al.* have shown ^{129}Xe NMR spectroscopy to be a powerful tool for determining micropore dimensions of zeolites. ^{129}Xe NMR spectroscopy has also been

Figure 29. a: The Variation of the ^{129}Xe NMR Chemical Shift Extrapolated to Zero Xe Gas Concentration (δ_z) Against the Mean Free Path ($\bar{l}$) of a Xe atom in Zeolite Pores of Known Dimensions. b: δ_z^{-1} versus $\bar{l}$ (Slope = $2.05 \times 10^{-3} \text{ ppm}^{-1}/\text{\AA}^{-1}$ and Y-Intercept of $4.22 \times 10^{-3} \text{ ppm}^{-1}$). 105/69

successfully applied to determine short distance crystallinity, structural defects, and cationic field strengths in zeolites.⁹³

Experimental

VI. Sample Origins

All coal samples were obtained from the Argonne National Laboratory Premium Coal Sample Program. The Ultimate analysis of the Argonne coals is presented in descending rank order in Table 15 on a dry mineral matter free (dmmf) basis. These coals were received in sealed ampules under a N_2 gas atmosphere pre-ground to -100 Tyler standard mesh (coal particles $> 174 \mu m$ in diameter). All coal sample ampules were opened and stored in a glovebox filled with nitrogen gas to minimize exposure to air. The Spherocarb sample was obtained from Analabs Inc., received and used at -60 Tyler standard mesh ($246 \mu m$ diameter particles).

VII. ^{129}Xe NMR Spectroscopy of Coals

A. Sample Preparation

Air Products 99.995% xenon gas was used in all experiments. Variable pressure NMR sample tubes were designed in this laboratory (Figure 30) and used in all experiments. Approximately 1.5 grams of each coal or 1

Coal	%C	%H	%N	%S ^b	%Cl	%F	%O ^c
Pocahontas No. 3	91.8	4.48	1.34	0.51	0.20	0.00	1.66
Upper Freeport	88.1	4.84	1.60	0.76	0.00	0.00	4.72
Lewiston-Stockton	85.5	5.44	1.61	0.67	0.13	0.00	6.68
Pittsburgh No. 8	85.0	5.43	1.68	0.91	0.12	0.00	6.90
Blind Canyon	81.3	5.81	1.59	0.37	0.03	0.00	10.88
Illinois No. 6	80.7	5.20	1.43	2.47	0.06	0.00	10.11
Wyodak-Anderson	76.0	5.42	1.13	0.48	0.03	0.00	16.90
Beulah-Zap	74.1	4.90	1.17	0.71	0.04	0.00	19.13

^a Coal samples presented on a dry mineral matter free (dmmf) basis.

^b % Organic Sulfur

^c % Oxygen calculated by difference.

Table 15. Ultimate Analysis of Argonne Coals.³

Figure 30. Illustration of a Variable Pressure NMR Sample Tube

Used for the ^{129}Xe NMR Spectroscopic Studies.

gram of the Spherocarb sample was transferred into the variable pressure NMR tubes in a glovebox filled with nitrogen gas using a 9 inch flared pasteur capillary pipette. The flared pipette was used to minimize coal adhering to the sides of the NMR tube above the excitation coils of the instrument. The threaded NMR sample tube cap was closed in the glovebox under a nitrogen gas atmosphere. The sample tube was immediately transferred to a vacuum apparatus for degasing.

The Spherocarb, Upper Freeport coal, and Illinois No. 6 coal were degased for no less than 6 hours at 10^{-5} torr on an all glass vacuum line equipped with a diffusion pump and a Barocel pressure sensor to measure xenon gas pressures. All the other coal samples were degased overnight at 10^{-6} torr on a Micromeritics Digisorb 2500 stainless steel vacuum apparatus equipped with an air cooled diffusion pump and a Datametrics differential capacitance-type pressure sensor to determine xenon gas pressures. All samples were otherwise untreated.

The samples were exposed to Xe gas on a Digisorb 2500 vacuum apparatus at room temperature. The Xe gas uptake was monitored as a function of time. The NMR sample tube cap was closed and the sample removed from the vacuum apparatus when no change in pressure was observed over a 30

minute time period, typically requiring a minimum exposure of 4 hours for the first Xe gas exposure. After acquiring the ^{129}Xe NMR spectrum, the NMR sample tube containing the coal was replaced on the vacuum apparatus, exposed to a greater xenon gas pressure, and equilibrated as previously described. Xe gas pressures greater than 1 atmosphere could not be directly measured on the adsorption apparatus without causing damage to the pressure manometers. Xe gas pressures greater than one atmosphere pressure were calculated using the Ideal Gas Equation. The dead volume above the coal in the NMR tube was calculated based on volume of a cylinder (the NMR sample tube) using Wilmad specifications for the internal radius of the NMR tube and the height above the coal. The number of moles of Xe added to the NMR tube were calculated by charging the calibrated volume of the adsorption apparatus with a known pressure of Xe gas. The known amount of Xe was condensed into the NMR tube by using liquid nitrogen cooling.

B. NMR Operating Parameters

All ^{129}Xe NMR spectra were obtained on a Bruker AM series 500 NMR spectrometer operating at 138.37 MHz. A sweep width of 83333.33 Hz (600 ppm) and a 90° pulse angle

were employed in all spectral accumulations. A two second recycle delay was used between pulses. The recycle delay was determined to be greater than $5 T_1$'s for the Argonne Illinois No. 6 coal and was assumed to be sufficient for the other coals. Typically, 1000-2000 transients were required for each coal to obtain a satisfactory signal-to-noise ratio while the Sphero carb sample required 300-500 spectral accumulations. A line broadening factor of 300 Hz was used for the Xe-coal spectra which was less than 5% of the natural line width of all the coals studied.

VIII. BET Tiling Experiment

A. Origin and Purification of Adsorption Gases.

The BET adsorbate gases were obtained from various sources: Aldrich gold label (99.9% minimum purity) cyclohexane; TCI American (99% minimum purity) cyclopentane; Columbia Organic (99.9% minimum purity) cyclobutane; Matheson Gas Company (99.9% minimum purity) cyclopropane; Blue Valley Company (99.998%) carbon dioxide; Blue Valley (99.999%) nitrogen; Matheson (99.99%) ethane; and Blue Valley Company (99.995%) helium. In a glovebag under a nitrogen atmosphere, cyclohexane, cyclopentane, and

cyclobutane, which are liquids at room temperature, were transferred to stainless steel gas collection bulbs pre-rinsed with a minimum of 5-20 ml aliquots of the transferred solvent. A brass $\frac{1}{4}$ inch standard Swagelok ball valve was placed on the stem of the gas collection bulb and closed in a glovebag filled with nitrogen gas. The gas bulb containing the adsorption solvent was connected to the Digisorb 2500 adsorption apparatus using a stainless steel flexible tube having standard $\frac{1}{4}$ inch Swagelok fitted ends. Purification of the adsorbate liquid was accomplished using a minimum of 5 consecutive freeze-pump-thaw cycles of the adsorbate under a diffusion pump vacuum of 10^{-6} torr.¹¹⁰ The listed gases were used as received with no further purification.

B. BET Gas Adsorption of Coals

The surface areas of the Argonne coals were determined using standard 5-point volumetric BET gas adsorption techniques.^{42,44} The adsorbate gases consisted of a homologous series of cyclic aliphatic alkanes (cyclopropane to cyclohexane), ethane, N_2 and CO_2 . The Argonne coals were transferred into an adsorption sample tubes in a nitrogen gas filled glovebox to prevent air oxidation of

the samples. All coal samples except the Illinois No. 6 coal were degased overnight at room temperature under a vacuum of 10^{-6} torr on a Micromeritics Digisorb 2500 stainless steel gas adsorption apparatus and were otherwise untreated. The vacuum apparatus was equipped with a Datametric's differential capacitance-type pressure sensor capable of measuring pressure differences as small as 10^{-4} torr. Twenty four hours equilibration for the first adsorption point and six hours equilibration for each subsequent point were allowed for the cyclic hydrocarbon gases. Six hours equilibration between adsorption points was used for all other gases except N_2 . The nitrogen surface areas of all the coals were determined using the Micromeritics Digisorb 2500 automated 5-point BET N_2 gas adsorption program.

The surface area measurements for the Illinois No. 6 coal were determined on an all glass vacuum apparatus equipped with a diffusion pump and a Barocel pressure sensor to measure the uptake of the adsorbate gases. The Illinois No. 6 coal samples were degased overnight at room temperature under a vacuum of 10^{-5} torr prior to the surface area determinations and were otherwise untreated. Six hour equilibration between each gas adsorption point was allowed for all the adsorbate gases except N_2 which was

determined on the Digisorb 2500.

The cross sectional area of the adsorbate molecules was determined using the method described by Emmett and Brunauer¹¹¹ which assumes the average cross sectional area of the adsorbed molecule corresponds to the plane of closest packing in the liquefied or solidified gas by the equation:

$$S = (4)(.866) \left(\frac{M}{4 \sqrt{2} A D} \right)^{\frac{2}{3}} \quad (22)$$

where S is the cross sectional area of the adsorbate, M is the molecular weight of the adsorbate, D is the density of the liquefied or solidified gas, and A is Avagadro's number. The densities of the liquefied hydrocarbon gases were obtained from reference 112.

IX. Small Angle X-ray Scattering of Coal Surfaces

The small angle X-ray scattering (SAXS) studies of the Argonne coals were performed at the Brookhaven National Laboratory (BNL) Facilities as a colaborative effort with Dr. K. Liang and Dr. P. Hall.¹¹³ A 2.5 GeV X-ray beam source was provide from the radiation emmitted from the BNL synchrotron light source. Argonne coal sample vials which

were sealed under nitrogen gas were opened in air and immediately transferred to an X-ray sample cell. The X-ray sample cell consisted of two aluminum plates having approximately 2 cm Kapton windows for the X-ray beam to enter and exit the sample cell. The X-ray scattering from the coal samples was determined by computer controlled monitoring the number of radioactive counts from the Geiger counter detector as a function of the angle of the detector with respect to the incident electron beam.

Results and Discussion

X. The Determination of the Fractal Dimensionality of the Argonne Coal's Surface by Small Angle X-ray Scattering Techniques.

All reactions involving solid coal require that the reagent first encounter the coal surface. The area of the coal surface accessible to interacting molecules and the types of interactions which occur on contact are important, often crucial parameters in predicting coal reactivity. The fractal dimensionality value of a surface is a way of expressing the different surface areas of a solid defined by adsorbed compounds of different sizes. A perfectly smooth flat surface will have a fractal dimensionality of 2.0. As a surface becomes more irregular, its fractal dimensionality increases, eventually approaching 3.0. For a perfectly smooth flat surface, the measured surface area will be independent of the size of the adsorbate molecule. As a surface becomes more convoluted or space filling, the surface contacted by a molecule becomes less as the size of the molecule increases (see Figure 22). The fractal dimensionality value of a surface provides a quantitative

measure of the degree of surface convolution or roughness. To define more precisely coal pore systems, a small angle X-ray scattering (SAXS) study was performed on five of the Argonne coals to determine the fractal dimensionalities of the coal surfaces.

Bale has demonstrated that the SAXS curve of Beulah Zap lignite can be described as a surface having a fractal dimensionality of 2.56.⁸⁹ The power law dependence of the X-ray scattering intensity on the scattering angle is indicative of pores bounded by noninteger dimensional surfaces (see Figure 24). We have performed a SAXS study of five Argonne coals varying in rank from 88.1% C (dmmf) to 74.1% C (dmmf) to determine the fractal dimensionality of the coal surfaces.

The SAXS studies were performed as a collaborative effort with Dr. Ken Liang¹¹³ and Dr. Peter Hall¹¹⁴. Figure 31 shows the SAXS curve of an Argonne Beulah Zap lignite. Similar to Bale's findings, a power law dependence was found between the X-ray scattering intensity ($I(q)$) and the scattering vector h where:

$$h = \frac{4\pi \sin \theta}{\lambda} \quad (24)$$

Figure 31. The X-ray Scattering Intensity as a Function of the X-ray Scattering Vector for Argonne Beulah Zap Lignite. 7/3

λ is the X-ray wavelength and θ is the scattering angle.¹¹⁴ The linearity of the SAXS curve indicates that the pores in this Beulah Zap lignite are bounded by a fractal surface. The fractal dimensionality of a surface is determined from the slope of $\log I(q)$ vs. $\log h$ from Equation 17 where:

$$\text{dimensionality} = 6 + \text{slope} \quad (25)$$

The slope of the X-ray scattering curve for the Beulah Zap lignite (Figure 31) is -3.65 giving a surface dimensionality of 2.35. The linearity of the power law dependence of the X-ray scattering intensity on the scattering vector indicates that pores, ranging from 1000 Å to 30 Å, in this Beulah Zap lignite are bounded by a fractal surface of dimensionality 2.35.

The SAXS curves of Argonne Wyodak-Anderson, Illinois No. 6, Pittsburgh No. 8, and Upper Freeport coals are shown in Figures 32 - 35 respectively. Similarly to the Beulah Zap coal, a linear dependence of $\log I(q)$ on $\log h$ is observed for all the coals examined in this study. The linearity of the SAXS data of these Argonne coals (Figures 31 - 35) indicates that pores ranging from 1000 Å to 30 Å in all these coals are bounded by fractal surfaces.

Figure 32. The X-ray Scattering Intensity as a Function of the X-ray Scattering Vector for Argonne Wyodak-Anderson Subbituminous Coal.¹¹³

Figure 33. The X-ray Scattering Intensity as a Function of the X-ray Scattering Vector for Argonne Illinois No. 6 Bituminous Coal.¹¹³

Figure 34. The X-ray Scattering Intensity as a Function of the X-ray Scattering Vector for Argonne Pittsburgh No. 8 Bituminous Coal.¹¹³

Figure 35. The X-ray Scattering Intensity as a Function of the X-ray Scattering Vector for Argonne Upper Freeport Bituminous Coal.¹¹³

The results of a fractal analysis of the Argonne coals are summarized in Table 16. The fractal dimensionalities of all the coals studied are between 2 and 3 as expected for fractal surfaces.⁸⁴ The Illinois No. 6 coal has the most convoluted surface ($D = 2.87$) of the coals studied and the Beulah zap lignite was found to have the least convoluted surface ($D = 2.35$).

XI. Fractal Analysis of the Argonne Coals Using Classical Gas Adsorption Techniques.

A. Choice of Adsorbate gases.

Gas adsorption techniques have been used to measure the dimensionality of many fractal surfaces.^{85,86,88,115} The measured surface area of any surface having a fractal dimensionality greater than 2 is dependent on the size of the adsorbate probe. The relationship between the measured surface area of a fractal solid and the dimensionality of the surface is given by Equation 16. A plot of the log of the number of molecules required for monolayer surface coverage (n , obtainable from the BET equation) vs. the log of the cross sectional area of the adsorbate (σ) will have a slope of $-D/2$ where D is the fractal dimensionality of

Argonne Coal	% C (dmmf)	Slope of X-ray Curve ^a	D _{SAXS}	Correlation Coefficient
Upper Freeport	88.1	-3.42	2.58	-0.999
Pittsburgh No. 8	85.0	-3.31	2.69	-0.999
Illinois No. 6	80.7	-3.13	2.87	-0.999
Wyodak-Anderson	76.0	-3.44	2.56	-0.999
Beulah Zap	74.1	-3.65	2.35	-0.999

a. The slope of $\log I(q)$ vs. $\log h$.

Table 16. Fractal Dimensionalities of the Argonne Coals
Determined from SAXS Curves Corresponding to
Coal Pore Diameters Ranging From 1000 Å to 30 Å.

the surface.⁸⁴

Applying gas adsorption techniques to determine the fractal dimensionality of a surface requires a careful choice of adsorbate probes. It is best if the adsorbate probes consist of an isotropic series of molecules which means the adsorbates must vary in size but be geometrically similar in shape.⁸⁶ The series of surface area probe molecules must not chemically interact with the adsorbent surface. Molecules which specifically interact with an adsorbent report surface areas which are erroneously too large due to a combination of adsorption and absorption by the solid. Solvent absorption in coals produces swelling (or expansion of the coal macromolecular network) resulting in adsorbate penetration into volumes where porosity and surface area did not originally exist.⁶¹

Considering adsorbate shapes and interactions, a homologous series of small cyclic hydrocarbons, cyclopropane to cyclohexane, was chosen to determine the fractal dimensionalities of the Argonne coals by gas adsorption. These nonpolar cyclic hydrocarbons are flat, or nearly so, and should be accessible to slit-like coal pores described by Bond's model (Figure 9).³⁸ Nonpolar saturated hydrocarbons are not expected to interact chemically with coals. Lucht and Peppas studied the

swelling of 14 coals varying in rank from 69.9% C (dmmf) to 94.2 %C by cyclohexane at 35°C.¹¹⁶ They determined that cyclohexane was a poor swelling solvent for all the coals studied. The degree of coal swelling by cyclohexane determined by the volumetric swelling ratio (described by Equation 3) had a maximum value of 1.2 for coals 69.9% C to 73% C (dmmf) and rapidly decreased to a value of 1.0 for coals greater than 77.0% C (dmmf). A swelling ratio of 1.0 represents a volumetric coal expansion of 0%. Larsen *et al.* found small volumetric swelling ratios varying from 1.0 to 1.2% volumetric coal expansion for an Illinois No. 6 coal (Figure 4) and a Bruceton coal (83.1% C, daf) by nonpolar organic solvents including cyclohexane.²⁹ The low volumetric swelling ratios indicate a lack of specific interactions between coals and nonpolar solvents. The use of nonpolar adsorbates removes complications arising from adsorbates capable of dissolving in coals rather than being adsorbed on their surface.

B. Fractal Analysis of the Gas Adsorption Data on the Argonne Coals.

BET surface areas of the Argonne coals were determined

using nitrogen, carbon dioxide, cyclopropane, cyclobutane, cyclopentane, cyclohexane, and ethane. The cross-sectional areas of the adsorbate molecules were determined by the method described by Emmett and Brunauer which considers the area of an adsorbed molecule to be the same as the plane of closest packing in the liquefied or solidified adsorbate gas (see Equation 23).¹¹¹ The determination of adsorbate cross-sectional areas using Equation 23 has been widely used to determine the surface area of solids.^{46,117,118} Table 17 lists the adsorbate gases used to determine the surface areas of the Argonne coals and their corresponding cross-sectional areas determined by Equation 23.

A fractal analysis of the gas adsorption data for all the coals was performed applying Equation 16. Plotting the log of the number of moles required for monolayer coverage (n) against log of the cross sectional area of the adsorbate molecule (σ) will have a slope of $-D/2$, where D is the fractal dimensionality of the surface.⁹⁰ A typical result of this fractal analysis on an Argonne Pittsburgh No. 8 coal is presented in Figure 36. The experimental adsorption temperature and the measured coal surface area are given for each adsorbate gas. N_2 and CO_2 surface areas were determined to check our results with published literature values of similar rank coals. Both measured N_2

Adsorbate Gas	Molecular Weight (g/mol)	Density ^a (g/cm ³)	σ^b (Å ²)
Cyclohexane	84.2	0.795	34.3
Cyclopentane	70.1	0.760	31.2
Cyclobutane	56.1	0.725	27.8
Cyclopropane	42.1	0.630	25.2
Ethane	30.1	0.448	25.3
Carbon dioxide	44.0	0.662	25:1
Nitrogen	28.0	0.813	16.2

a. Liquid densities of the Adsorbate gases were obtained from reference 111.

b. The cross-sectional area of the adsorbate gases were determined using Equation 23.

Table 17. The Cross-Sectional Areas of the Adsorbate Gases Used to Determine the Surface Areas of the Argonne Coals.

Figure 36. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Pittsburgh No. 8 Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

and CO_2 surface areas for this Pittsburgh coal are within the surface area ranges for 83% C (daf) coals correlated by Gan, Nandi, and Walker (Figure 12).⁵¹

Carbon dioxide adsorption is believed to measure the total surface areas of coals based on the agreement between CO_2 adsorption, SANS, and SAXS surface areas of coals^{57,59,61} (see however reference 57). The cross-sectional areas of CO_2 and cyclopropane are very similar ($25.1 \text{ \AA}^2$ and $25.2 \text{ \AA}^2$ respectively, determined from Equation 22). Despite the similar size of CO_2 and cyclopropane, the surface area of this Pittsburgh coal determined by CO_2 adsorption was 6 times larger than the coal surface area determined by cyclopropane adsorption (see Figure 36). If CO_2 measures the total surface area of coals, then cyclopropane is not accessible to all of the Pittsburgh coal's porosity. It is possible that the cyclopropane surface area is much smaller than the CO_2 surface area for this Pittsburgh coal simply due to the difference in the geometrical shape of the two adsorbate molecules. Bond's pore model (Figure 9) describes coals as molecular sieves having slit-like pores connected by capillary constrictions (bottle-necked pores).³⁸ Cyclopropane, which is flat, may not be able to penetrate into the bottle-necked pore system of coals, while the cylindrical CO_2 molecule is not

restricted by capillary coal pore constrictions.

Ethane adsorption was chosen to determine if the geometrical shape of the adsorbate probe is responsible for the low surface area of the Pittsburgh coal determined by cyclopropane adsorption. Ethane, cyclopropane, and CO_2 are all of similar cross-sectional area (the cross-sectional area of ethane is $25.3 \text{ \AA}^2$). Ethane and CO_2 are both cylindrical in shape. The mean molecular diameter of ethane and CO_2 are $4.42 \text{ \AA}$ and $3.95 \text{ \AA}$ respectively based on the Lennard-Jones force constants from gas viscosity measurements.⁷⁴ Ethane and cyclopropane, both being nonpolar saturated hydrocarbon gases, are expected to have the same interactions with coals. The measured ethane and cyclopropane BET surface areas of the Pittsburgh No. 8 coal are very similar ($37 \text{ m}^2/\text{g}$ and $31 \text{ m}^2/\text{g}$ respectively). Based on the close agreement of the ethane and cyclopropane coal surface areas, the geometrical shape of the adsorbate probe cannot be governing the measured coal surface area.

To determine if adsorption on the Pittsburgh coal surface was responsible for the difference between the CO_2 surface area and the measured hydrocarbon surface areas, a fractal analysis of the BET gas adsorption data was performed. The fractal dimensionality of a surface can be determined by gas adsorption as demonstrated in Figure 23.

A plot of the log of the moles required for monolayer coverage (n) against the log of the cross-sectional area of the adsorbate gases (σ) will have a slope of $-D/2$ where D is the fractal dimensionality of the surface. Figure 36 shows the fractal analysis of the Pittsburgh coal based on the adsorption of the cyclic hydrocarbon gases. The slope of the plot in Figure 36 was -7.9 which corresponds to a fractal dimensionality of 16 for this Pittsburgh coal. This is an impossible dimensionality value for any surface and contradicts the fractal dimensionality of 2.69 determined from our SAXS study (Figure 34). The impossibly high dimensionality value of 16 for the Pittsburgh coal indicates that the surface areas measured by the hydrocarbon gases are not governed by the surface geometry of the coal.

The observed steep surface area dependence on the size of the hydrocarbon adsorbate gases is similar to the dependence of diffusion rates on penetrant size through glassy polymers (see Figures 16 and 17). Coals are glassy polymers under these experimental conditions.^{19,23} Smaller molecules diffuse faster through glassy polymers than larger molecules^{74,78} and would report higher (non-equilibrium) surface areas. The hydrocarbon gases reach only a small portion of the pores in the Pittsburgh coal,

that portion depending on their diffusion rates. CO_2 , being slightly soluble in coals, can rapidly diffuse through coals reaching pores which are closed to insoluble molecules.^{60,61} Due to the solubility of CO_2 in coals, surface areas determined by CO_2 adsorption will be overestimated, but this effect is thought to be small.⁶¹

The only other explanation for the steep surface area dependence on hydrocarbon adsorbate size (Figure 36) is that coal surface areas are not being measured, just the solubility of the probe molecule in the coal. This argument is controverted by recent neutron diffraction studies of coal pores and the agreement between CO_2 surface areas and those determined from SAXS and SANS experiments (Table 6, page 54).^{57,119} Winans stirred an Argonne Pittsburgh No. 8 coal (85% C, dmmf) with d_6 -benzene (a non-swelling solvent) and d_5 -pyridine (a good coal swelling solvent) to study the neutron scattering by the deuterated solvents in the Pittsburgh coal.¹¹⁹ The d_6 -benzene and d_5 -pyridine have similar neutron scattering length densities ($5.35 \times 10^{10} \text{ cm}^{-2}$ and $5.69 \times 10^{10} \text{ cm}^{-2}$ respectively) but gave very different SANS curves. Based on the shapes of the SANS curves of both deuterated solvents in the Pittsburgh coal, Winans suggested that the deuterated benzene and deuterated pyridine are both located in coal

pores. The pyridine swollen Pittsburgh coal has a different SANS shape than the benzene-coal mixture due to pyridine's ability to cause coal structural rearrangements which change the geometry of the coal pores from roughly spherical (for untreated coals) to elongated, cylindrical pores in the presence of good swelling solvents like pyridine.¹¹⁹

A steep dependence of the measured hydrocarbon surface areas on adsorbate size was found for all the Argonne bituminous coals. The fractal analysis of Argonne: Pocahontas No. 3; Upper Freeport; Lewiston-Stockton; Blind Canyon; and Illinois No. 6 coals are presented in Figures 37 - 41 respectively. The N_2 and CO_2 surface areas of all these Argonne bituminous coals are within the range reported by Gan, Nandi, and Walker for coals of similar rank (Table 6).⁵¹ Periodically, determinations of coal surface areas were repeated to check for reproducibility. Duplicate surface areas are marked with an asterisk and the average value of the duplicates are reported. All duplicate surface areas of the coals were found to be within $\pm 3 \text{ m}^2/\text{g}$ of their average value.

The surface areas of the bituminous coals determined by the adsorption of the hydrocarbon gases are much less than the corresponding coal surface areas determined by CO_2

Figure 37. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Pocahontas No. 3 Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

Figure 38. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Upper Freeport Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

Figure 39. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Lewiston-Stockton Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

Figure 40. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Blind Canyon Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

Figure 41. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Illinois No. 6 Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

adsorption. In some cases, the ethane surface areas of the coals were greater than the corresponding cyclopropane surface areas which may be attributable to the difference in shape of these two hydrocarbons. In all cases, ethane and cyclopropane reported much lower coal surface areas than CO_2 . The diffusion of the linear ethane through the coals may be along its "long" axis allowing ethane to diffuse more quickly through the coals than cyclopropane. Hopfenberg has seen this effect with the diffusion of linear alkanes through polymers.⁷⁴

A fractal analysis was performed based on the cyclic hydrocarbon adsorption on the coals and the dimensionality values are presented in Table 18 along with the dimensionalities determined by SAXS. All of the fractal dimensionality values determined by gas adsorption on the Argonne coals are impossibly large, ranging from 11 to 23. Based on the same rationale presented for the Pittsburgh No. 8 coal, the porosity of these bituminous coals are not accessible by diffusion through a pore network but can only be reached by diffusion through solid coal. It is the diffusion rates of the adsorbate molecules through the coals that govern the measured surface area of that coal.

To verify slow diffusion of the hydrocarbon gases

Coal	%C dmmf	D SAXS	D Ads.	Slope Ads.	Correlation Coefficient ^a
Pocahontas					
No. 3	91.8	----	12	-5.8	-0.998
Upper					
Freeport	88.1	2.58	11	-5.5	-0.995
Lewiston-					
Stockton	85.5	----	15	-7.4	-0.942
Pittsburgh					
No. 8	85.0	2.69	16	-7.9	-0.987
Blind					
Canyon	81.3	----	14	-6.7	-0.990
Illinois No.6	80.7	2.87	23	-11.6	-0.999
Wyodak-					
Anderson	76.0	2.56	11	-5.3	-0.867
Beulah Zap	74.1	2.35	---	----	-----

a. Linear correlation coefficient of the fractal analysis based on the cyclic hydrocarbon gas adsorption.

Table 18. Comparison of the Fractal Dimensionalities of the Argonne Coals Determined by SAXS and Gas Adsorption of Cyclic Hydrocarbon Gases (Cyclopropane - Cyclohexane)

through the bituminous coals, ethane uptake on an Argonne Illinois No. 6 coal was followed for 130 hours at 177 K and the data are presented in Table 19. The Illinois No. 6 coal was evacuated overnight at 10^{-5} torr on an all glass adsorption apparatus equipped with a Barocel diaphragm pressure sensor capable of measuring gas pressures as low as 10^{-3} torr. Since the ethane adsorption experiment was conducted at a pressure below 1 atmosphere, any leaks in the sample holder containing the Illinois No. 6 coal or vacuum system would be manifested as an increase in pressure. Ethane adsorption was continuous during the course of this experiment and had not reached equilibrium when the experiment was terminated. The uptake of the cyclic hydrocarbon gases was also monitored for the first 24 hours of the surface area measurements for the Argonne coals. A diffusion analysis of the uptake of the cyclic hydrocarbon gases on the Argonne coals verifying slow diffusion of the hydrocarbons through the bituminous coals will be presented and discussed in the next section of this thesis.

A fractal analysis of the adsorption of the cyclic hydrocarbon gases on Argonne Beulah Zap lignite and Argonne Wyodak-Anderson subbituminous coals is presented in Figures 42 and 43 respectively. The N_2 and CO_2 surface areas for

Time (hours)	Ethane Gas Pressure (Torr)
0	99.429
0.02	40.090
0.08	36.748
0.17	35.502
0.33	34.162
0.75	32.098
1.0	30.923
1.5	30.068
2.0	29.360
3.0	28.431
4.5	27.650
6.3	25.320
8.0	25.268
27	24.083
54	23.262
108	23.143
131	23.098

Table 19. Ethane Uptake as a function of time on 0.1190 g
of Argonne Illinois No. 6 Coal at 177 K.

Figure 42. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Beulah Zap Lignite (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

Figure 43. Fractal Analysis of the Cyclic Hydrocarbon Gas Adsorption on Argonne Wyodak-Anderson Coal (n is the Number of Moles Required for Monolayer Surface Coverage Obtained from the BET Equation). The Adsorbate Gas is Given Followed by the Adsorption Temperature and the Measured BET Surface Area.

both coals are within the ranges reported in the literature by Gan, Nandi, and Walker for coals of similar rank (see Table 6).⁵¹ The measured surface areas of the Beulah Zap lignite by the cyclic hydrocarbon gases varied from 5 m²/g to 8 m²/g and are identical within experimental error. These coal surface areas are about 50 fold less than their corresponding areas measured by CO₂ adsorption. One explanation for the invariance of the measured surface area on the size of the cyclic hydrocarbon adsorbates is that the Beulah Zap lignite has a dimensionality of 2.0. This is inconsistent with the fractal dimensionality of 2.35 for the Beulah Zap lignite measured by our SAXS studies and inconsistent with the area measured with CO₂. The high oxygen content of this lignite (21%) makes this coal a polar material. It is likely that this high polarity makes the nonpolar hydrocarbons insoluble in the coal, preventing the penetration of the nonpolar hydrocarbon gases into the coal. Only the external portion of the Beulah Zap lignite surface is covered by the hydrocarbon gases, and they accurately report a low coal surface area. The variation in the low surface areas expected for this low dimensional lignite surface are too small to be resolved by an experiment as imprecise (± 3 m²/g) as the gas adsorption technique used.

The surface areas measured by adsorption of the cyclic hydrocarbon gases on the Wyodak subbituminous coal (Figure 43) were much more scattered than the results for the other coals. Similar to the Beulah Zap lignite, this subbituminous coal has a high oxygen content (19%, daf). This subbituminous coal exhibits a transitional behavior between the linearity observed for the fractal analysis of the cyclic hydrocarbon adsorption on the bituminous coals (having oxygen contents ranging from 3 to 13%, daf) and the hydrocarbon surface area invariance found for the Beulah Zap lignite.

XII. Diffusion Analysis of the Cyclic Hydrocarbon Sorption by the Argonne Coals.

A. The Measurement of the Cyclic Hydrocarbon Uptake as a Function of Time by the Argonne Coal.

While determining the surface areas of the Argonne coals, the uptake of the cyclic hydrocarbons was monitored as a function of time to determine the transport mechanisms (Fickian, anomalous, or Case II) of these nonpolar gases through the coals. The uptake of the cyclic hydrocarbons on all the coals was determined at penetrant relative pressures ($\frac{P}{P^0}$, where P is the measured pressure and P^0 is

the saturated vapor pressure of the adsorbate gas) ranging 0 to 0.06 - 0.11. To determine the surface areas of the Argonne coals by the BET method (Equation 5), the volume of the gas adsorbed within an adsorbate relative pressure range of 0.05 - 0.35 is monitored.⁴⁴ The BET theory of gas adsorption is typically performed at $0.35 \leq \frac{P}{P^0} \leq 0.05$ to prevent multilayer adsorption on the solid surface.⁴⁵ To obtain adsorbate relative pressures between 0.05 to 0.35, the gas adsorption experiments were performed at temperatures below room temperature. Cyclopropane, ethane and CO₂ were used at -78°C by submerging the coal samples in a dry-ice/acetone bath. Cyclobutane uptake by the coals was studied at a temperature of -10°C using a saturated NaCl/ice water bath. Cyclopentane and cyclohexane uptake experiments were performed at 0° C using an ice water bath. All constant temperature baths were well stirred during the adsorption experiments. Adsorbate relative pressures at the experimental temperature were calculated using the Clausius-Claperon equation:

$$\log P^0 = - \frac{a}{T} + b + c \log T + D(T) \quad (26)$$

where P^0 is the adsorbate saturated vapor pressure, T is the adsorption temperature in degrees Kelvin, a , b , c , and d are the virial coefficients of the adsorbate gases

obtained from reference 120.

The manifold of the Digisorb 2500 adsorption apparatus has a calibrated volume of 29.542 cm³ which is maintained at a constant temperature of 40° C by the instrument. A temperature gradient is established between the Digisorb 2500 manifold (40° C) and the sample holders containing the coals (-78° to 0°C, depending on the identity of the adsorbate gas). The standard procedure to correct for the temperature difference between the manifold and the coal samples is to calculate what the sample volume of the coal and the dead volume of the sample container would be if the experiment were performed with no temperature gradient using helium gas and Boyle's law:

$$V_d = \left(\frac{P_d - P_e}{P_e - P_{e'}} \right) V_k \quad (27)$$

where V_k is the calibrated manifold volume, V_d is the helium dead volume, P_d is the helium pressure in the known volume, P_e is the helium equilibrium pressure established by opening the known volume to the unknown volume, and $P_{e'}$ is the previous helium equilibrium pressure.⁴² The helium dead volume is the volume that the sample and the sample holder would occupy if the adsorption experiment were performed at a uniform temperature (the temperature of the

adsorption manifold). The weight of the adsorbate taken up by the coals was determined by:

$$Wt_a = \left(\frac{P_d * V_k}{RT} - \frac{(P_d - P_t) * V_d}{RT} \right) * MW_a \quad (28)$$

where Wt_a is the weight of adsorbate taken up, P_d is the pressure of the adsorbate gas in the known manifold volume V_k , R is the ideal gas constant, T is the manifold temperature in degrees Kelvin, P_t is the adsorbate pressure at time t when the valve connecting the manifold to the sample container is opened, and MW_a is the molecular weight of the adsorbate gas.

The time dependence of cyclohexane uptake by a Pittsburgh No. 8 coal is shown in Figure 44. Cyclohexane uptake by this Pittsburgh coal was continuous during the course of the experiment and had not reached equilibrium after 4 days, at which time the experiment was terminated. Fickian diffusion is characterized by an initial rapid uptake of an adsorbate by a solid which approaches a maximum value when the concentration of the penetrant is uniform throughout the solid (see Figure 13, page 63).⁶⁶ The long continuous uptake of cyclohexane by the Pittsburgh coal is similar to penetrant uptake curves resulting from anomalous diffusion through glassy polymers (Figures 14 and

Figure 44. Cyclohexane Uptake on Argonne Pittsburgh No. 8 Coal at 273K (Relative Pressure 0 $\rightarrow$ 0.1).

Experiment Performed by P. Mulieri at Lehigh University.

15, page 71).^{66,73,74}

The diffusion exponent (n) was calculated by Equation 13 to characterize the diffusional mechanism (Fickian, anomalous, or Case II) of cyclohexane uptake by the Pittsburgh coal. To correct for buoyancy and adsorption of cyclohexane on the Pittsburgh coal, the weight of cyclohexane taken up as a function of time is extrapolated to zero time and subtracted from the uptake data as described by Hopfenberg.⁷⁴ The initial cyclohexane uptake by the Pittsburgh coal before and after the correction for buoyancy and cyclohexane adsorption are shown in Figures 44 and 45 respectively. The diffusional exponent (n) can be determined by Equation 13 by plotting the log of the weight of adsorbate taken up vs. log time, where the resulting slope is equal to n .⁷⁰ If the uptake of a penetrant through a solid is governed by pure Fickian diffusion, n will be equal to 0.43 while if the penetrant uptake is governed by pure Case II relaxation, n will equal 0.85 (see Table 9, page 84). Anomalous diffusion of a penetrant through a spherical solid will have a diffusional exponent between 0.43 and 0.85.⁷⁰ The determination of the diffusional exponent is only valid for analysis of the first 60% of the total uptake by the solid, since molecular diffusion of penetrants (Fickian) is typically much faster

Figure 45. Initial Cyclohexane Uptake by Argonne Pittsburgh No. 8 Coal at 273K. The Cyclohexane Uptake by the Pittsburgh Coal is Extrapolated to Zero Time to Correct for Cyclohexane Adsorption on the Coal Particles.

Experiment Performed by P. Mulieri at Lehigh University.

then polymer (Case II) relaxation.¹²¹

A plot of log the mass of cyclohexane taken up by the Pittsburgh coal vs. log time is shown in Figure 46. The slope of the plot in Figure 46, which is equal to the diffusional exponent, is 0.51. A diffusional exponent of 0.51 indicates that the uptake of cyclohexane in this Pittsburgh coal is governed by anomalous diffusion (Table 9) assuming the shape of the powdered coal particles to be roughly spherical. The grinding and sieving of coals creates particles of various shapes whose overall shape approximates spherical particles.^{49,122} Anomalous diffusion is typically only observed for the uptake of penetrants through polymers below their glass transition temperatures.⁷⁰ There has been a reported case of anomalous uptake of allylchloride by polyvinylacetate (PVA) 10°C above the glass transition temperature of the PVA polymer.¹²³ Coals are glassy at the experimental conditions^{19,23} under which anomalous diffusion of penetrants through glassy polymers are typically observed.^{64,65}

The uptake of cyclopropane, cyclobutane, cyclopentane, and cyclohexane by the Argonne coals as a function of time is presented in Figures 47 - 50 respectively. Cyclohexane uptake by a powdered polystyrene (Supelco Co.) at 273 K was

Figure 46. Determination of the Diffusional Exponent (n) for Cyclohexane Uptake by Argonne Pittsburgh No. 8 Coal at 273K. The Diffusional Exponent was Calculated by Equation 13 Based on the First 60% of the Total Cyclohexane Uptake (Solid Line) as Described by Reference 69.

Figure 47. Cyclopropane Uptake by the Argonne Coals at 195K as a Function of Time.

Figure 48. Cyclobutane Uptake by the Argonne Coals at 263K as a Function of Time.

Figure 49. Cyclopentane Uptake by the Argonne Coals at 273K as a Function of Time.

Figure 50. Cyclohexane Uptake by the Argonne Coals at 273K as a Function of Time.

also examined as a comparison to the coals and is presented in Figure 50. The diffusional exponents of the cyclic hydrocarbon uptakes by the coals were calculated in the same manner previously described for the cyclohexane uptake by the Pittsburgh coal and the results are shown in Table 20. The diffusional exponents were greater than 0.43 indicative of anomalous diffusion except for cyclopentane on the Upper Freeport coal, which is abnormal compared to the other bituminous coals. Based on the diffusional exponent values (Table 20) the uptake of the cyclic hydrocarbon gases by the Argonne coals is characterized by anomalous diffusion. The diffusional exponents calculated for the uptake of the cyclic hydrocarbons on the Beulah Zap lignite were all between 0.31 and 0.44, indicating Fickian diffusion of the cyclic hydrocarbon gases through this lignite.

The extraordinarily steep dependence of the measured surface area on adsorbate size is similar to diffusion rates through glassy polymers on molecular size observed for both Fickian and Case II penetrant sorption into glassy polymers.^{74,78} Anomalous diffusion is typically only observed for the diffusion of organic molecules through glassy polymers^{64,65} (see however reference 123). Coals are glassy polymers under the gas adsorption experimental

Coal	Diffusional Exponent (n)			
	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane
Pocahontas No. 3	0.56	0.55	0.47	0.46
Upper Freeport	0.45	---	0.43	0.47
Pittsburgh No. 8	0.62	---	0.56	0.51
Lewiston-Stockton	0.55	0.60	0.51	0.47
Blind Canyon	0.60	0.58	0.59	0.52
Wyodak-Anderson	0.57	0.55	0.55	0.59
Beulah Zap lignite	0.31	0.44	0.44	0.42
Polystyrene	---	---	---	0.73

Table 20. Diffusional Exponents of the Uptake of the Cyclic Hydrocarbon Gases on the Argonne Coals and a Polystyrene Sample.

conditions described in this thesis.^{19,23} Based on the anomalous diffusion of the cyclic hydrocarbon gases through the bituminous coals, the hydrocarbons may reach only a small portion of the coal pores, that portion being dependent on their diffusion rates. Those diffusion rates fall very quickly as the molecular size increases, as expected for diffusion through a glassy polymer.^{74,78} These slow diffusion rates are responsible for the low hydrocarbon surface coal surface areas compared to the high CO₂ coal surface areas.

Anomalous diffusion of the hydrocarbon gases into the Beulah Zap lignite does not occur, presumably due to the high polarity of this coal (21% O, daf). It is possible that the high polarity of this lignite makes the nonpolar hydrocarbons insoluble in this coal. CO₂ is soluble in coals, diffuses rapidly reaching closed pores, and reports a large total pore surface area.

The gas adsorption studies presented in this thesis indicate that most pores in coals are closed. They cannot be reached by diffusion through a pore network but can only be reached by diffusion through solid coal. The pores in coals may be envisioned as isolated "bubbles" which are not interconnected. CO₂ gives accurate total surface areas of coals because it dissolves in and rapidly diffuses through

solid coals, reaching all the internal coal pores. CO_2 coal surface areas are irrelevant to penetrants which are only slightly soluble or insoluble in coals since these penetrants can only reach a small portion of the total coal porosity. The diffusion rate of an adsorbate through the solid coal controls the determined pore size. For large molecules involved in direct liquefaction and most organic reactions, the effective surface area of these coals is very small, only a few m^2/g .

The consequences of this structural model for coal processing and reactions involving solid coal are significant. Coals cannot be considered high (hundreds of m^2/g) surface area materials having an easily accessible pore network to all reagents. For large and insoluble molecules, these coals will be a low surface area, impermeable solid.

XIII. Determination of the Distribution of Micropores in the Argonne Coals by ^{129}Xe NMR Spectroscopy.

A. The Average Micropore Size of a Standard Carbonaceous Molecular Sieve Determined by ^{129}Xe NMR Spectroscopy.

^{129}Xe NMR spectroscopy has been successfully applied to determine micropore size ($< 20 \text{ \AA}$) and surface characteristics of zeolites.^{93,96,100,107} The factors affecting the measured ^{129}Xe NMR chemical shift of Xe gas adsorbed in a microporous solid are given by Equation 20 (page 104). The two major factors affecting the ^{129}Xe NMR chemical shift in monovalent cationic zeolites are the frequency of Xe-Xe collisions ($\delta_{\text{Xe-Xe}}$) and the frequency of collisions between Xe atoms and micropore walls (δ_s).

The ^{129}Xe NMR chemical shift is quantitatively related to the void volume of the micropore containing the Xe atom(s).^{93,109} The frequency of Xe-Xe atom collisions in a porous solid is dependent on the Xe gas pressure and the pore dimensions. As the concentration of Xe gas in a microporous solid increases, the Xe-Xe atom collision frequency increases. An increase in Xe-Xe atom collisions results in a downfield shift of the measured ^{129}Xe NMR

resonance.^{93,100,107} The contribution of Xe-Xe atom collisions to the measured ^{129}Xe NMR chemical shift can be eliminated by extrapolation of the ^{129}Xe NMR chemical shift to zero Xe pressure. At zero Xe gas pressure, the probability of a Xe-Xe atom collision is zero and the chemical shift at zero Xe concentration (δ_z) is related to the collision frequency between Xe atoms and pore walls. The smaller the pore in which a Xe atom is trapped, the greater will be the collision frequency between Xe atoms and pore walls. As the collision frequency between Xe atoms and pore walls increases, the average distortion to the symmetrical Xe electron cloud increases resulting in a downfield shift in the observed ^{129}Xe NMR spectrum.

Fraissard and co-workers have developed a correlation between the δ_z and the mean free path of a Xe atom entrapped in zeolite cavities of known dimensions (Figure 29, page 118).^{109,124} The mean free path of the Xe atom in the zeolite is related to the average diameter of a cylindrical zeolite cavity by Equation 21 and a spherical zeolite cavity by Equation 22 (page 115).

Zeolites are alumina-silicates and chemically different from carbonaceous materials such as coals. To test this NMR technique on a carbonaceous molecular sieve, a standard 15 Å diameter Sphero carb sample (Analabs

Incorporated) was studied. The ^{129}Xe NMR spectra as a function of decreasing Xe gas pressure are presented in Figure 51 after 300 - 500 NMR spectral accumulations. There is a clear upfield chemical shift of the ^{129}Xe NMR resonance with decreasing Xe gas pressure in this Spherocarb sample. The ^{129}Xe NMR chemical shift extrapolated to zero Xe gas pressure (δ_z) is 57.2 ppm for this Spherocarb sample as shown in Figure 52. This corresponds to a Xe mean free path of $5.5 \text{ \AA}$ based on the relationship graphically illustrated in Figure 29 (page 118). Assuming the shape of the Spherocarb pores to be spherical, an average pore diameter of $15.4 \text{ \AA}$ was calculated from Equation 22 (page 115). This value agrees remarkably well with the pore diameter of $15 \text{ \AA}$ reported by Analabs. The relationship between δ_z and the mean free path of Xe trapped in a pore was found to be a valid means of determining average pore diameters of zeolite cavities and pores in a carbonaceous molecular sieve (Spherocarbs), and this NMR technique was applied to the Argonne coals.

B. Determination of the Average Micropore Diameter of the Argonne Coals.

Figure 51. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in 15 Å Diameter Spherocarbs Shown in Descending Xe Gas Pressure.

Figure 52. ^{129}Xe NMR Chemical Shift Dependence on Xe Gas Pressure for Xe Adsorbed in 15 Å Diameter Spherocarbs.

The ^{129}Xe NMR spectra as a function of decreasing Xe gas pressure on Argonne Pocahontas No. 3 coal are shown in Figure 53. The signal-to-noise ratio of the ^{129}Xe -Spherocarbs NMR spectra was much greater than the signal-to-noise ratio of the ^{129}Xe -coal NMR spectra, despite the fewer spectral accumulations required for the Xe-Spherocarb sample. Spherocarbs have a narrow micropore size distribution while coals have a broad pore size distribution.^{48,59,125} At the same Xe gas concentration, there would be a larger population of Xe atoms in similar environments for Xe trapped in a solid with a narrow micropore size distribution than Xe trapped in a solid with a broad micropore size distribution. The broad coal pore size distribution may be responsible for the poorer signal-to-noise ratio of the ^{129}Xe -coal NMR resonances compared to the ^{129}Xe -Spherocarb resonance.

The resonance furthest upfield in Figure 53 is due to Xe in pores greater than 20 Å in diameter or Xe gas between powdered coal particles and is assigned a chemical shift value of 0 ppm by convention.¹⁰⁰ The downfield resonance in Figure 53 has a ^{129}Xe NMR chemical shift dependence on Xe gas pressure which extrapolates to 162 ppm at zero Xe concentration as shown in Figure 54. The ^{129}Xe NMR

Figure 53. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Pocahontas No. 3 Coal, Shown in Descending Xe Gas Pressure.

chemical shift dependence on Xe gas pressure is typical behavior of Xe in micropores.^{93,126} Based on the center of the downfield resonance, a mean free path of $0.8 \text{ \AA}$ was calculated for Xe in the micropores of the Pocahontas coal by:

$$i = \left(\frac{1}{\delta_z} - a \right) / b \quad (29)$$

where δ_z is the ^{129}Xe NMR chemical shift extrapolated to zero Xe concentration, i is the mean free path of a Xe atom in a micropore, b and a are the slope and intercept of δ_z^{-1} vs. i based on zeolites of known cavity dimensions (Figure 29, page 118). Assuming spherical pores, an average pore diameter of $6.0 \text{ \AA}$ was calculated for this Pocahontas No. 3 coal. Spherical pores were assumed based on recent SANS¹¹⁹ and spin probe electron spin resonance (EPR) methods¹²⁵ which suggest the average shape of untreated coal pores are spherical.

The asymmetry of the ^{129}Xe NMR pressure dependent resonances (Figure 53) made the exact determination of the center of the ^{129}Xe -coal resonance difficult. This uncertainty in determining the center of the Xe-coal

Figure 54. ^{129}Xe NMR Chemical Shift Dependence on Xe Gas Pressure for Xe Adsorbed in Argonne Pocahontas No. 3 Coal.

resonance does not create a problem in determining the average micropore diameter of the Argonne coals since a ± 5 ppm error in determining the center of the Xe resonance would only cause a $\pm 0.16 \text{ \AA}$ difference in the calculated micropore diameter.

This thesis has presented evidence suggesting that the majority of the pores in coals are closed to the external surface and can only be reached by diffusion through solid coal. Molecules which are soluble in coals can rapidly diffuse through coals, reaching porosity which is only accessible to insoluble molecules by slow diffusion through glassy solid coal. Reucroft and Patel dilatometrically have shown that Xe swells the 3 coals examined in their study (83.8% C, 78.3% C, 65.8% C, daf) but to a smaller extent than CO_2 .⁵⁹ Walker and Kini found a close agreement between the surface areas of 6 coals varying in rank from 95.2% C to 72.7% C (daf) calculated from CO_2 and Xe gas adsorption (Table 21).¹¹⁷ Apparently, Xe is sufficiently polarizable to swell coals slightly and thereby rapidly diffuse through solid coals reaching coal porosity which is closed to insoluble molecules.

The ^{129}Xe NMR chemical shift dependence on Xe gas pressure for Argonne Pittsburgh No. 8, Upper Freeport, Lewiston-Stockton, Blind Canyon, Wyodak-Anderson, and

Coal (% C, daf)	Surface Area (m ² /g)				
	N ₂	Kr	CO ₂	Xe	CO ₂
	(-196°C)	(-78°C)	(-78°C)	(0°C)	(25°C)
95.2	34	176	246	226	224
90.0	<i>Nil</i>	96	146	141	146
86.2	<i>Nil</i>	34	107	109	125
83.6	<i>Nil</i>	20	80	62	104
79.2	11	17	92	84	132
72.7	22	84	198	149	139

Table 21. Surface Area of Coals Measured by Different
Adsorbate Gases.¹¹⁷

Beulah Zap lignite are presented in Figures 55 - 60 respectively. Similar to the Pocahontas No. 3 coal, all of the ^{129}Xe NMR spectra for these Argonne coals had two primary resonances. The resonance furthest upfield is due to the free Xe gas peak and assigned a chemical shift value of 0 ppm. The downfield resonance is presumably due to Xe trapped in micropores of these Argonne coals. The average micropore diameter of the Argonne coals based on the ^{129}Xe -coal NMR resonance was determined by the same procedure described for the Argonne Pocahontas coal. The mean free path of a Xe atom based on the ^{129}Xe NMR chemical shift extrapolated to zero Xe concentration and the average micropore diameters of all the Argonne coals, assuming spherical coal pores,^{119,125} are presented in Table 22.

The widths of the ^{129}Xe NMR resonances of Xe gas in the coal micropores (Figures 53 and 55-60) are assumed to be due to a distribution of micropore sizes in these Argonne coals. Botto has recently reported the determination of the range of micropore sizes of Argonne Upper Freeport, Wyodak-Anderson, and Illinois No. 6 coals, based on ^{129}Xe NMR spectroscopy.¹²⁷ A ^{129}Xe NMR spectrum of Xe adsorbed in an Argonne Upper Freeport coal (Xe gas pressure of 570 torr) determined by Botto is shown in

Figure 55. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Pittsburgh No. 8 Coal, Shown in Descending Xe Gas Pressure.

Figure 56. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Upper Freeport Coal, Shown in Descending Xe Gas Pressure.

Figure 57. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Lewiston-Stockton Coal, Shown in Descending Xe Gas Pressure.

Figure 58. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Blind Canyon Coal, Shown in Descending Xe Gas Pressure.

Figure 59. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Wyodak-Anderson Coal, Shown in Descending Xe Gas Pressure.

Figure 60. ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Beulah Zap Lignite, Shown in Descending Xe Gas Pressure.

Argonne Coal	% C	δ_z^a	i^b	Average Micropore diameter	Linear ^c Corr. Coef.
	(dmmf)	($\text{\AA}$)	($\text{\AA}$)	($\text{\AA}$)	
Pocahontas No. 3	91.8	162	0.3	6.0	0.99
Upper Freeport	88.1	136	1.3	7.0	0.97
Pittsburgh No. 8	85.5	171	0.5	5.4	0.92
Lewiston-Stockton	85.0	176	0.4	5.2	0.99
Blind Canyon	81.3	171	0.5	5.4	0.95
Illinois No. 6	80.7	179	0.4	5.2	0.96
Wyodak Anderson	76.0	159	0.8	6.0	0.93
Beulah Zap	74.1	165	0.9	6.2	0.90

a. δ_z is the ^{129}Xe NMR chemical shift extrapolated to zero Xe concentration.

b. i is the mean free path of a Xe atom in the coal micropores based on i vs. δ_z found by Fraissard for zeolites of known structure (Figure 20).

c. The linear correlation coefficient of the extrapolation of the center of the ^{129}Xe -coal NMR chemical shift to zero Xe gas pressure.

Table 22. Average Micropore Diameters of the Argonne Coals Determined by ^{129}Xe NMR Spectroscopy.

Figure 61 after 60,000 spectral accumulations with a 0.5 sec pulse delay. Botto used a pascal line simulation program *Linesim*¹²⁸ to suggest that the width of the ^{129}Xe -coal resonance is due to Xe trapped in two different micropore coal regions. *Linesim* deconvolutes overlapping resonances in an NMR spectrum based on the number of individual components assigned by the NMR operator and the asymmetry of the convoluted NMR resonance.¹²⁹ Botto's use of *Linesim* to deconvolute the resonances for the ^{129}Xe -coal peak of Xe adsorbed in an Upper Freeport coal is illustrated by the two dashed lines in Figure 61. The free Xe gas peak (referenced to 0 ppm) observed in Botto's NMR experiment, which is not due to Xe adsorbed in the micropores of the Upper Freeport coal, is highly asymmetric. Based on the asymmetry of free Xe gas peak, it does not seem wise to base any structural conclusions on the asymmetry of the other peak. The widths of the ^{129}Xe -coal NMR resonances presented in this thesis are assumed to be due to a distribution of micropore sizes in the coals and not due to different pore regions as suggested by Botto. To more precisely define the origin of the broadness of the ^{129}Xe -coal NMR resonances, a Hahn T_2 experiment was performed.

Figure 61. ^{129}Xe NMR Spectrum of 569 Torr Xe Gas Pressure Adsorbed in Argonne Upper Freeport Coal. The Dashed Line Indicates the ^{129}Xe -Coal Resonance Deconvoluted Into Two Different Pore Regions Using a Resonance Deconvolution Simulation Program (*Linesim*¹²⁷).¹²⁶

C. T_2 Study of the ^{129}Xe NMR Resonance of Xe Adsorbed in
Argonne Upper Freeport Coal and Analab's Spherocarbs

A Hahn T_2 experiment¹³⁰ was performed on Argonne Upper Freeport coal to determine if the width of the ^{129}Xe downfield resonance (Figure 56) results from a distribution of pore sizes or is due to magnetic susceptibility broadening. Magnetic susceptibility broadening typically occurs in the NMR of solids. The limited motional freedom of molecular groups in a solid causes a distribution of chemical shift values depending on the orientation of the molecular groups with respect to the NMR magnetic field.¹³¹ The distribution of chemical shifts in a solid sample typically appears as a broad, unresolved NMR resonance.

The rotating frame model which describes the net nuclear magnetization changes in a Cartesian coordinate system will be used to describe the Hahn T_2 experiment. Detailed descriptions of the rotating frame model illustrating the NMR experiment have been extensively published.¹³⁰⁻¹³² The rotating frame model considers the precession of nuclear magnetic moments to be aligned with a static magnetic field (B_0). The static magnetic field (B_0) is considered to be along the Z-axis of a Cartesian

coordinate system. A second magnetic field (B_1) is applied in an orthogonal direction to B_0 in the form of a radio frequency pulse. The applied magnetic field (B_1) projects the net nuclear magnetization vector into the X-Y plane which induces a current in the NMR receiver coils which are located in the X-Y plane.

T_1 or spin lattice relaxation is associated with the decay of the macroscopic nuclear moment vector along the Z-axis. T_2 is transverse relaxation (or spin-spin relaxation) and is associated with the decay of the macroscopic nuclear moment in the X-Y plane. All relaxation processes which decrease the projection of the macroscopic nuclear component in the X-Y plane of the NMR rotating frame model are considered T_2 relaxation mechanisms.¹³¹ The Hahn Spin echo pulse sequence for determining T_2 relaxation times are presented in Figure 62. The delay time τ after the $\pi/2$ pulse must be the same delay time applied after the π pulse in a Hahn T_2 experiment. The Hahn T_2 experiment represented by the rotating frame model is illustrated and described in Figure 63.¹²⁹ The $\pi/2$ pulse is required to project the net macroscopic nuclear components into the X-Y plane. During the first time τ , the nuclear spins begin to precess at their characteristic Larmor frequencies and "fan out" away

Figure 62. Hahn T_2 Pulse Sequence Where τ is a Variable Delay Time Applied After the First $\pi/2$ Pulse and After a π Pulse. ^{130,133}

The spin echo signal is formed by the NMR pulse sequence described by Equation 30. a) At time $(t) = 0^-$ the net magnetization vector (M_0) is in thermal equilibrium along the z-axis. b) The location of the net magnetization vector after a $\pi/2$ pulse. c) During the time τ , the magnetization (δM) vector has precessed an angle θ resulting from the magnetic field inhomogeneity. d) the π pulse inverts the direction of the magnetization vector δM . e) at time 2τ all elements of the magnetization have re-focused along the +y-direction.

63
 Figure 62. The Hahn T_2 Experiment Expressed in Terms of the Rotating Frame Model of NMR Spectroscopy. 129732

from each other. The application of a π pulse inverts the direction of the fanning out process and causing the individual spins to refocus after the second time τ at which time the FID is acquired. The acquired NMR signal is called a spin echo. Any loss in the NMR signal intensity as a function of varying the time τ is a result of T_2 relaxation if τ times are sufficiently short to eliminate spin diffusion.¹³¹

Spin-lattice relaxation, T_1 , does not contribute to the measured intensity difference in the Hahn spin echo experiment. During the first time interval τ , T_1 relaxation occurs. The π pulse inverts the direction of the z-component which has developed during the first time τ and eliminates any T_1 relaxation contribution by having an equal τ time before spectral accumulation. The net magnetization producing the spin echo ($M(2\tau)$) is:

$$M(2\tau) = M_0 e^{-2\tau/T_2} \quad (30)$$

and M_0 is the thermal equilibrium magnetization.¹³⁰ For Xe in coals, the log of the Hahn echo peak intensity of the ^{129}Xe NMR signal will be a linear function of 2τ if the observed resonance signal is due to Xe in one pore site and the resonance line width is a result of magnetic

susceptibility broadening.

The ^{129}Xe NMR spectra applying the Hahn spin echo pulse sequence to 3 atmospheres of Xe gas adsorbed in the Upper Freeport coal are shown in Figure 64 as a function of decreasing τ times. The ^{129}Xe NMR resonance intensities not only decrease as a function of increasing τ times but the overall peak shape changes with τ as well. Plotting the log of the ^{129}Xe signal intensity as a function of 2τ (Figure 65) shows non linear dependence of the NMR peak intensity at two arbitrary chemical shift values (184 ppm and 174 ppm) as a function of τ . If the width of the ^{129}Xe -coal resonances were due solely to magnetic susceptibility line broadening, one characteristic T_2 value for the coal resonances is expected.¹³⁰ The log of the NMR signal intensity is a linear function of 2τ (Equation 30) if the width of an NMR resonance is solely due to a single T_2 value. The lack of linearity observed for Xe in the Upper Freeport coal indicates the width of the ^{129}Xe -coal NMR resonance is due to two or more different T_2 relaxation times, attributed to Xe atoms in different environments. These different environments are presumably due to Xe atoms in a coal pores with a distribution of sizes.

The Hahn spin echo experiment was also performed on Xe

Figure 0.4 ^{129}Xe NMR Spectra of 3 Atmospheres Xe Gas Pressure Adsorbed in Argonne Upper Freeport Coal Applying the Hahn T_2 Pulse Sequence (Equation 30). The ^{129}Xe -Coal Spectra are Presented as a Function of Decreasing Time Delay (τ).

6T
Figure : The ^{129}Xe NMR Resonance Intensity Dependence on the Variable Time Delay (τ) Applying the Hahn T_2 Pulse Sequence (Equation 30) to Argonne Upper Freeport Coal and Analab's Spherocarbs.

gas adsorbed in a Sphero carb sample at a pressure of 400 torr. Figure 65 shows that the log of the intensity of the ^{129}Xe echo signal is a linear function of 2τ for the Sphero carbs. The ^{129}Xe NMR resonance in the Sphero carbs is due to Xe in one type of environment as indicated by the linearity of log spin echo signal intensity vs. 2τ . When Xe gas was adsorbed in a mixture of two zeolites (CaA and NaY) having two different cavity size dimensions, a distinct ^{129}Xe NMR resonance was observed for each zeolite (Figure 28).⁹⁴ Xe adsorbed in a microporous solid having a distribution of pore sizes would be expected to have a characteristic ^{129}Xe NMR resonance for each different pore size in which the Xe atom is trapped. Xe, in a distribution of pore sizes, would have a distribution of T_2 relaxation times as is observed for the Xe-Upper Freeport coal resonance.

D. ^{129}Xe NMR Chemical Shift Pressure Dependence on Argonne Illinois No. 6 Coal

The ^{129}Xe NMR spectra as a function of decreasing Xe gas pressure adsorbed in Argonne Illinois No. 6 coal are shown in Figure 66. The furthest upfield resonance is due to the free Xe gas peak and is assigned a chemical shift

66
Figure 22: ^{129}Xe NMR Spectra of Xe Gas Adsorbed in Argonne Illinois No. 6 Coal, Shown in Descending Xe Gas Pressure. Peak A Shows a ^{129}Xe NMR Chemical Shift Dependence on Xe Gas Pressure. The ^{129}Xe NMR Chemical Shift of Resonance B is Independent of Xe Gas Pressure.

value of 0 ppm. ^{129}Xe in the Illinois No. 6 coal gives rise to two distinct resonances. The peak furthest downfield (peak A) shows a chemical shift dependence on Xe gas pressure and extrapolates to 179 ppm at zero Xe gas pressure. This is what is expected of Xe in a pore. Applying the same data treatment to peak A of the Illinois No. 6 coal as was applied to the other Argonne coals, an average micropore diameter of $5.2 \text{ \AA}$ was calculated assuming spherical coal pores.^{119,125}

The ^{129}Xe NMR chemical shift of resonance B (Figure 66) is independent of Xe gas pressure. One possibility for peak B is that its resonance is due to micropores which can only accommodate one Xe atom. This is implausible because the ^{129}Xe NMR chemical shift increases as pore size decreases,¹²⁴ and peak A has a greater ^{129}Xe NMR chemical shift than peak B. Peak B is tentatively assigned to Xe dissolved in the Illinois No. 6 coal. Reucroft and Patel have shown that Xe slightly soluble in three Kentucky coals ranging from 65.8% C to 83.8% C (daf).⁶⁰

The ^{129}Xe NMR spectra of 6 atmospheres of Xe gas adsorbed in an untreated Argonne Illinois No. 6 coal and the insoluble portion of a THF extracted residue of the Illinois No. 6 coal are shown in Figure 67. The resonance assigned as peak B is absent in the THF extracted residue

67
Figure 66. ^{129}Xe NMR Spectra of 6 Atmospheres Xe Gas Pressure Adsorbed in An Argonne Illinois No. 6 Coal and A THF Extracted Illinois No. 6 Coal Residue.

of the Illinois No. 6 coal. Peak B is most likely due to Xe dissolved in the extractable portion the Illinois No. 6 coal. Nishioka and Larsen examined the pyridine extractability of an untreated and a chlorobenzene treated Argonne Pittsburgh No. 8 coal.¹³⁴ Comparison of the pyridine extractability of the untreated Pittsburgh coal to the pyridine extractability of the coal after stirring with chlorobenzene at 115° C for one hour, one day and one week is shown in Table 23. Chlorobenzene is a coal plasticizer which increases the motion of the coal molecular segments and does not hydrogen bond to the coal.¹³⁴ The pyridine extractability of the Pittsburgh coal decreases from an extraction yield of 44% (for the chlorobenzene untreated coal) to 32% when the coal is pre-treated with chlorobenzene for 1 week at 115°C. The decrease in the coal pyridine extractability was not a result of simply heating the coal to 115°C prior to pyridine extraction. The pyridine extractability of the Pittsburgh coal heated to 115°C in a non-oxidizing atmosphere (nitrogen) for one week was unchanged from the pyridine extractability of the untreated coal (Table 23). Coal-coal molecular rearrangements in the presence of chlorobenzene, to a lower free energy conformation, are most likely responsible for the decrease in pyridine extractability compared to the untreated coal.

Coal Treatment	Extraction Yield (%)
None ^a	44
Heated 1 week in N ₂ (115°C)	45
Heated 1 hour in Ph-Cl (130°C)	41
Heated 1 day in Ph-Cl (130°C)	40
Heated 1 week in Ph-Cl (113°C)	32
a. The Argonne Pittsburgh coal was soxhlet extracted at 115° C.	

Table 23. Effect of Chlorobenzene (Ph-Cl) Pre-treatment on the Pyridine Extractability of an Argonne Pittsburgh No. 8 Coal.¹³⁴

When the THF extractable portion of the coal is removed, the solubility of the Xe in the coal decreases for the same reason pyridine extractability decreases upon pretreatment with chlorobenzene (Table 23). The decrease in Xe solubility in the Illinois No. 6 THF residue is confirmed by the absence of the ^{129}Xe NMR resonance B (Figure 67, page 211).

The center of the ^{129}Xe NMR resonance in the untreated Illinois No. 6 coal has an chemical shift of 206 ppm at 6 atmospheres Xe gas pressure. The center of ^{129}Xe NMR chemical shift of the Illinois THF residue has a chemical shift of 190 ppm. The 16 ppm upfield change in the chemical shift of peak A upon THF extraction of the Illinois No. 6 coal may be a result of a change in the pore shape and/or distribution caused during the swelling of the Illinois No. 6 coal by THF.^{119,125}

The ^{129}Xe NMR spectra of Xe adsorbed in the Argonne coals is most likely due to Xe in the micropores of the coals. The close agreement between the determined average pore size of 15.2 Å for the Spherochars with the manufacture's reported value of 15 Å demonstrates the applicability of this NMR technique to carbonaceous microporous solids. The ^{129}Xe NMR spectra of Xe adsorbed in the Argonne coals (Figures: 53; 55-60; and 66, peak A)

show a chemical shift dependence on Xe gas pressure. This is what is expected of Xe in a pore. The Hahn spin echo experiment on the Upper Freeport coal indicates that the width of the ^{129}Xe NMR resonance for this coal is due Xe adsorbed in more than one site in the coal. The Hahn T_2 experiment on the Upper Freeport coal indicates that the width of the ^{129}Xe resonances of Xe adsorbed in this coal is not solely due to magnetic susceptibility line broadening. The width of the ^{129}Xe -Upper Freeport NMR coal resonance is most likely due to Xe adsorbed in a distribution of coal micropore sizes. Since the ^{129}Xe NMR resonance of Xe in the Upper Freeport coal was typical of all the Argonne coals studied (except resonance B of the Illinois No. 6 coal), the broad ^{129}Xe -coal resonances are attributed to Xe gas adsorbed in a distribution of micropores in all the Argonne coals.

Guet calculated macropore and micropore size distributions of a Provence lignite, Mericourt low volatile bituminous coal, and an Escarpelle semi-anthracite coal obtained from the French GRECO minibank coal supply.¹³⁶ Guet analyzed small angle X-ray scattering curves of the French coals using a Fourier Transform technique to obtain coal pore size distributions by:

$$\gamma(r) = \frac{1}{I_0 I_e V (P_1 - P_2) \phi_1 \phi_2} \int_0^{\infty} 4\pi S^2 I(S) \frac{\sin 2\pi S r}{2\pi S r} dS \quad (31)$$

where $\gamma(r)$ is a geometrical correlation function which depends on the size and shape of the pores scattering the X-ray beam, I_0 is the incident X-ray beam intensity, I_e is the X-ray intensity scattered by the sample, V is the irradiated sample volume, P_1 is the electron density of carbon, P_2 is the electron density of the pore scattering the X-ray beam, ϕ_1 is the volumetric fraction of matter in coal, ϕ_2 is the volumetric fraction of pores in coal, S is the X-ray scattering vector (defined by Equation 24), and r is a vector joining two distinct points of the system. The macropore and micropore size distributions of the Providence lignite, the Mericourt bituminous, and the Escarpelle semi-anthracite coals are shown in Figures 68-70. All three coals have a micropore size distribution determined from the Fourier transform of the X-ray scattering curves which correlates with the average micropore diameters of the Argonne coals determined by ^{129}Xe NMR spectroscopy (Table 22). This Fourier transform technique could not account for the X-ray scattering from the mineral matter content of the coals which may account for negative pore size distribution limits. Guet confirmed that the micropore size distributions of the three French coals obtained this X-ray

68
Figure 68. Pore Size Distribution of a Providence Lignite
 Coal Determined by Small Angle X-ray Diffraction. 34-130

109
Figure 68. Pore Size Distribution of a Mericourt Low
 Volatile Bituminous Coal Determined by Small Angle X-ray
 Diffraction. 134 735

70
Figure 69. Pore Size Distribution of an Escarpelle Semi-Anthracite Coal Determined by Small Angle X-ray Diffraction: 134 135

scattering technique (Equation 31) are valid¹³⁶ but there may be problems in interpreting X-ray and neutron scattering curves due to coal micropore scattering. The X-ray and neutron scattering intensities from coal pores less than $10 \text{ \AA}$ in diameter provide such a weak contribution to the total scattering intensity in the presence of mesopores ($20 \text{ \AA}$ to $200 \text{ \AA}$) that micropore scattering is typically unresolvable from background noise.^{137,138} The poor resolution typically associated with X-ray scattering intensities at angles corresponding to coal micropores may invalidate the micropore size distributions obtained by Guet.¹³⁹

XIV. Micropore Size Distributions of the Argonne Coals by ^{129}Xe NMR Spectroscopy.

The width at half height of the ^{129}Xe NMR resonances of Xe in the Argonne Pocahontas No. 3 coal as a function of Xe gas pressure is shown in Table 24. The width at $\frac{1}{2}$ height as a function of Xe gas pressure for the ^{129}Xe -coal NMR resonance remained constant. Similarly, Fraissard found that the width at $\frac{1}{2}$ height as a function of Xe gas pressure remained constant for the ^{129}Xe NMR resonance of Xe gas adsorbed in NaY zeolites (Figure 26, page 106).¹⁰⁰

A similar invariance on the width at half height of the ^{129}Xe -coal resonances on Xe gas pressure was found for all the Argonne coals. Since the width of the ^{129}Xe NMR resonances of Xe adsorbed in the Argonne coals was independent of Xe gas pressure, the pore size distributions of the Argonne coals were determined at the highest Xe concentration which had the best signal-to-noise ratio.

The ^{129}Xe NMR spectra of each Argonne coal at the highest Xe gas pressure were transferred from an Aspect 3000 computer of the Bruker AM 500 NMR spectrometer to an IBM compatible computer using Columbia University's *Kermit*¹⁴⁰ communications software package. Each ^{129}Xe NMR spectrum of the Argonne coals was converted from a Two's Complement hexadecimal format to an integer file using a BASIC program developed by O. Yamada and P. C. Wernett at Lehigh University.

The integer files containing the ^{129}Xe spectral information of Xe in the Argonne coals were converted to micropore size distributions using *Statgraphics*¹⁴¹ statistical computer program. The data points defining the ^{129}Xe NMR coal spectra were converted to a chemical shift scale by:

^{129}Xe -Coal Resonance (ppm)	Xe Gas Pressure (torr)
45	315
41	500
41	680
43	820
45	1670
41	2920

Table 24. The Width of the ^{129}Xe NMR Argonne Pocahontas
No. 3 Coal Resonance as a Function of Xe Gas Pressure

$$\delta = Dp * Sw / (SFO + 01) \quad (32)$$

where δ is the ^{129}Xe NMR chemical shift, Dp is the data point number, Sw is the spectral sweep width, SFO and 01 are the ^{129}Xe NMR resonance frequency and frequency offset (center band frequency) respectively. The ^{129}Xe NMR chemical shift scale was shifted to correlate with the ^{129}Xe NMR chemical shift at zero Xe concentration from extrapolation of the ^{129}Xe chemical shift dependence on Xe gas pressure observed for all the coals (Table 22). The ^{129}Xe chemical shift scale was converted to a corresponding pore diameter using the semi-empirical relationship developed by Demarquay and Fraissard correlating the ^{129}Xe NMR chemical shift at zero Xe concentration with the mean free path of a Xe atom adsorbed in model zeolites (Figure 29).^{109,124}

The micropore size distributions of Argonne Pocahontas No. 3, Pittsburgh No. 8, Upper Freeport, Lewiston-Stockton, Blind Canyon, Illinois No. 6, Wyodak-Anderson coals and Beulah Zap lignite determined by ^{129}Xe NMR spectroscopy are presented in Figures 71 - 78. The micropore size distributions of the Argonne coals were found to range from 3.9 Å to 10 Å in diameter as determined by ^{129}Xe NMR spectroscopy. The Argonne coal micropore size

71
Figure 10. Micropore Size Distribution of Argonne
 Pocahontas No. 3 Coal Determined by ^{129}Xe NMR Spectroscopy.

72
Figure 1. Micropore Size Distribution of Argonne
Pittsburgh No. 8 Coal Determined by ^{129}Xe NMR Spectroscopy.

73
Figure 72. Micropore Size Distribution of Argonne Upper Freeport Coal Determined by ^{129}Xe NMR Spectroscopy.

74
Figure 12. Micropore Size Distribution of Argonne Lewiston-Stockton Coal Determined by ^{129}Xe NMR Spectroscopy.

75
Figure 7a. Micropore Size Distribution of Argonne Blind Canyon Coal Determined by ^{129}Xe NMR Spectroscopy.

76
Figure 1 Micropore Size Distribution of Argonne Illinois
 No. 6 Coal (Peak A, Figure 65) Determined by ^{129}Xe NMR
 Spectroscopy.

77
Figure 6. Micropore Size Distribution of Argonne Wyodak-Anderson Coal Determined by ^{129}Xe NMR Spectroscopy.

7b
Figure . Micropore Size Distribution of Argonne Beulah
 Zap Lignite Determined by ^{129}Xe NMR Spectroscopy.

distributions determined by ^{129}Xe NMR are similar to those found for the French coals (Figures 68 - 70) determined by Guet using X-ray scattering techniques.¹³⁶

The presence of the gaussian shaped distributions of micropore sizes of the Argonne coals (Figures 71 - 78) indicates that the coal micropores are not bounded by fractal surfaces. If the coal micropores were fractal, there would be an increasing slope from higher to lower ^{129}Xe NMR chemical shift values and no Gaussian shaped ^{129}Xe -coal NMR resonance would be observed. This thesis has demonstrated by small angle X-ray scattering techniques that coal pores ranging from $1000 \text{ \AA}$ to $30 \text{ \AA}$ are bounded by fractal surfaces (Figures 31 - 35, pages 132, 134-137). The presence of a non-fractal ^{129}Xe NMR micropore size distribution for all the Argonne coals may appear contradictory. The difference between fractal surfaces encountered in nature and ideal fractal surfaces is that natural fractals are not self-similar over all scale lengths.¹⁴² Naturally occurring fractal materials have both an upper and lower size limit at which the material is no longer fractal. The microporosity of the coals may be smaller than the fractal lower limit at which the pores of the coals are no longer bounded by a fractal surface.

This NMR technique is a promising, convenient method for determining the micropore size distributions for microporous solids such as coals, requiring only a vacuum apparatus equipped with a pressure measuring device, high purity Xe gas, and an NMR spectrometer.

XVI. CONCLUSIONS

A. Pore Structure of Coals

The fractal dimensionality is a global measure of the roughness of a surface. The fractal dimensionality value of all surfaces must lie between 2 and 3. A surface having a fractal dimensionality value of 2.0 indicates that the surface is perfectly smooth and flat. A fractal dimensionality of a surface that approaches 3 indicates that the surface is so irregular and convoluted that it begins to occupy space. The small angle X-ray scattering curves of the five Argonne coals presented in this thesis indicate that the pores ranging from $1000 \text{ \AA}$ to $30 \text{ \AA}$ in diameter are bounded by fractal surfaces. The fractal dimensionality of the coal surfaces vary significantly with coal rank. The Argonne Beulah Zap lignite was found to have the least convoluted surface (a fractal dimensionality of 2.35) while the Argonne Illinois No. 6 coal had the most irregular surface (fractal dimensionality of 2.87) of all the coals studied. The origin of the variation of the fractal dimensionality with coal rank is unknown and requires further study.

An attempt to determine the fractal dimensionality of the Argonne coals using gas adsorption experiments failed. The surface area of all the Argonne coals was determined using an homologous series of cyclic aliphatic hydrocarbons (cyclopropane to cyclohexane), ethane, nitrogen, and carbon dioxide. For all the bituminous coals, the dependence of the measured surface area on the size of the adsorbate probe was found to be much greater than could be explained if adsorption on the coal surface controlled the uptake of these molecules.

The generally accepted pore model of coals, that of an interconnected network of bottle-necked pores linked by slit like cavities, is inconsistent with the gas adsorption results presented in this thesis. Ethane, cyclopropane, and carbon dioxide all have similar cross-sectional areas. Ethane, a cylindrical molecule, and cyclopropane, which is planar, have different shapes and slit like or bottle-necked pores would discriminate between them. Both molecules give much lower BET coal surface areas than carbon dioxide, which is similar in shape to ethane (both cylindrical) and similar in size to cyclopropane and ethane.

A diffusional analysis of the uptake of the cyclic hydrocarbon gases as a function of time by the Argonne

bituminous coals indicates that the uptake of these cyclic hydrocarbons is governed by anomalous diffusion. Anomalous diffusion describes penetrant uptakes by solids which are controlled by both Fickian diffusion and Case II relaxation controlled diffusion. Anomalous diffusion is typically only observed for the uptake of penetrants by polymers below their glass transition temperature. Coals are glassy materials at and below room temperature in which all the experiments presented in this thesis were performed. Fickian diffusion involves the migration of a penetrant molecule into pre-existing holes in the solid while Case II relaxation involves solvation of the solid by the penetrant resulting in the creation of porosity in the solid where it did not originally exist. Fickian diffusion and Case II relaxation both show a steep penetrant diffusion rate dependence on the size of the penetrant molecule. The coal surface area differences between the hydrocarbon gases and carbon dioxide are most likely due to sharply different diffusion rates of these adsorbates through solid coal. The hydrocarbon gases reach only a small portion of the total coal porosity, that portion dependent on their diffusion rates through the coal. These diffusion rates decrease rapidly as the molecular size of the hydrocarbon increases which would explain the observed steep coal surface area dependence on the size of the hydrocarbon

adsorbate molecule. Carbon dioxide is soluble in coals, diffuses rapidly reaching pores closed to insoluble molecules, and reports a large total pore surface area. The carbon dioxide coal surface areas will be slightly overestimated due to the solubility of carbon dioxide in coals, but this effect has been shown to be small.

The majority of the pores in coals are closed to the external surface. Most pores in coals cannot be reached by diffusion through a pore network but can only be reached by diffusion through solid coal. Carbon dioxide gives accurate total surface areas of coals because it dissolves in and rapidly diffuses through solid coals reaching all coal pores. Coal surface areas measured by carbon dioxide adsorption are irrelevant to molecules which are only slightly soluble or insoluble in coals for these molecules can only reach a small portion of the total coal porosity.

The consequences of this structural model for coal processing and reactions involving solid coal are significant. Coals cannot be considered as high (hundreds of m^2/g) materials which are easily penetrable by all reagents. For large molecules involved in direct coal liquefaction and most organic reactions involving solid coal, the effective surface area of coals will be very small, only a few m^2/g . The fine grinding of coals before

reaction with reagents will be necessary to expose maximum coal surface to reagents limited by a slow mass transport through solid coals. Pre-treatment of coals with solvents which will cause coal to become a rubbery rather than a glassy material should also enhance the diffusion rates of reagents through coals and thus increase reactivity.

B. Micropore Size Distributions of the Argonne Coals

The Xenon atom is highly sensitive to its environment. Any perturbation to the highly symmetrical Xe electron cloud can be observed by monitoring the ^{129}Xe NMR chemical shift. Fraissard *et al.* have successfully developed the use of ^{129}Xe NMR spectroscopy to determine cavity size dimensions and structural defects in zeolites. This NMR technique has been extended to determine the average pore diameter of a standard 15 Å diameter carbonaceous molecular sieve (Spheroocarbs) and to determine micropore size (< 20 Å diameter pores) distributions of the Argonne coals.

Fraissard *et al.* using zeolites of known cavity dimensions, have shown that the ^{129}Xe NMR chemical shift extrapolated to zero Xe gas pressure is directly related to the mean free path of a Xe atom in a zeolite cavity. The ^{129}Xe NMR chemical shift must be extrapolated

to zero Xe gas pressure to eliminate any NMR chemical shift contribution of Xe-Xe atom collisions. The validity of this NMR technique to determine micropore size distributions in carbonaceous solids, such as coals, was determined using a Sphero carb molecular sieve. The average micropore diameter of $15.4 \text{ \AA}$ for the Sphero carb sample agreed remarkably well with the manufacturer's reported value of $15 \text{ \AA}$ indicating the applicability of ^{129}Xe NMR for determining micropore sizes in carbonaceous materials as well as zeolites.

^{129}Xe -coal NMR resonances were found to be broad with respect to the ^{129}Xe -Sphero carb resonance. A Hahn T_2 NMR experiment was performed on an Argonne Upper Freeport coal to more precisely define the origin of the broadness of the ^{129}Xe -coal NMR resonances. The Hahn T_2 experiment indicated that the Xe atom is in different environments within the coal and therefore the broadness of the ^{129}Xe -coal NMR resonance is not solely due to magnetic susceptibility broadening. The different environments of Xe atoms in the Argonne coals is believed to be due to Xe atoms in a distribution of coal micropore sizes.

All of the Argonne coals were found to have a Gaussian shaped distribution of micropores ranging from $5 \text{ \AA}$ to $10 \text{ \AA}$ in diameter based on their ^{129}Xe NMR chemical shift

extrapolated to zero Xe gas pressure. The Gaussian coal micropore size distribution indicates that the coal pores less than $10 \text{ \AA}$ in diameter are not bounded by fractal surfaces. Fractal surfaces encountered in nature are not self-similar over all scale lengths. Naturally occurring fractals have both an upper and lower size limit at which the material ceases to be fractal. The coal surface bounded by micropores are most likely below the lower limit at which the Argonne coals are no longer fractal.

A Fourier analysis of the X-ray scattering curves of three French coals performed by Guet shows a close agreement between the micropore size distributions of these 3 French coals using X-ray scattering and the Argonne coals using ^{129}Xe NMR spectroscopy. The validity of the micropore size distributions of the French coals using X-ray scattering is questionable since the X-ray scattering intensity at angles corresponding to coal pores less than $10 \text{ \AA}$ in diameter is typically too weak to base any structural information on.

^{129}Xe NMR spectroscopy has potential as an important tool for monitoring microporous dimensions of coals. ^{129}Xe NMR of coals may provide important future applications to monitor changes in coal micropores upon exposure to chemical reagents.

XVI. Consequences of Pore Structure Model on Future Coal Science

Most of the chemistry and industrial processes involving solid coal have been developed with the assumption that coals contain an interconnected pore network. The experimental results presented in this thesis indicate that coals do not have a pore network. The design of coal conversion reactions, solvent swelling of coals, and coal desulfurization are directly affected by the way a scientist views the pore structure of coals. The concept that the pores in coals may be considered as isolated "bubbles" and not an interconnected pore network will have a significant impact on the future development of new coal processing technologies.

The ability of a solvent to swell glassy coals will have important applications in allowing reagents to penetrate into the solid coal. Good coal swelling solvents will plasticize glassy coals converting them to rubbery materials. Swelling solvents can no longer be considered to penetrate into coals through a pore network. A solvent that can swell coals will establish a moving solvent front. The coal ahead of the solvent front will be a glassy

material while the part of the coal that the solvent has penetrated will be a rubbery material. The rate at which the solvent front moves through the coal as well as effectiveness of solvent to expand or swell coal macromolecules are crucial parameters in characterizing the swelling power of a solvent for coals.

Coal conversion reactions involve transformation of solid coal to gas and liquid products. Liquefaction is the conversion of solid coals to liquid products and coal gasification is the conversion of solid coals to gaseous products. The ultimate goal of industrial coal conversion reactions is to transform solid coals to a liquid or gaseous state, increasing the hydrogen content of the coal, reducing the heteroatom content of coal, and removal of the mineral matter of coals. Many of the industrial coal conversion processes require a hydrogen donor solvent or molecular hydrogen, and a transition metal catalyst to reduce aromatic moieties in coals to unsaturated hydrocarbons. The transition metal catalyst must be able to penetrate into coals to increase their effectiveness for coal hydrogenation in liquefaction or gasification reactions. Since these transition metal catalysts cannot penetrate coals through an open pore network, pre-treatment of coals with solvents which will cause coals to be rubbery

materials or fine grinding of coal to increase the exposed surface area of the coal will be a crucial step to increase the yield of coal conversion products.

The desulfurization of coals is important for improving the conversion yield of coals to synthetic fuels. The sulfur in coals is not only an environmental pollutant when burning coals but also poisons transition metal catalysts used in coal conversion reactions. A commonly employed industrial method for removal of pyritic sulfur in coals employs the oxidation of pyrite using Fe(III). For the pyrite oxidation of coals to be effective, the Fe(III) reagent must be able to penetrate through the solid coal to reach the pyritic sulfur. This will require fine grinding of the coal or pre-treatment of the coal with a good swelling solvent prior to the introduction of the Fe(III) oxidizing agent. Pre-swelling of the coal or fine grinding will increase the mass transport rate of the Fe(III) oxidizing reagent through the coal and hence increase the effectiveness of pyrite removal from coals.

These are only a few examples of how the coal pore model presented in this thesis will change the future of coal science. This new coal pore model is a significant contribution to understanding coal structure and should aid in the development of new and better methods for

utilizing coals as a source of future energy.

REFERENCES

1. Van Krevelen, D. W. *Coal* (2nd Reprint) Elsevier Scientific Publishing Company: New York, NY, 1981.
2. Ting, F. T. C. in *Analytical Methods for Coal and Coal Products*, C. Karr Jr., Editor, Academic Press, Inc.: New York, NY, 1978.
3. Vorres, K. S. *Users Handbook for the Argonne Premium Coal Sample Program* Argonne National Laboratories, Argonne, IL, 1989.
4. Wiser, W. H. in *Prepr. Pap.- Am. Chem. Soc., Div. Fuel Chem.* 1975, 20(2), 122.
5. Given, P. G. *Fuel* 1960, 39, 147-153.
6. Heredy, L. A.; Wender, I. *Prepr. Pap.- Am. Chem. Soc., Div. Fuel Chem.* 1980, 25(4), 38-45.
7. Solomon, P. R. *New Approaches in Coal Chemistry* ACS Symp. Ser. 169, American Chemical Society: Washington, D. C., 1981.
8. Shin, J. H. *Fuel* 1984, 63, 1187-1196.
9. Liotta, R.; Brons, G. *J. Am. Chem. Soc.* 1981, 103, 1735-1742.
10. Cronauer, D. C.; Ruberto, R. G. *Investigation of the Mechanism of Reactions Involving Oxygen-Containing Compounds in Coal Hydrogenation* Electric Power Research Institute Report AF-913, Palo Alto, CA, 1979.

11. Blom, L.; Edelhausen, L.; van Krevelen, D. W. *Fuel* 1957, 36, 135-153.
12. Attar, A.; Corcoran, W. H. *Ind. Eng. Chem., Prod. Res. Dev.* 1977, 16, 168.
13. Green, T.; Kovac, J.; Brenner, D.; Larsen, J. W. in *Coal Structure* R. A. Meyers, Editor, Academic Press: New York, NY, 1982.
14. Larsen, J. W.; Wei, Y.-C. *Energy Fuels* 1988, 2, 344-350.
15. Hirsch, P. B. *Proc. Roy. Soc. (London)* 1954, A226, 143-169.
16. Solum, M. S.; Pugmire, R. J.; Grant, D. M. *Energy Fuels* 1989, 3, 187-193.
17. Grigoriew, H. *Fuel* 1990, 69, 840-845.
18. Ito, O.; Akiho, S.; Nozawa, T.; Hatano, M.; Iino, M. *Fuel* 1989, 68, 335-340.
19. Brenner, D. *Fuel* 1985, 64, 167-173.
20. Rabek, J. F. *Experimental Methods in Polymer Chemistry* John Wiley and Sons: New York, NY, 1980.
21. Cody, G. D.; Larsen, J. W.; Siskin, M. *Energy Fuels* 1988, 2, 340-344.
22. Larsen, J. W.; Baskar, A. J. *Energy Fuels* 1987, 1, 230-232.

23. Lucht, L. M.; Larson, J. M.; Peppas, N. A. *Energy Fuels* 1987, 1, 56-58.
24. Painter, P. C.; Park, Y.; Sobkowiak, M.; Coleman, M. M. *Energy Fuels* 1990, 4, 384-393.
25. Couchman, P. R. *Macromolecules* 1978, 11, 1156-1161.
26. Simha, R.; Boyer, R. F. *J. Chem. Phys.* 1962, 37, 1003-1007.
27. Small, P. A. *J. Appl. Chem.* 1953, 3, 71-80.
28. Hildenbrand, J. H.; Scott, L. L. *The Solubility of Non-Electrolytes* (3'rd Edition) Reingold Publishing Company Corporation: New York, NY, 1950.
29. Larsen, J. W.; Green, T. K.; Kovac, J. *J. Org. Chem.* 1985, 50, 4729-4735.
30. Liotta, R.; Brons, G.; Isaacs, J. *Fuel* 1983, 62, 781-791.
31. Hall, P. J.; Marsh, H.; Thomas, K. M. *Fuel* 1988, 67, 863-866.
32. Griffiths, D. M.; Marshall, K.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1*, 1974, 70, 400-410.
33. Whitehurst, D. D.; Mitchell, T. O.; Farcasiu, M. *Coal Liquefaction* Academic Press: New York, NY, 1980.
34. Quinga, E. M. Y.; Larsen, J. W. *Energy Fuels* 1987, 1, 300-304.

35. Ishida, T.; Matsui, M.; Inoue, M.; Hirano, H.; Yamashita, M.; Sugiyama, K.; Sugiura, M.; Tomita, K. *J. Am. Chem. Soc.* 1985, 107, 3305-3314.
36. Mallya, N.; Stock, L. M. *Fuel* 1986, 65, 736-738.
37. Liotta, R. *Fuel* 1979, 58, 724-728.
38. Bond, R. L. *Nature* 1956, 178, 104-105.
39. Gregg, S. J.; Pope, M. I. *Fuel* 1959, 38, 501-505.
40. Ganguli, N. C.; Mukherjee, P. N.; Lahiri, A. *Fuel* 1961, 40, 525-526.
41. Sharkey, A. G., Jr.; McCartney, J. T. in *Chemistry of Coal Utilization, Second Supplementary Volume*; M. A. Elliot, Editor, John Wiley and Sons: New York, NY, 1981.
42. Mahajan, O. P.; Walker, P. L., Jr. in *Analytical Methods for Coal and Coal Products*, Vol. I, C. Karr Jr., Editor, Academic Press: New York, NY, 1979.
43. Marsh, H. *Carbon* 1987, 25, 49-58.
44. Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* 1938, 60, 309-319.
45. Lowell, S. *Introduction to Powder Surface Area* John Wiley and Sons: New York, 1979.
46. Kini, K. A. *Fuel* 1964, 43, 173-180.

47. Yang, R. T.; Saunders, J. T. *Fuel* 1985, 64, 616-620.
48. Van der Sommen, J.; Zwietering, P.; Eillebrecht, B. J.
M. Van Krevelen, D. W. *Fuel* 1955, 34, 444-448.
49. Walker, P. L. Jr. *Phil. Trans. R. Soc. Lond.* 1981, A300, 65-81.
50. Otake, Y.; Suuberg, E. M. *Fuel* 1989, 68, 1609-1612.
51. Gan, H.; Nandi, S. P.; Walker, P. L. Jr. *Fuel* 1972, 51,
272-277.
52. Anderson, R. B.; Bayer, J.; Hofer, L. J. E. *Fuel* 1965,
44, 443-452.
53. Maggs, F. A. P. *Nature (London)* 1952, 169, 793-794.
54. Grimes, W. R. in *Coal Science*, Vol. I M. L. Gorbaty, J. W.
Larsen, and I. Wender, Editors, Academic Press: New York,
NY, 1982.
55. Porod, G. *Kolloid-Z.* 1951, 124, 83-114.
56. Lin, J. S.; Hendricks, R. W.; Harris, L. A.; Yust, C.
S. *J. Appl. Cryst.* 1978, 11, 621-625.
57. Spitzer, Z.; Ulicky, L. *Fuel* 1977, 55, 212-224.
58. Setek, M.; Snook, I. K.; Wagenfeld, H. K. *Determination of
the Microstructure of Wet and Dry Brown Coal by Small Angle X-Ray
Scattering in The Chemistry of Low Rank Coals* Schnobert,
H. H., Editor, American Chemical Society:
Washington, D. C., 1984, pp. 95-108.

59. Gethner, J. S. *J. Appl. Phys.* 1986, 59, 1068-1085.
60. Reucroft, P. J.; Patel, H. *Fuel*, 1986, 65, 816-820.
61. Walker, P. L., Jr.; Verma, S. K.; Rivera-Utrilla, J.; Khan, M. R. *Fuel* 1988, 67, 719-726.
62. Stacy, W. O.; Jones, J. C. *Fuel* 1986, 65, 1171-1173.
63. Crank, J.; Park, G. S. *Diffusion in Polymers* Academic Press: New York, NY, 1968.
64. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers* Elsevier Scientific Publishing Company: New York, NY, 1976.
65. Frisch, H. L. *Polym. Eng. Sci.* 1980, 20, 2-13.
66. Berens, A. R.; Hopfenberg, H. B. *Polymer* 1978, 19, 489-496.
67. Hsieh, S. T.; Duda, J. L. *Fuel* 1987, 66, 170-177.
68. Berens, A. R. *Polymer* 1977, 18, 697-704.
69. Vieth, W. R.; Howell, J. M.; Hsieh, J. H. *J. Membr. Sci.* 1976, 1, 177-183.
70. Barr-Howell, B. D.; Peppas, N. A.; Winslow, D. N. *Chem. Eng. Commun.* 1986, 43, 301-315.
71. Ritger, P. L.; Peppas, N. A. *Fuel* 1987, 66, 815-826.

72. Ensore, D. J.; Hopfenberg, H. B.; Stannett, V. T.
Polymer 1977, 18, 793-800.
73. Barr-Howell, B. D.; Peppas, N. A.; Squires, T. G. *J. Appl. Polym. Sci.* 1986, 31, 39-53.
74. Berens, A. R.; Hopfenberg, H. B. *J. Membr. Sci.* 1982, 10, 283-303.
75. Crank, J. *The Mathematics of Diffusion* Oxford University Press: London, 1956.
76. Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Theory of Gases and Liquids* John Wiley and Sons: New York, NY, 1954.
77. Stannett, V. in *Diffusion in Polymers* J. Crank and G. S. Park, Editors, Academic Press: New York, NY, 1968.
78. Holley, R. H.; Hopfenberg, H. B.; Stannett, V. *Polym. Eng. Sci.* 1970, 10, 376-382.
79. Hsieh, S. T. *The Penetration of Solvent Vapor Into Coal Particles* Ph.D. Thesis, Department of Chemical Engineering, Pennsylvania State University, 1984.
80. Barr-Howell, B. D.; Howell, J. M.; Peppas, N. A.
Thermochimica Acta 1987, 116, 153-159.
81. Erbatur, G.; Erbatur, O.; Davis, M. F.; Maciel, G. E.
Fuel 1986, 65, 1265-1272.
82. Long, F. A.; Richman, D. *J. Am. Chem. Soc.* 1960, 82,

513-519.

83. Cody, G.; Davis, A. *Energy Fuels* in press.
84. Farin, D.; Peleg, S.; Yavin, D.; Avnir, D. *Langmuir* 1985, 1, 399-407.
85. Farin, D.; Volpert, A.; Avnir, D. *J. Am. Chem. Soc.* 1985, 107, 3368-3370.
86. Pfeifer, P.; Avnir, D. *J. Chem. Phys.* 1983, 79, 3558-3565.
87. Fripiat, J. J.; Gatineau, L.; Van Damme, H. *Langmuir* 1986, 2, 562-567.
88. Avnir, D.; Farin, D.; Pfeifer, P. *Nature (London)* 1984, 308, 261-263.
89. Bale, H. D.; Schmidt, P. W. *Phys. Rev. Lett.* 1984, 53, 596-599.
90. Avnir, D.; Farin, D.; Pfeifer, P. *J. Chem. Phys.* 1983, 79, 3566-3571.
91. Erdelyi, A. *Asymptotic Expansions* Dover Publishing: New York, NY, 1956.
92. Guinier, A.; Fournet, G.; Walker, C. B.; Yudowitch, K. L. *Small Angle Scattering of X-Rays* John Wiley and Sons: New York, 1955.
93. Fraissard, J.; Ito, T. *Zeolites* 1988, 8, 350-361.

94. Spinguel-Huet, M. A.; Ito, T.; Fraissard, J. *Structure and Reactivity of Modified Zeolites* P. Jacobs, Editor, Elsevier Science Publishers: Amsterdam, 1984.
95. Chmelka, B. F.; Ryoo, R.; Liu, S. B.; de Menorval, L. C.; Radke, C. J.; Petersen, E. E.; Pines, A. *J. Am. Chem. Soc.* 1988, 110, 4465-4467.
96. Johnson, D. W.; Griffiths, L. *Zeolites* 1987, 7, 484-487.
97. Davis, M. E.; Saldarriaga, C.; Montes, C.; Hanson, B. E. *J. Phys. Chem.* 1988, 92, 2557-2560.
98. Stengle, T. R.; Reo, N. V.; Williamson, K. L. *J. Phys. Chem.* 1981, 85, 3772-3775.
99. Miller, K. W.; Reo, N. V.; Uiterkamp, A. I. M. S.; Stengle, D. P.; Stengle, T. R.; Williamson, K. L. *Proc. Nat. Acad. Sci.* 1981, 78, 4946-4949.
100. Ito, T.; Fraissard, J. *J. Chem. Phys.* 1982, 76, 5225-5229.
101. Buckingham, A. D.; Schaefer, T.; Schneider, W. G. *J. Chem. Phys.* 1960, 32, 1227-1233.
102. Onsager, L. *J. Am. Chem. Soc.* 1936, 58, 1486-1493.
103. Rummens, F. H. A. *Chem. Phys. Lett.* 1975, 31, 596-598.
104. One amagat is the density of a gas under standard conditions.

105. Jameson, C. J.; Jameson, A. K.; Cohen, S. M. *J. Chem. Phys.* 1973, 59, 4540-4546.
106. Jameson, A. K.; Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* 1979, 53, 2310-2321.
107. Ito, T.; de Menorval, L. C.; Guerrier, E.; Fraissard, J. P. *Chem. Phys. Lett.* 1984, 111, 271-274.
108. Ito, T.; Fraissard, J. *J. Chem. Soc., Faraday Trans. I* 1987, 83, 451-462.
109. Springuel-Huet, M.; Demarquay, J.; Ito, T.; Fraissard, J. in *Innovations in Zeolite Material Science* P. J. Grobet et al., Editors, Elsevier Scientific Publishers: Amsterdam, 1988.
110. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Edition Pergamon Press: New York, NY, 1988.
111. Emmett, P. H.; Brunauer, S. *J. Am. Chem. Soc.* 1937, 59, 1553-1564.
112. Gallant, R. W. *Physical Properties of Hydrocarbons* Gulf Publishing Company: Houston, TX, 1968.
113. The small angle X-ray scattering studies of the Argonne coals involved a collaborative effort with Dr. P. J. Hall and Dr. K. Liang of Exxon Engineering and Research Company Incorporated, Annandale, NJ.
114. Foster, M. D.; Jensen, K. F. *Fuel* 1990, 69, 88-96.

115. Ross, S. B.; Smith, D. M. *Langmuir* 1988, 4, 977-982.
116. Lucht, L. M.; Peppas, N. A. *Erdoel Kohle, Erdgas, Petrochemie* 1987, 40, 483-485.
117. Walker, P. L.; Kini, K. A. *Fuel* 1965, 44, 453-459.
118. Ng, S. H.; Fung, D. P. C.; Kim, S. *Fuel* 1984, 63, 1564-1569.
119. Winans, R. E.; Thyagarajan, P. *Energy Fuels* 1988, 2, 356-358.
120. Demaison, J.; Huttner, W.; Starck, B.; Buck, I.; Tischer, R.; Winnewisser, M. *Landolt-Bornstein Zahlenwerte Und Funktionen Aus Physik, Chemie, Astronomie, Geophysik, Technik* (Volume II/6), K.-H. Hellwege and A. M. Hellwege Editors, Springer-Verlag: New York, NY, 1974.
121. Vrentas, J. S., Duda, J. L.; Hou, A.C. *J. Appl. Polym. Sci.* 1984, 29, 399-406.
122. Lucht, L. M.; Peppas, N. A. *J. Appl. Polym. Sci.* 1987, 33, 1557-1566.
123. Meares, P. *J. Polym. Sci.* 1958, 27, 405-418.
124. Demarquay, J.; Fraissard, J. *Chem. Phys. Lett.* 1987, 136, 314-318.
125. Goslar, J.; Kispert, L. D. *Energy Fuels* 1989, 3, 589-594.

126. Ripmeester, J. A. *J. Mag. Res.* 1984, 56, 247-253.
127. Tsiao, C.; Botto, R. E. *Energy Fuels* 1991, 5, 87-92.
128. *Linesim* program version 880101 by P. Barron, Bruker Instruments Inc. (Australia) Pty. Ltd.
129. C. Thibault, Bruker Instruments Inc.,
personal communication
130. Slichter, C. P. *Principles of Magnetic Resonance*, 3rd Edition
Springer-Verlag: New York, NY, 1990.
131. Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd Edition
Academic Press: New York, NY, 1988.
132. Martin, M. L.; Delpuech; J.-J.; Martin, G. J. *Practical
NMR Spectroscopy* Heyden: Philadelphia, PA, 1980.
133. Benn, R.; Gunther, H. *Angew. Chem.* 1983, 22, 350-380.
134. Nishioka, M.; Larsen, J. W. *Energy Fuels* 1990, 4, 100-106.
135. Guet, J. M. *Coal Science Technology* (Volume 15)
Elsevier Scientific: New York, NY, 1990.
136. Guet, J. M. *Personal Communication*.
137. Tricker, M. J.; Grint, A.; Audley, G. J.; Church, S.
M.; Rainey, V. S.; Wright, C. J. *Fuel* 1983, 62, 1092-1095.
138. Schmidt, P. W.; Kwak, C. Y.; Kalliat, M. *Prepr. Pap. - Am.
Chem. Soc., Div. Fuel Chem.* 1983, 28(4), 75-80.

139. P. J. Hall *Personal Communication*.

140. *Kermit* Interface Communications Package, Columbia University: New York, NY, 1988.

141. *Statgraphics* Version 4.0, By Statistical Graphics Corporation Incorporated: Rockville, MD, 1989.

142. Borman, S. *Chem. Eng. News* 1991, 69 (16), 28-35.8. P. J. Hall *Personal Communication*.

139. *Kermit* Interface Communications Package, Columbia University: New York, NY, 1988.

140. *Statgraphics* Version 4.0, By Statistical Graphics Corporation Incorporated: Rockville, MD, 1989.

141. Borman, S. *Chem. Eng. News* 1991, 69 (16), 28-35.

139. P. J. Hall *Personal Communication*.

140. *Kermit Interface Communications Package*, Columbia University: New York, NY, 1988.

141. *Statgraphics Version 4.0*, By Statistical Graphics Corporation Incorporated: Rockville, MD, 1989.

142. Borman, S. *Chem. Eng. News* 1991, 69 (16), 28-35. S. P. J. Hall *Personal Communication*.

139. *Kermit Interface Communications Package*, Columbia University: New York, NY, 1988.

140. *Statgraphics Version 4.0*, By Statistical Graphics Corporation Incorporated: Rockville, MD, 1989.

141. Borman, S. *Chem. Eng. News* 1991, 69 (16), 28-35.

PART 2

Inverse Gas Chromatography

Book 99
Chap 11

Section A
Inverse Gas Chromatography of Coal and Polymer Surfaces

Introduction

Inverse gas chromatography (IGC) is used routinely to determine interaction energies of polar and nonpolar molecules with polymers.¹⁻⁹ Above the glass-to-rubber transition temperature (T_g), the technique is sensitive to properties of the *bulk* polymer.¹⁰ Below T_g , the technique has been used to determine interactions at polymer *surfaces*.^{2-9,11} Broad peaks are often observed below T_g .^{4,7-9,12} Broad peaks often result when injected molecules diffuse into the stationary phase bulk.¹³ If diffusion into the bulk polymer is occurring below T_g , the technique is not sensitive to surface interactions only, bringing into doubt the use of IGC to obtain polymer surface thermodynamics. Because we wanted to use IGC to determine adsorption thermodynamics for molecules interacting with the surface of the complex macromolecular solid, coal, it was necessary to determine if the technique is sensitive to surface interactions only.¹⁴ Others have studied the behavior of the retention volumes, but the behavior of the peak widths below T_g has not been experimentally demonstrated.^{4,7-10,15} We studied peak broadening for several adsorbates on two glassy polymers and a coal.

Two important parameters in IGC are the retention volume and the peak width or peak broadening. At temperatures above and near T_g , the origin of IGC retention volumes and peak broadening are well understood.^{10,16-21} Because injected molecules diffuse rapidly through the polymer above T_g , the retention volumes represent thermodynamic interactions of injected molecules with the bulk

polymer.^{10,16,18,20} The flowrate dependence of the peak widths has been used to determine diffusion coefficients in the polymer bulk.²²⁻²⁶ At temperatures within about 50°C of T_g , nonequilibrium diffusion, characterized by a kinetically-controlled (flowrate-dependent) retention volume, sets in.^{16-21,27} The retention volumes are characteristic of the distance the injected molecules travel into the bulk and they cannot be used to determine equilibrium thermodynamic properties. The peak width and retention volume behavior in this regime are complex and depend on several factors including the nature of the injected molecules, the polymer thickness, and the polymer crystallinity.^{16-18,21,28}

For IGC on glassy polymers at temperatures below T_g , it has been demonstrated that for sufficiently small injection sizes the requirements of linear chromatography are met, the retention volumes do not shift with flow velocity, and they are sensitive to the polymer surfaces.^{4-9,18,27,29-31} IGC peaks below T_g are non-Gaussian and first moments should be used to calculate retention volumes.³² When peak broadening is caused by nonlinear chromatography, the retention volumes shift and the peaks broaden with increasing injection amount because a range of sites of different energies is sampled, strongest first.¹³ Below T_g , retention volumes were constant with injection amount for polar and nonpolar adsorbates on polycarbonate, for alkanes on Kevlar, for alkanes and chloromethanes on polymer-coated glass beads, for alkanes on a polyester, and for various adsorbates on cellulose.^{4-9,29} This is taken as evidence that, at sufficiently low injection

amounts, linear chromatography holds for these systems.^{4-9,29} Injection size-dependent peaks were reported for tetrachloroethane, butyl acetate, and dioxane on Kevlar at unknown injection sizes and for ether and acetone on polymer-coated glass beads at injection sizes below 0.1 ml.^{7,8} At larger injection sizes, adsorption isotherms have been determined from IGC peaks for adsorbates on polymers below T_g .^{16,29} Only anti-Langmuir type isotherms corresponding to increased adsorbate-adsorbate interaction energies at higher injection amounts were observed for *n*-decane on poly(methyl methacrylate) (PMMA), and for *n*-decane, dioxane, and *n*-alcohols on cellulose.^{16,29} Retention volumes below T_g were shown to be independent of column flow velocity for *n*-hexadecane on polystyrene (PS), for *n*-octane and carbon tetrachloride on poly(vinyl acetate), and for alkanes on cellulose, demonstrating that these retention volumes were not affected by nonequilibrium diffusion into the polymer.^{18,27,30} Braun and Guillet showed that accessible surface areas calculated from the retention volumes were similar to the specific surface area for *n*-hexadecane on PS, demonstrating that the retention volumes are sensitive to the polymer surfaces.¹⁸ Glass and Larsen showed that retention volumes for alkanes on Illinois No. 6 coal depend on the coal particle size, demonstrating that the retention volumes are sensitive to the external surface of the coal.³¹ These data provide evidence that linear chromatography holds at sufficiently low injection amounts and that nonequilibrium diffusion is not affecting the retention volumes below T_g . Studies of the flowrate and injection size

dependence of the peak broadening are needed to provide further evidence that surface properties only are contributing to IGC below T_g .

Peak broadening below T_g has not been studied in detail, but several different explanations have been offered for the broad peaks.^{10,12,15,19,33} It was thought that diffusion into the polymer bulk was occurring so that bulk interactions were in part responsible.^{10,12,15} It was thought that "soluble" molecules diffused into the bulk polymer and reported both bulk and surface properties, while insoluble molecules did not diffuse into the polymer and as a result reported only surface properties.^{10,15} However, Braun and Guillet stated that the solubility does not determine the tendency to diffuse into the bulk at temperatures near T_g .¹⁹ It was also thought that IGC peaks below T_g might result from a combination of nonlinear and nonideal chromatographic effects.¹² If both of these effects were operating simultaneously, it would be difficult if not impossible to extract meaningful information from the IGC peaks.³⁴ Katz and Gray thought that the broad peaks they observed for *n*-alkanes on cellophane were probably caused by diffusion in the gas phase.³³

The origin of the peak broadening below T_g remains uncertain. Studies reported here of the flowrate and injection size dependence of IGC peaks for adsorbates on PS, PMMA, and Illinois No. 6 coal show that the broad peaks are not caused by diffusion into the bulk.

Experimental

Experiments were conducted using the apparatus described previously.³¹ The GC was a Hewlett Packard 5890 with a flame ionization detector. Briefly, the adsorbate gas of interest was admitted to a vacuum manifold and then to a Valco injection valve (0.015 or 0.100 ml sample loop). The pressure of gas in the injection loop was determined with a Baratron (MKS Instruments) gauge located in the vacuum manifold. This allowed injection of known amounts of gas onto the column.

Gases were 99% purity or better. Liquids were obtained from Aldrich in "sure-seal" bottles and subjected to at least three freeze-pump-thaw cycles before being introduced into the vacuum manifold at pressures below their vapor pressures.

PMMA and PS beads were obtained from Polysciences, Inc. PMMA was used as received (200 μ m beads) or was coated onto Chromosorb W AW 80/100 mesh (Supelco, Inc.) by evaporation from methylene chloride. 4.09 g of PMMA beads were packed into a 1/8 inch O.D., 2.1 mm I.D. stainless steel column 154.2 cm long. 1.76 g of Chromosorb containing 4.13% weight loading PMMA was packed into a 1/8 inch O.D., 2.1 mm I.D. stainless steel column 134.9 cm in length. PS beads were sieved to 60/40 mesh and 3.37 g packed into a 1/8 inch O.D., 2.1 mm I.D. stainless steel column 154.3 cm in length. The columns were heated at temperatures slightly above T_g (at 110°C for PMMA and at 105°C for PS) overnight in helium before each day's experiments.

Argonne premium Illinois No. 6 coal was sieved to 60/70 mesh

and 3.95 g packed into a 1/8 inch O.D., 2.1 mm I.D. stainless steel column 153.5 cm in length. The column was heated at 150°C in helium for 2 weeks and overnight before each day's experiments. Extracted coal was prepared by extracting Illinois No. 6 coal of 40/60 mesh particle size in a Soxhlet extractor for several days in tetrahydrofuran (THF). The coal was dried in a vacuum oven at 110°C overnight. 3.88 g of the coal was packed into a stainless steel column 152.9 cm long, 1/8 inch O.D., and 2.1 mm I.D. The column was heated in helium at 250°C for 2 weeks and overnight before each day's experiments.

For PMMA and PS, injections were made over the temperature range 30 to 55°C, with injector and detector temperatures at 70°C. For coal, injections were made over the temperature range 30 to 150°C with injector and detector temperatures at 150 to 180°C. The temperature of the chromatograph oven was accurate to $\pm 0.1^\circ\text{C}$ and was unchanged within 0.2°C of the recorded temperature over different parts of the oven.

Flowrates, determined from the GC mass flow control readout and checked periodically with a bubble meter, ranged from 5 to 40 ml/min. They were corrected for water vapor. The column pressure drop was measured with a pressure transducer (Omega Engineering, Inc.) on the column inlet and a barometer in the ambient atmosphere. Typical pressure drops were 1 to 2 atm. Retention volumes were corrected using the pressure drop correction term j .³⁵ Average linear flow velocities, $\bar{u}$, were calculated from the column length, l , and the dead time, t_m ($\bar{u} = jl/t_m$).³⁶ Column dead times

were determined using columns containing glass beads of the same average particle diameter as the polymer and coal columns.

Data from the GC were sent via a modified 16-bit Keithley A/D board to a PC. Points were collected at a rate of one per second and input to LabCalc software (Galactic Industries, Corp.). The retention volumes of the peaks were calculated from the first moments which were determined by integrating the peaks. Peak standard deviations were measured at 0.607 times the height (at this height, the standard deviation in time units, $\sigma_{(t)}$, equals half the peak width).³⁷

Results and Discussion

Figure 1 shows IGC peaks for n-pentane on PS. These data are typical of those used to determine retention volumes for polar and nonpolar adsorbates on PS, PMMA, and Illinois No. 6 coal at temperatures below the glass transition temperature. The first moments of the peaks in this regime remained constant over a range of about a factor of 5 in injection amount. Retention volumes that are independent of injection amount were observed by others for polar and nonpolar adsorbates on different polymers below T_g .^{4-9,29} These observations demonstrate that at sufficiently small injection sizes, the linear region of the adsorption isotherm is being sampled. Linear chromatography holds. The broad peaks in this regime (Figure 1) cannot be caused by nonlinear chromatography. Assuming close packing of n-pentane on the PS surface, the injection sizes in Figure 1 correspond to about 0.1% surface

coverage of the polymer in the column. If the adsorbate is occupying 1/100th of the column (~1.5 cm) this corresponds to 10% surface coverage. The distribution of adsorbate on the column is not known, so the true surface concentration cannot be determined.

At higher injection amounts, peak tailing was observed. See Figure 2. Others have observed peak tailing below T_g for ethanol on Kevlar.⁷ Because tails lead to increased first moments, tailed peaks cannot be used to determine retention volumes.³⁸ In order to stay below the tailing regime, and to obtain accurate first moments, very small injection sizes are required. We constructed a vacuum manifold to inject these small amounts of adsorbate onto the columns. The tailed peaks reported by others probably resulted because they could not inject sufficiently small amounts (syringes were used).

The tails observed by us and by others for IGC on glassy polymers may result from "slow kinetics".³⁹ The term "slow kinetics" is used to describe the existence of sites in the column ("slow sites") that have relatively long time constants.³⁹ These slow sites may be the result of limited diffusion into the bulk and/or very strong interactions with the stationary phase.^{39,40} Giddings has used a two site model to describe the GC peaks that result from slow kinetics.⁴⁰ Briefly, the model is based on two distinct populations of sites, one with a relatively rapid time constant and the other with a very long time constant.⁴⁰ If a significant number of injected molecules occupy the slow sites, the GC peak will have a tail.⁴⁰ It is possible that on glassy

polymers, some adsorbates, especially strongly interacting ones, may give tailed peaks. At larger injection sizes, we observed peak tailing that increased with increasing injection size for alkanes and polar adsorbates on PMMA, PS, and Illinois No. 6 coal. This behavior is in contrast to the behavior expected for a range of adsorption energies (nonlinear chromatography), where long retention times contribute less to the peak as the injection size is increased. As long as data are collected at small enough injection sizes, tailing does not contribute to the retention volumes.

If the peak broadening is caused by diffusion into the bulk polymer, then either equilibrium or nonequilibrium diffusion must be occurring during the experiments. Equilibrium diffusion may be due to either bulk diffusion or gas diffusion and is described by the van Deemter equation.⁴¹ From the van Deemter equation, when peak broadening is caused by diffusion into the bulk, the peak width (measured as the standard deviation in volume units, $\sigma_{(v)}$) increases with increasing flow velocity.⁴¹ When peak broadening is caused by diffusion in the gas phase, $\sigma_{(v)}$ decreases with increasing flow velocity.⁴¹ The van Deemter equation, however, assumes that the peak width is much less than the retention time, a condition which does not hold below T_g (Figures 1 and 2).⁴¹ The van Deemter equation cannot be used to refute gas or bulk diffusion as peak broadening mechanisms below T_g . We use a different argument to show that diffusion into the polymer is not responsible for peak broadening below T_g .

If equilibrium diffusion is occurring, then the adsorbates must diffuse through the entire polymer during the experiment. Table I shows retention times for alkanes on PS, PMMA, and Illinois No. 6 coal along with the diffusion coefficients determined from static sorption experiments for the same systems.^{42,43} The average diffusion distances, $\langle x \rangle$, were calculated using Fick's second law, $\langle x \rangle = 2(Dt/\pi)^{1/2}$ where D is the diffusion coefficient and t is the diffusion time (set equal to the IGC retention time).⁴⁴ The values of $\langle x \rangle$ in Table I are therefore upper limits for the distance that the injected molecules can diffuse into the polymer during our IGC experiments. It is seen from the Table that the maximum diffusion depth possible during our experiments is about two orders of magnitude less than the polymer thickness (r) for the five systems listed. The adsorbates cannot diffuse through the entire polymer depth during the IGC experiments. Any diffusion into the polymer occurring during the experiments must be nonequilibrium diffusion.

If nonequilibrium diffusion is responsible for peak broadening, the retention times decrease with increasing flowrate.¹⁸ As reported by others, we observed that the retention volumes below T_g are independent of flow velocity (see Figure 3).^{18,27,30} Nonequilibrium diffusion cannot be responsible for the peak broadening. These data (Figure 3 and Table I) demonstrate diffusion into the polymer is not occurring during IGC below T_g .

Figure 4 shows that the peaks for benzene on PMMA and n-pentane on Illinois No. 6 coal decrease with increasing flowrate. The ratio of standard deviation in time units to the retention

time, $\sigma_{(t)}/t_R$, is constant with flow velocity. See Figure 5. Because $\sigma_{(v)} = \sigma_{(t)} * F$, where F is the flowrate, this means that the standard deviation in volume units is constant with flow velocity. The behavior displayed in Figure 5, a constant standard deviation $\sigma_{(v)}$ with flowrate, was observed for every system we studied, including n-alkanes on PS and PMMA, tetrahydrofuran and dimethyl sulfoxide on PMMA, and n-alkanes and a wide range of polar molecules on Illinois No. 6 coal. We never observed any other dependence of peak width on flow velocity. The behavior in Figures 4 and 5 does not follow the flowrate-dependent behaviors associated with equilibrium diffusion and predicted by the van Deemter equation nor the flowrate-dependent behavior observed for nonequilibrium diffusion.^{16,41}

The data demonstrate that neither isotherm nonlinearity nor diffusion into the polymer are responsible for peak broadening below T_g . The only other mechanisms which could be responsible for the broad peaks are gas diffusion or surface desorption. Both of these mechanisms give retention volumes that are sensitive to interactions with the polymer surface only. IGC below T_g is sensitive to surface interactions only and the retention volumes at sufficiently low injection sizes may be used to determine polymer adsorption thermodynamics.

Acknowledgement

Support of this work by the U.S. Department of Energy through grant number DE-FG22 89PC9757 is gratefully acknowledged.

Table I Comparison of average diffusion distance, $\langle x \rangle$, with polymer thickness, r , for hydrocarbons in PS, PMMA, and Illinois No. 6 coal assuming that the diffusion time is equal to the IGC retention time.

Polymer	Adsorbate	IGC Retention Time (min) ^{a),b)}	Diffusion Coefficient (cm ² /sec) ^{c)}	$\langle x \rangle$ (μm) ^{d)}	r (μm)
PS	<u>n</u> -butane	0.59 (33°C, 6.9 ml/min.)	$1.6 \cdot 10^{-12}$ (30°C) ^{e)}	0.84	500
PS	<u>n</u> -pentane	0.75 (33°C, 7.2 ml/min.)	$6.3 \cdot 10^{-13}$ (30°C) ^{e)}	0.60	500
PMMA	<u>n</u> -pentane	0.40 (45°C, 16.2 ml/min.)	$3.2 \cdot 10^{-16}$ (30°C) ^{e)}	0.01	200
PMMA	<u>n</u> -hexane	1.20 (40°C, 20.8 ml/min.)	$5.0 \cdot 10^{-17}$ (30°C) ^{e)}	0.01	200
Illinois No. 6 Coal	methane	3.60 (30°C, 3.1 ml/min.)	$\sim 10^{-12}$ (30°C) ^{f)}	1.70	230

^{a)} determined from the first moments of the IGC peaks

^{b)} numbers in parentheses are temperatures and flowrates at which measurements were made

^{c)} numbers in parentheses are temperatures of diffusion experiments

^{d)} calculated using the equation $\langle x \rangle = 2(Dt/\pi)^{1/2}$ assuming a diffusion time, t , equal to the IGC retention time

^{e)} diffusion coefficients from reference 43

^{f)} diffusion coefficients from reference 44

References

1. Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds. *Inverse Gas Chromatography*, ACS Symposium Series 391; ACS: Washington, DC, 1989.
2. Gray, D. G. *Prog. Polym. Sci.* **1977**, *5*, 1-60.
3. Saint Flour, C.; Papirer, E. *J. Coll. Int. Sci.* **1983**, *91*, 69.
4. Anhang, J.; Gray, D. G. In *Physicochemical Aspects of Polymer Surfaces*, vol. 2; Mittal, K. L., Ed.; Plenum: New York, 1983; pp. 659-667.
5. Deng, Z.; Schreiber, H. P. In *Contemporary Topics in Polymer Science (Int. Symp. Multiphase Macromolecular Systems (1988))*, vol. 6; Culbertson, B. M., Ed.; Plenum: New York, 1989; p. 385-400.
6. Boluk, M. Y.; Schreiber, H. P. *Polymer Composites* **1989**, *10*, 215-221.
7. Briscoe, B. J.; Roach, S.; Williams, D. R. In *Interfacial Phenomena in Composite Materials*; Jones, F., Ed.; Butterworths: Guilford, 1989; pp. 132-137.
8. Tiburcio, A. C.; Manson, J. A. *J. Appl. Polym. Sci.* **1991**, *42*, 427-438.
9. Panzer, U.; Schreiber, H. P. *Macromolecules* **1992**, *25*, 3633-3637.
10. Smidsrød, O.; Guillet, J. E. *Macromolecules* **1969**, *2*, 272.
11. Schultz, J.; Lavielle, L. In *Inverse Gas Chromatography*, ACS Symposium Series 391; Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds.; ACS: Washington, DC, 1989; pp. 185-202.
12. Gray, D. G.; Guillet, J. E. *Macromolecules* **1972**, *5*, 316-321.

13. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; Chapter 2.
14. Coals are complex macromolecular solids with glass transition temperatures thought to be about 250°C. Green, T. K.; Kovac, J.; Brenner, D.; Larsen, J. W. In *Coal Structure*, Meyers, R. A., Ed.; Academic: New York, 1982; p. 199. b) Ritger, P. L.; Peppas, N. A. *Fuel* 1987, 66, 815.
15. Galin, M.; Rupprecht, M. C. *Polymer* 1978, 19, 506-512.
16. Gray, D. G.; Guillet, J. E. *Macromolecules* 1974, 7, 244-247.
17. Braun, J.-M.; Lavoie, A.; Guillet, J. E. *Macromolecules* 1975, 8, 311-315.
18. Braun, J.-M.; Guillet, J. E. *Macromolecules* 1975, 8, 882-888.
19. Braun, J.-M.; Guillet, J. E. *Macromolecules* 1976, 9, 340-344.
20. Braun, J.-M.; Guillet, J. E. *Macromolecules* 1976, 9, 617-621.
21. Courval, G. J.; Gray, D. G. *Can. J. Chem.* 1976, 54, 3496-3507.
22. Gray, D. G.; Guillet, J. E. *Macromolecules* 1973, 6, 223-227.
23. Tait, P. J. T.; Abushihada, A. M. *J. Chromatographic Sci.* 1979, 17, 219-223.
24. Munk, P.; Card, T. W.; Hattam, P.; El-Hibri, M. J.; Al-Saigh, Z. Y. *Macromolecules* 1987, 20, 1278-1285.
25. Pawlisch, C. A.; Bric, J. R.; Laurence, R. L. *Macromolecules* 1988, 21, 1685-1698.
26. Arnould, D.; Laurence, R. L. In *Inverse Gas Chromatography*, ACS Symposium Series 391; Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds.; ACS: Washington, DC, 1989; pp. 87-106.

27. Deshpande, D. D.; Tyagi, O. S. *Macromolecules* **1978**, *11*, 746-751.
28. Lipatov, Y. S.; Nesterov, A. E. *Macromolecules* **1975**, *8*, 889-894.
29. Tremaine, P. R.; Gray, D. G. *J. Chem. Soc. Faraday Trans. I* **1975**, *71*, 2170-2185.
30. Dorris, G. M.; Gray, D. G. *J. Coll. Int. Sci.* **1980**, *77*, 353-362.
31. Glass, A. S.; Larsen, J. W. *Energy Fuels*, submitted.
32. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; p. 73.
33. Katz, S.; Gray, D. G. *J. Coll. Int. Sci.* **1981**, *82*, 318-351.
34. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; p. 86.
35. Littlewood, A. B. *Gas Chromatography*, 2nd ed.; Academic: New York, 1970; p. 28.
36. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; p. 51.
37. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; p. 82.
38. Curl, R. L.; McMillan, M. L. *AIChE J.* **1966**, *12*, 819.
39. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; p. 53.
40. Giddings, J. C. *Dynamics of Chromatography*, vol. 1; Marcel Dekker: New York, 1965; pp. 75-79.
41. Van Deemter, J. J.; Zuiderweg, F. J.; Klinkenberg, A. *Chem.*

Eng. Sci. 1956, 5, 271.

42. Berens, A. R.; Hopfenberg, H. B. *J. Memb. Sci.* 1982, 10, 283.

43. Walker, P. L., Jr.; Austin, L. G.; Nandi, S. P. In *Chemistry and Physics of Carbon*, vol. 2.; Walker, P. L., Ed.; Marcel Dekker: New York, 1966.

44. Atkins, P. W. *Physical Chemistry*, 2nd ed.; Freeman & Co.: San Francisco, 1978; p. 839.

Figure Captions

Figure 1. IGC peaks for different injection amounts of n-pentane on polystyrene. Column temperature=33°C, flowrate=7.2 ml.min. A, 8.0×10^{-6} μmol ; B, 4.0×10^{-6} μmol ; C, 2.4×10^{-6} μmol .

Figure 2. IGC peaks for different injection amounts of n-pentane on extracted Illinois No. 6 coal. Column temperature=110°C, flowrate=30.4 ml/min. A, 2.2×10^{-4} μmol ; B, 1.7×10^{-4} μmol ; C, 1.4×10^{-4} μmol ; D, 1.2×10^{-4} μmol ; E, 1.0×10^{-4} μmol ; F, 5.4×10^{-5} μmol ; G, 2.5×10^{-5} μmol ; H, 1.5×10^{-5} μmol .

Figure 3. Plots of retention volume, V_N , vs. linear flow velocity, $\bar{u}$, for alkanes on PMMA and Illinois No. 6 coal. A, cyclopropane on Illinois No. 6 coal, 130°C, $\blacktriangle$; B, benzene on PMMA, 52°C, $\circ$; C, n-pentane on Illinois No. 6 coal, 110°C, $\triangle$; D, ethane on Illinois No. 6 coal, 80°C, $\blacksquare$; E, propane on Illinois No. 6 coal, 110°C, $\square$; F, neopentane on Illinois No. 6 coal, 90°C, ∇ .

Figure 4. IGC peaks for benzene on poly(methyl methacrylate) and for n-pentane on Illinois No. 6 coal. To make clear changes in peak width, the curves have been shifted along the time axis to bring their peak maxima into coincidence. Ticks on the x-axis indicate one minute intervals. Peak widths were measured at 0.607 times the height. A, benzene on PMMA, column temperature=52°C, injections=0.015 ml at 0.010 Torr. (a) flowrate=23.2 ml/min.,

width=0.78 min., retention time=1.70 min. (b) flowrate=27.9 ml/min., width=0.66 min., retention time=1.49 min. (c) flowrate=34.1 ml/min., width=0.60 min., retention time=1.29 min. B, n-pentane on Illinois No. 6 coal, column temperature=110°C, injections=0.015 ml at 0.013 Torr. (a) flowrate=28.4 ml/min., width=0.80 min., retention time=1.10 min. (b) flowrate=35.1 ml/min., width=0.68 min., retention time=1.00 min. (c) flowrate=42.7 ml/min., width=0.53 min., retention time=0.79 min.

Figure 5. Plots of the ratio of standard deviation in time units to retention time, $\sigma_{(t)}/t_R$, vs. linear flow velocity, $\bar{u}$, for adsorbates on poly(methyl methacrylate) and Illinois No. 6 coal. A, methane on Illinois No. 6 coal, column temperature=50°C, •; B, cyclopropane on Illinois No. 6 coal, column temperature=100°C, Δ; C, benzene on PMMA, column temperature=52°C, ▲; D, neopentane on Illinois No. 6 coal, column temperature=90°C, ◦.

1.3

Minutes

0

Arbitrary Units

Arbitrary Units

9570

Back-up
Blank

Introduction

Measuring thermodynamics for adsorption on polymeric surfaces is difficult using static techniques because diffusion of the adsorbate into the polymer usually occurs during the experiment, leading to simultaneous measurement of bulk and surface properties.¹ In contrast, inverse gas chromatography (IGC) is a dynamic technique (injected molecules flow past the stationary phase) which provides a way to limit the contact time of the adsorbate with the surface. This can prevent diffusion into the bulk polymer making possible the measurement of surface properties. We present here thermodynamic data obtained by inverse gas chromatography for adsorption of hydrocarbons and noble gases on Illinois No. 6 coal. The data provide insight into the surface structure and chemistry of this complex glassy polymer.

Interactions at coal surfaces are of both fundamental and practical importance. Reactions that occur during coal liquefaction and beneficiation involve disruption or modification of forces at coal surfaces such as maceral-maceral, maceral-mineral, and coal-solvent interfaces. Understanding the forces at these interfaces should lead to improvements in coal processing. Knowledge of the interactions occurring at both maceral and mineral surfaces will help optimize the design of coal cleaning processes. Before it reaches reaction sites inside bulk coal, a reagent encounters the coal surface. It may react there or diffuse into the coal. In either event, the

interactions at the surface play a crucial role. Any interaction with coal is first an interaction with coal surfaces. An understanding of coal surfaces is important for understanding reactions with coal and for a complete understanding of coal structure and chemistry.

If coal surface properties are to be measured, penetration of adsorbed molecules into the bulk must be prevented during the experiment. Polymers are known to absorb molecules into their bulk, rates for absorption in rubbers being typically several orders of magnitude faster than those in glasses.² Although coal is a glassy polymer with a high glass to rubber transition temperature, rates of penetration of molecules into bulk coal are still fairly rapid, with penetration beginning immediately after adsorption.^{3,4} Static sorption data for uptake of toluene vapor by a bituminous coal obtained by Hsieh and Duda illustrate the behavior.⁴ Solvent molecules first adsorb on the coal surface, then begin to diffuse into the bulk. Since the transition from surface adsorption to bulk penetration is continuous, static sorption determines coal surface properties in the presence of competing bulk diffusion. In contrast, gas chromatography is a dynamic technique and it has the potential to determine surface properties without interference from bulk diffusion.¹

Inverse gas chromatography differs from analytical gas chromatography. The interest in analytical GC is separating an injected mixture into its components, whereas the interest in inverse GC is the interactions of a single pure solute with the

stationary phase. Inverse gas chromatography is routinely used to obtain thermodynamic data for interactions at carbon black and inorganic solid surfaces, as well as to obtain solution thermodynamic data for liquids and rubbery polymers.^{5,6} Its application to glassy polymer surfaces (including coal) is less straightforward because broad peaks are often observed.⁷⁻⁹ However, it has been shown that the broad peaks are not caused by bulk diffusion or heterogeneous surface energies at the injection sizes used in our experiments and that IGC provides thermodynamic data for interactions of hydrocarbons with coal and glassy polymer surfaces.⁹

In order to obtain thermodynamic values characteristic only of the surface-adsorbate interactions, data must be collected in the concentration range called the region of "linear chromatography." This corresponds to the "Henry's law" region in solution thermodynamics. The concentration of the adsorbate on the surface is so low that only surface-adsorbate interactions are important. The region of linear chromatography is characterized by the invariance of retention volume with the amount injected. For coals, this requires very small injection sizes.⁹ In fact, a vacuum line had to be constructed to accurately measure the small injection amounts required. All data reported in this paper were obtained in the region of linear chromatography.

There have been several attempts to obtain coal surface thermodynamic data using IGC. Bulashov et al. obtained data for

polar and nonpolar organic molecules on a low-rank coal.¹⁰ Their retention times were low and their injection sizes ($0.1 \mu\text{l}$) were most likely higher than the limit for linear chromatography. This conclusion is supported by their statement that, "A decrease in the size of the sample leads to an increase in the retention time and to a considerable diffusion of the peak."¹⁰ Larsen et al. used IGC to determine adsorption enthalpies for organic molecules on a Bruceton coal.¹¹ Their injection sizes were $\sim 0.1 \mu\text{l}$ and their measured adsorption heats were less exothermic than heats of condensation and less exothermic than adsorption heats for the same molecules on graphitized carbon black, indicating saturation of the coal surface.¹¹ Their thermodynamic data therefore do not measure interactions at the coal surface and are of little value. Roy and Guha applied IGC to several coals, including lignite, bituminous, and anthracite.¹²⁻¹⁴ They also used injection sizes above $0.1 \mu\text{l}$. The peak maxima for some of their probes decrease with increasing injection size, and the peak profiles are not superimposable, indicating that kinetic processes may be operating.^{13,14} The exact process(es) responsible for the peak shifts is difficult to ascertain without additional data, but may involve heterogeneous coal-solute interactions as well as bulk absorption of the solute.¹⁵ Arnett et al. used IGC to study an anthracite coal.¹⁶ These authors stated that their experiments were conducted at infinite dilution, but injection sizes were not given. Their heats of adsorption for organic bases on anthracite coal were similar to

those on graphite.¹⁶

It seems likely that all of these studies except that of Arnett et al. used solute amounts sufficient to saturate the coal surfaces.^{10-14,16} The maximum injection size necessary for saturation is typically 10^{-3} μ l or less for adsorbent stationary phases.¹⁵ Since the surface area of coal accessible during IGC is probably less than that for a typical (porous) adsorbent, the maximum injection size for linear chromatography of coal surfaces is likely to be much less than 10^{-3} μ l.

We present thermodynamic data for nonpolar hydrocarbons on Illinois No. 6 coal obtained using injection sizes five orders of magnitude smaller than those used in previous IGC studies of coals.¹⁰⁻¹⁴ The retention volumes for IGC peaks in this regime are independent of injection amount and are characteristic of the thermodynamic interaction between the solute and the coal.⁹ Plots of the logarithm of retention volume over temperature vs. inverse temperature (van't Hoff plots) may therefore be used to determine the isosteric adsorption heats, q_{st} .⁶ The integral adsorption entropies, ΔS° , may be determined from q_{st} and the retention volume.^{5,17} Isosteric adsorption heats for hydrocarbons on extracted, demineralized, and heated coal reflect changes that occur at the coal surface as a result of these treatments. The effect of changing the coal particle size on the retention volumes indicates that the retention volumes are sensitive to the external surface of the coal.

Experimental

Experiments were conducted using the apparatus shown in Figure 1 with helium as the carrier gas using a Hewlett Packard 5890 gas chromatograph with both TCD and FID detectors. 0.03 inch stainless steel tubing was used between the GC valve and the column inlet to minimize dead volume. Gas samples at pressures of 0.01 to 10.0 Torr were injected from a glass vacuum manifold (base pressure 10^{-3} Torr or less) using a Valco 8-port sample valve with 0.015 and 0.100 ml sample loops. Pressures were measured with a 1 Torr Baratron gauge (MKS Instruments, Inc.) or a mercury manometer attached to the sample reservoir. Peak areas were proportional to injection amount and were the same for a given injection size of a particular adsorbate on coal and on glass beads, indicating that all of the adsorbate injected appeared in the peak.

Gases were 99% purity or better. Liquids obtained from Aldrich in "sure-seal" bottles were subjected to at least three freeze-pump-thaw cycles before being introduced as gases at pressures below their vapor pressures.

Argonne premium Illinois No. 6 coal was sieved to give the desired fraction (40/60, 60/70, or 80/100 mesh) and about 4 grams were packed into 1/8 inch O.D., 2.1 mm I.D. stainless steel columns about 1.5 meters in length. The coal particle density was 1.3 g/ml.¹⁸ The coal was degassed in a stream of helium at 150°C overnight before each day's experiments. For experiments on heated coal, the coal was heated at each temperature, i.e.,

150°C, 200°C, or 250°C, in helium for at least 2 weeks before any IGC experiments were performed and at the same temperature overnight before the day's experiments. Extracted coal was prepared by extracting Illinois No. 6 coal of the desired particle size in tetrahydrofuran (THF) in a Soxhlet extractor for several days.¹⁹ Demineralized coal was prepared by refluxing coal of the desired particle size in a 1M citric acid solution for 24 hours.²⁰ The coal was washed exhaustively in a Soxhlet extractor with distilled water. The demineralized and the extracted coal particles were heated in a vacuum oven at 110°C overnight. They were packed into stainless steel columns as above and dried at the desired temperature (150, 200, or 250°C) in a flow of helium until the GC baseline stabilized (about 2 weeks). The columns were heated overnight in helium before each day's experiments.

Data were collected in various temperature ranges between 30 and 250°C, with injector and detector temperatures at 180 to 250°C. The temperature of the chromatograph oven was accurate to $\pm 0.1^\circ\text{C}$ and was constant to within 0.2°C over different parts of the oven. Flowrates ranged from 3 to 40 ml/min. They were determined using the electronic flow sensor on the gas chromatograph, and checked periodically with a bubble meter. The column pressure drop was determined using a pressure transducer (Omega Engineering, Inc.) on the column inlet and a barometer for measuring atmospheric pressure. Typical pressure drops were about 1 to 2 atm. Retention volumes were corrected for varying

flow velocity in the column using the pressure drop correction term, j .⁶

Columns of the same length, diameter, and containing the same mesh fraction particles but filled with glass beads instead of coal were used to determine the column dead volumes. Retention times for several hydrocarbons on a given glass bead column gave the same dead volumes, within experimental error.

Data were collected with a PC using Lab Calc software (Galactic Industries Corp.) at a rate of one point per second. Peak first moments, determined by integrating the peaks, were used to calculate the retention volumes.¹⁵ Each retention volume was determined from the average of five to nine IGC peaks. The reported errors in the retention volumes are the standard deviations for these measurements. Adsorption enthalpies were determined from plots of the natural logarithm of retention volume over temperature vs. inverse temperature (van't Hoff plots) at three to six temperatures covering a temperature range of at least 30°. The reported errors for the adsorption enthalpies are the standard errors from the linear regression fits. Adsorption entropies were calculated using de Boer's approach, assuming a standard gaseous state with a pressure of 1.01×10^6 dyne/cm² (1 atm) and a standard adsorbed state with a pressure of 0.338 dyne/cm.²¹ Errors in the adsorption entropies were calculated by error propagation from adsorption enthalpy and retention volume errors.

Results and Discussion

For the solute amounts used in our experiments, it has been shown that the retention volumes for hydrocarbons on coal are independent of injection amount and the retention volumes characterize the equilibrium interaction between the adsorbate and the surface.⁹ The isosteric heats of adsorption, q_{st} , can therefore be obtained from plots of the natural logarithm of the retention volume over temperature vs. inverse temperature (van't Hoff plots, see equation 1) and the integral entropies of adsorption, ΔS° , can be obtained from q_{st} and the retention volume (see equation 2).^{6,15}

The isosteric heat of adsorption is the enthalpy change for transfer of one mole of the adsorbate from the ideal gas phase to the surface at infinite dilution on the surface. It is a partial molal quantity and the adsorption process is exothermic. The integral entropy of adsorption is the entropy change on transferring one mole of the adsorbate from the ideal gas phase to the surface where the surface concentration is that which gives a surface pressure of 0.338 dyne/cm. This standard state was defined by de Boer and is commonly used.²¹

The adsorption entropy is a function of the surface concentration which depends on the surface area of the coal. The value for the adsorption entropy changes with the value selected for the surface area of the coal accessed by the adsorbate. The surface area of coals is currently a matter of some controversy.^{22,23} We cannot use BET surface areas measured with

these hydrocarbons because those values include the surface area accessed by slow diffusion of the adsorbate; diffusion which does not occur during the rapid IGC experiment. We have used the external surface areas calculated from the particle size. The choice of surface area affects the absolute value of the entropy but not the change in entropy. Thus our data will accurately show how the entropy changes as the adsorbate or the coal changes, but the absolute values are dependent on the value assumed for the surface area. Sufficient data are included to permit the reader who dislikes our choice of surface area to recalculate ΔS° for any surface area.

The isosteric adsorption heat, q_{st} , and the integral adsorption entropy, ΔS° , are ultimately derived from the retention volume.^{5,17} The defining equation is

$$\ln \left[\frac{V_N}{T} \right] = \frac{q_{st}}{RT} + \ln R + \ln s + K_{s,o}. \quad (1)$$

Here, V_N is the net retention volume, R is the gas constant, s is the surface area accessible to the solute, and $K_{s,o}$ is the preexponential factor. See reference 24 for a complete explanation of this equation. q_{st} is obtained in a straightforward way from a plot of $\ln(V_N/T)$ vs. $1/T$.

The equation used to determine the entropy from V_N is more complex. Equation 1 can be rewritten as

$$\begin{aligned}\Delta S^\circ &= -\frac{Q_{st}}{T} + R + R \ln \left[\frac{p'}{\pi} \right] + R \ln V_s \\ &= -\frac{Q_{st}}{T} + 31.61 \frac{\text{cal}}{\text{mole}^\circ} + R \ln \left[\frac{V_N}{s} \right]\end{aligned}\quad (2)$$

where p' ($=1 \text{ atm} = 1.01 \times 10^6 \text{ dyne/cm}^2$) and π ($=0.338 \text{ dyne/cm}$) come from the chosen standard state.²¹ See references 17 and 21 for a derivation of this equation.²⁵ Note that V_s (in cm), the retention volume corrected for coal surface area (see equation 3), is used in the calculation.

$$V_s = \frac{V_N}{s} \quad (3)$$

If it is assumed that the particles in the column are spherical, s can be determined from²⁶

$$s = \frac{3}{\rho r} \quad (4)$$

where ρ is the particle density (1.3 g/ml for the coal) and r is the particle radius.¹⁸ Surface areas from equation 4 with r set equal to the average particle radius of the mesh fraction of coal in the column were used in the calculation of ΔS° .

The above equations (1 and 2) can be used to obtain isosteric adsorption heats and adsorption entropies from the retention volumes if the retention volumes are independent of injection amount, because this behavior is a condition for linear chromatography.^{5,6,15} Figure 2 shows data, typical of that used to calculate q_{st} , for *n*-pentane on Illinois No. 6 coal. The retention volumes for *n*-pentane (Figure 2) were obtained using injection sizes of 1.0×10^{-4} to $1.9 \times 10^{-5} \mu\text{mol}$ of gas. This

represents a reduction in injection size by a factor of 10^5 over those used in previous IGC studies of coals.¹⁰⁻¹⁴ (0.1 μ l of liquid corresponds to about 10^{-5} mol.) The retention volumes were independent of injection amount over this range of injection size, as seen from the coincidence of the peak maxima in the figure.

At some injection size ($\sim 2 \times 10^{-4}$ μ mole for n-pentane), although the maxima still coincided, the peaks began to tail (Figure 3). Peak tailing increased with increasing injection size. For methane, ethane, and cyclopropane, the peak maxima were independent of injection size over at least a 100 fold range. Data for ethane are shown in Figure 3. For the other gases, peak maxima (as well as retention times) remained constant over at least a 10 fold range below the injection size at which troublesome tailing was encountered. Retention volumes could not be accurately determined from tailed peaks, because the tail caused an increase in the calculated first moments.²⁷ For all adsorbates studied, peak first moments were constant over a range of injection size from the smallest detectable peak to the regime where tailing was first observed. Retention times determined from peaks in this regime were used to calculate q_{st} and ΔS° .

The cause of the peak tailing in these systems is not known. It may be column overload or slow diffusion into the bulk.^{6,15,28} Isotherm nonlinearity (heterogeneous surface or bulk interactions) has been ruled out as a source of tailing in these systems.⁹ Assuming close packing of the solute on the coal

surface, the injection sizes where tailing begins to set in for *n*-pentane ($\sim 10^{-4}$ μmol) corresponds to a specific surface area of about 10^{-5} m^2/g , much less than the external surface area of the coal in the column (~ 0.01 m^2/g). However, the distribution of solute in the column and on the coal surface is not known making it impossible to calculate the real surface coverage.

There is a problem with using such very small injection sizes. A small set of uniform strong binding sites not typical of the whole surface may be selectively sampled. That three different adsorbates studied over more than a 100 fold variation in injection size showed no change in peak maxima argues against selective adsorption. The observed values for q_{st} are consistent with adsorption on carbonaceous surfaces.²⁹

The observed retention volumes are independent of the flowrate. This is strong evidence that the retention volumes are being measured at thermodynamic equilibrium. Whenever the solute-stationary phase interactions are due to nonequilibrium absorption into the bulk of the solid, retention volumes can no longer be used to determine thermodynamic interactions between the solute and stationary phase.³⁰ The retention volume then is a function of the depth of penetration of the solute into the stationary phase. This situation is characterized by retention volumes that decrease with increasing column flowrate.³⁰ The retention volumes for all hydrocarbons we studied on Illinois No. 6 coal were constant, independent of flowrate, demonstrating that nonequilibrium diffusion into the bulk coal was not occurring

(Figure 4).^{9,30}

The data demonstrate that the retention volumes are sensitive to the external coal surface area. Plots of $\ln(V_N/T)$ vs. $1/T$ are shown in Figure 5. The slopes of the plots give q_{st}/R , while the y-intercepts of the plots are determined by the last three terms in equation 1. For a given adsorbate on a given coal, $K_{s,o}$ is constant, $\ln R$ is constant, but the retention volume decreases with decreasing surface area. This leads to decreasing y-intercepts with decreasing coal surface area.

The y-intercepts for the plots in Figure 5 decrease with increasing coal particle size. This indicates that the retention volumes are sensitive to the external surface of the coal in the column. If the internal surface of the coal was accessible to the adsorbates; the retention volumes would not be sensitive to the coal particle size. The IGC data provide support for the idea that the internal surface of coal is not connected to the external surface. This conclusion differs from the "classical" view of coal structure, but is consistent with recent studies of coal surfaces.^{31,22,23}

Retention volumes acquired at temperatures of 30 to 150°C were used to determine isosteric adsorption heats of hydrocarbons on Illinois No. 6 coal. Figure 6 shows a plot of $\ln(V_N/T)$ vs. $1/T$ (a van't Hoff plot) for n-hexane on Illinois No. 6 coal previously heated to 150°C. The plot has a constant slope over the temperature range 100 to 150°C. Retention volumes for all of the hydrocarbons and inert gases we studied on Illinois No. 6

coal gave linear van't Hoff plots.

Changes in the slopes of plots of $\ln(V_N/T)$ vs. $1/T$ are often observed when the stationary phase undergoes a reversible transition, i.e., a glass to rubber transition.²⁴ Recently, Hall and Mackinnon reported a low temperature glass to rubber transition (in the range ~ 80 to 130°C) for Wyodak coal (75%C) based on a differential scanning calorimetry study.³² Reversible low temperature ($\sim 150^\circ\text{C}$) transitions were observed during differential scanning calorimetry of Illinois No. 6, Pittsburgh No. 8, and Blind Canyon coals by Yun et al.³³ The IGC data for n-hexane on Illinois No. 6 coal show no evidence for such a low temperature transition.

The adsorption heats of inert gases and linear alkanes on Illinois No. 6 coal increase linearly with adsorbate polarizability, α . Figure 7 displays adsorption heats (obtained from van't Hoff plots) for inert gases and hydrocarbons on Illinois No. 6 coal heated to 150°C . Data for original, extracted, and demineralized Illinois No. 6 coal are shown. The plots are linear for all adsorbates except neopentane, discussed below. Not surprisingly for these nonpolar adsorbates, the interactions are dominated by van der Waals and dispersion interactions.

Comparison of adsorption heats for alkanes on Illinois No. 6 coal with those on graphitized carbon (Table I) demonstrates that greater interaction strengths exist for hydrocarbons with Illinois No. 6 coal than with graphitized carbon.²⁹ The

adsorption heats for the coal are more exothermic (except for Ar and CH₄) than those for graphitized carbon black. For Illinois No. 6 coal, the increase in adsorption heat per CH₂ group in the adsorbate is about 2.1 kcal/mol between propane and n-hexane compared to about 1.6 kcal/mol for linear alkanes on graphitized carbon black.³⁷ The increase in adsorption heat per CH₂ group ranges from about 1.0 to 3.0 kcal/mol for carbons, depending on the history of the carbon.^{17,38} A higher concentration of surface atoms on Illinois No. 6 coal compared to graphitized carbon black could explain these observations.³⁹ The higher adsorption heats found for hydrocarbons on more highly-oxidized and on less highly graphitized carbon surfaces have been ascribed to a greater proportion of geometric irregularities or to greater surface heterogeneity.^{17,38}

Neopentane does not fit on the line with the other (linear) alkanes on original and extracted Illinois No. 6 coal (Figure 7). Increased branching decreases the adsorbate's surface-to-volume ratio so the branched adsorbate cannot approach the surface as closely as a linear adsorbate.⁶ Because van der Waals interactions depend steeply on the distance between the adsorbate and the surface ($1/r^6$), bulky adsorbates report lower adsorption heats than linear ones with the same number of carbon atoms.⁶ This effect has been observed on carbon black and polymer surfaces.⁴⁰

Adsorption heats for hydrocarbons on demineralized and extracted Illinois No. 6 coal differ from those on the original

coal (Figure 7), demonstrating that changes occur at the coal surface as a result of extraction and demineralization.

Adsorption heats for hydrocarbons on extracted Illinois No. 6 coal are similar to those for hydrocarbons on graphitized carbon black.²⁹ After demineralization, the heats are less exothermic than those for the original coal but are more exothermic than those for the extracted coal.

A linear relationship was found between the adsorption heats and entropies for hydrocarbons on both original and extracted Illinois No. 6 coal heated to 150°C (Figure 8). All of the points (including those for neopentane) fall on the same line. This effect, observed for vapor-liquid condensation and solubilities, is known as the isokinetic relationship or the compensation effect.⁴¹ The existence of the isokinetic effect indicates that adsorption of hydrocarbons on extracted and on original Illinois No. 6 coal surfaces involve the same types of interactions, as expected for van der Waals surface interaction forces. Because both q_{st} and ΔS° were derived from the same V_N data, significant statistical criticism can be made of the isokinetic plot.⁴¹

Figure 9 shows the effects of heating the original Illinois No. 6 coal on the measured adsorption heats. The heats become less exothermic after heating the coal to 200°C and are even less exothermic after heating to 250°C. The adsorption heat for *n*-hexane on the original coal heated to 250°C is the same as that for the extracted coal. This indicates that heating Illinois No.

6 coal to 250°C or extracting with THF results in alterations which give rise to surfaces with similar nonpolar interactions.

The changes in the adsorption heats caused by the various treatments are irreversible. For example, once the coal has been exposed to a temperature of 200°C, the adsorption heats are less exothermic than those for the coal heated at 150°C no matter what the measurement temperature range (below 200°C). Likewise for the coal heated to 250°C. The effect of coal extraction on the surface is also irreversible. The adsorption heat for a given hydrocarbon on the extracted coal is independent of the temperature (between 30 and 250°C) at which the data are acquired. Heating the extracted coal does not alter the adsorption heat. These observations demonstrate that heating Illinois No. 6 coal at 200 to 250°C results in irreversible changes in surface structure. Extracting Illinois No. 6 coal with tetrahydrofuran results in irreversible changes in surface structure which give rise to adsorption heats similar to those caused by heating the coal at 250°C.

The similar adsorption heats obtained for hydrocarbons on Illinois No. 6 coal heated at 250°C or extracted in tetrahydrofuran lend support to the conclusions of others that heating coal at 200 to 300°C or extracting with a good solvent causes an irreversible structural relaxation of the bulk coal.^{42,43} The IGC data demonstrate that this relaxation is also felt at the coal surface. The surface interactions become less exothermic, consistent with a rearrangement of the coal to give a

lower surface energy.

The similar adsorption heats for the demineralized, extracted, and original Illinois No. 6 coals all heated at 250°C provides evidence that the presence of mineral matter does not have an effect on van der Waals interactions at these coal surfaces. Heating the original or extracted coal at 250°C should leave the coal mineral matter intact.

Inverse gas chromatography is now the only way to obtain thermodynamic data for adsorption at the coal surface, uncomplicated by diffusion into the bulk. The data generate a picture of a surface which is similar to other carbons and interacts with nonpolar adsorbates primarily by van der Waals and dispersion forces. This is not surprising. It is surprising that mild heat treatment and exposure to aqueous citric acid should alter the surface, and in the same direction. The IGC technique works with polar molecules and other coals and we shall be reporting these results in other papers.

Acknowledgement

Support of this work by the U.S. Department of Energy through grant DE-FG22 89PC9757 is gratefully acknowledged. We thank Bob Hunsicker for preparing the demineralized coal.

Table I. Retention volumes, V_N , negative adsorption heats, $-q_{st}$, and integral adsorption entropies, ΔS° , for inert gases and alkanes on Illinois No. 6 coal obtained by inverse gas chromatography and adsorption heats, Q_o , on graphitized carbon^{a)}.

Adsorbate	Measurement Temp Range ^{b)} (°C)	Adsorbate Area ^{c)} (Å ²)	Adsorbate Polarizability ^{d)} (Å ³)	$V_N^e)$ (ml)	$-q_{st}^f)$ coal (kcal/ /mol)	$Q_o^a)$ carbon (kcal/ mol)	$\Delta S^\circ g)$ coal (cal/ mol*K)
Ar	30-90	14.2	20.1	1.67 ±0.17	2.6 ±0.4	2.4	11.9 ±0.2
CH ₄	30-90	17.2	32.7	3.56 ±0.17	3.1 ±0.3	3.0	12.1 ±0.1
Xe	60-100	19.3	51.9	6.90 ±0.24	5.6 ±0.4	4.2	8.0 ±0.1
C ₂ H ₆	80-120	22.4	56.3	12.6 ±0.0	6.4 ±0.4	4.3	5.8 ±0.2
cyclo- C ₃ H ₆	80-130	25.8	72.3	55.0 ±1.2	9.9 ±0.7	6.4	-1.0 ±0.0
C ₃ H ₈	90-130	27.1	79.4	37.2 ±0.4	9.2 ±0.5	7.3	0.5 ±0.0
n-C ₄ H ₁₀	100-130	34.6	102	81	11.5 ±0.4	8.6	0.2
neo-C ₅ H ₁₂	80-130	40.6	125	28.9 ±1.0	8.9 ±0.7	7.0	-4.6 ±0.1
n-C ₅ H ₁₂	115-140	38.9	126	389	13.5 ±0.4	9.1	-6.8
n-C ₆ H ₁₄	110-130	43.6	149	733	15.7 ±0.5	11.2	-11.3

- a) isosteric adsorption heats on graphitized carbon, Q_o , from ref. 29.
- b) indicates temperature range for van't Hoff plots.
- c) cross sectional areas of the adsorbates, calculated using the equation $(B/N)^{2/3}$ from ref. 34 where B is the molar volume and N is Avogadro's number. Values of B from refs. 35 or 36.
- d) polarizability, α , calculated from the formula $\alpha = [3M/\rho N] * [(n^2 - 1)/(n^2 + 2)]$ where M is the molecular mass, ρ is the density, N is Avogadro's number, and n is the refractive index using refractive indices and densities from ref. 35.
- e) net retention volumes, V_N , of the adsorbates on Illinois No. 6 coal at 90°C from IGC experiments or extrapolated from plots of $\ln (V_N/T)$ vs. $1/T$. Extrapolated values have no errors reported.
- f) negative isosteric adsorption heats, $-q_{st}$, for the adsorbates on Illinois No. 6 coal calculated from van't Hoff plots of the IGC retention volumes using equation 1.
- g) integral adsorption entropies, ΔS° , for adsorbates on Illinois No. 6 coal from IGC retention volumes (equation 2) at 90°C except for extrapolated values which were calculated using retention volumes at higher temperatures. Extrapolated values have no errors reported.

References

1. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; Chapter 10.
2. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*; Elsevier: New York, 1976; p. 403ff.
3. Ritger, P. L.; Peppas, N. A. *Fuel* **1987**, *66*, 815.
4. Hsieh, S. T.; Duda, J. L. *Fuel* **1987**, *66*, 170.
5. Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*, Plenum: New York, 1969.
6. Littlewood, A. B. *Gas Chromatography*, 2nd ed.; Academic: New York, 1970.
7. Gray, D. G.; Guillet, J. E. *Macromolecules* **1972**, *5*, 316.
8. Panzer, U.; Schreiber, H. P. *Macromolecules* **1992**, *25*, 3633.
9. Glass, A. S.; Larsen, J. W., submitted to *Macromolecules*.
10. Bulashov, V. M.; Kogan, L. A.; Popov, V. K.; Ol'shanetskii, L. G. *Solid Fuel Chem.* **1975**, *9*, 64.
11. Larsen, J. W.; Kennard, L.; Kuemmerle, E. W. *Fuel* **1978**, *57*, 309.
12. Guha, O. K.; Roy, J. *Fuel Sci. Technol.* **1983**, *2*, 103.
13. Guha, O. K.; Roy, J. *Fuel Process. Technol.* **1985**, *11*, 113.
14. Guha, O. K.; Roy, J. *Fuel* **1985**, *64*, 1164.
15. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; Chapter 2.
16. Arnett, E. M.; Hutchinson, B. J.; Healy, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 5255.
17. Crescenti, G.; Mangani, F.; Mastrogiacomo, A. R.; Palma, P.

J. Chromatogr. **1987**, *392*, 83.

18. Vorres, K. S.; *Users Handbook*, Argonne Premium Coals.
19. Linares-Solano, A.; Mahajan, O.P.; Walker, P. L., Jr. *Fuel* **1979**, *58*, 327.
20. Larsen, J. W.; Pan, C.-S.; Shawver, S. *Energy Fuels* **1989**, *3*, 557.
21. de Boer, J. H. *The Dynamical Character of Adsorption*; Oxford University: London, 1953; Chapter 6.
22. Larsen, J. W.; Wernett, P. C. *Energy Fuels* **1988**, *2*, 719.
23. Larsen, J. W.; Wernett, P. C. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37*, 849.
24. Braun, J.-M.; Guillet, J. E. *Macromolecules* **1975**, *8*, 882.
25. Reference 17 contains a numerical error in the calculation of $R\ln(p'/\pi)$ which we have corrected here.
26. Lowell, S. *Introduction to Powder Surface Area*; Wiley & Sons: New York, 1979; p. 5.
27. Curl, R. L.; McMillan, M. L.; *A. I. Ch. E. J.* **1966**, *12*, 819.
28. Purnell, H. *Gas Chromatography*; Wiley & Sons: New York, 1962.
29. a) Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*, Plenum: New York, 1969; pp., 26, 57, 59. b) Avgul, N. N.; Kiselev, A. V. In *Chemistry and Physics of Carbon*; P. L. Walker, Jr., Ed.; Marcel Dekker: New York, 1970, p. 33.
30. Courval, G. J.; Gray, D. G. *Can J. Chem.* **1976**, *54*, 3496.
31. Zwietering, F.; Van Krevelen, D. W. *Fuel* **1954**, *33*, 331.
32. Hall, P. J.; Mackinnon, A. J. *Prepr. Pap.-Am. Chem. Soc.,*

Div. Fuel Chem. **1992**, 37, 872.

33. Yun, Y.; Otake, Y.; Suuberg, E. M. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1991**, 36, 1314-1324.

34. Emmett, P. H.; Brunauer, S. J. *Am. Chem. Soc.* **1937**, 59, 1553.

35. Weast, R. C., Ed. *Handbook of Chemistry and Physics*, CRC: Boca Raton, Florida, 1982.

36. *Landolt-Börnstein Zahlenwerte und Funktionen*, Pt. 2, Sect. A; Springer-Verlag: Berlin, 1960.

37. Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*; Plenum: New York, 1969; p. 26.

38. Elkington, P. A.; Curthoys, G. J. *Phys. Chem.* **1969**, 73, 2321.

39. Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*; Plenum: New York, 1969; p. 58.

40. a) Littlewood, A. B. *Gas Chromatography*, 2nd ed.; Academic: New York, 1970; p. 102ff. b) Kiselev, A. V.; Yashin, Ya. I. *Gas-Adsorption Chromatography*, Plenum: New York, 1969; p. 28ff. c) Gray, D. G.; *Prog. Polym. Sci.* **1977**, 5, 1.

41. Exner, O. In *Progress in Physical Organic Chemistry*, vol. 10; Streitweiser, A. S., Jr.; Taft, R. W., Eds. Wiley: New York, 1973.

42. Larsen, J. W.; Mohammadi, M. *Energy Fuels* **1990**, 4, 107.

43. a) Yun, Y.; Suuberg, E. M. *Energy Fuels* **1992**, 6, 328. b) Yun, Y.; Suuberg, E. M. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1992**, 37, 856.

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Chromatographic peaks for n-pentane on THF-extracted Illinois No. 6 coal heated to 150°C. Column temperature=110°C, flowrate=30.3 ml/min. y-axis ticks represent 0.16 mV intervals. A, 1.0×10^{-10} mol; B, 7.0×10^{-11} mol; C, 3.2×10^{-11} mol; D, 1.9×10^{-11} mol.

Figure 3. Chromatographic peaks for ethane on Illinois No. 6 coal heated to 150°C. Column temperature=80°C, flowrate=6.6 ml/min. y-axis ticks represent 4.0 mV intervals for peak A. Other peaks have been expanded along the y-axis to the same height as peak A. A, 1.1×10^{-8} mol; B, 8.1×10^{-10} mol, expanded x5.5; C, 2.8×10^{-10} mol, expanded x16; D, 7.3×10^{-11} mol, expanded x30.

Figure 4. Retention volume vs. linear velocity, $\bar{u}$, for hydrocarbons on Illinois No. 6 coal heated to 150°C. A, cyclopropane, 130°C ($\blacktriangle$); B, n-pentane, 110°C ($\circ$); C, ethane, 80°C ($\blacksquare$); D, propane, 110°C ($\square$); E, neopentane, 90°C (∇).

Figure 5. Van't Hoff plot for n-hexane on original Illinois No. 6 coal heated to 150°C. Retention volumes were acquired over the temperature range 100 to 150°C.

Figure 6. $\ln (V_N/T)$ vs. $1/T$ for n-butane, neopentane, and methane on different particle size fractions of Illinois No. 6 coal heated to 150°C. Each of the three columns contained 4g of coal. A-C: n-butane; A, 80/100 (•), B, 60/70 (■), C, 40/60 (▼). D-F: neopentane; D, 80/100 (◦), E, 60/70 (◊), F, 40/60 (▼). G-I: methane; G, 80/100 (◆), H, 60/70 (▲), I, 40/60 (□).

Figure 7. Adsorption heat versus electronic polarizability, α , for original, THF-extracted, and demineralized Illinois No. 6 coal from van't Hoff plots of IGC retention volumes. All coals were heated to 150°C. Lines are drawn through points for the n-alkanes and inert gases. ◦, original; Δ, demineralized; •, extracted.

Figure 8. Adsorption entropies versus adsorption heats for hydrocarbons and inert gases on original and on THF-extracted Illinois No. 6 coal. Data acquired for coals heated to 150°C. ◦, hydrocarbons and inert gases on original coal; •, hydrocarbons on extracted coal.

Figure 9. Adsorption heats versus polarizability for original and demineralized Illinois No. 6 coal heated to different temperatures. ◦, hydrocarbons and inert gases on original coal heated to 150°C (repeat of data in Figure 7); ■, n-butane and n-hexane on original coal heated to 200°C; Δ, n-butane, n-pentane, n-hexane on demineralized coal heated to 200 and 250°C; ▲, n-

hexane on original coal heated to 250°C.

15

time (minutes)

0

intensity (mV)

Introduction

Studies of interactions at coal surfaces are important for understanding the fundamental nature of coal as well as for improved coal processing. Coal cleaning involves polar solutes and the coal surface. Surface interactions may play a role in determining the success or failure of reactions in bulk coal. Knowledge of adsorbate-coal interaction strengths would provide information necessary for understanding both of these situations. However, rapid penetration of solutes into the coal precludes accurate determinations of solute-coal surface interaction energies. Penetration of most organics into the bulk coal begins immediately after adsorption.¹⁻⁴ Unless the adsorption step can be distinguished from the absorption which quickly follows, surface properties cannot be measured.

Inverse gas chromatography (IGC) is a useful technique for measuring adsorption thermodynamics at coal surfaces.² The adsorbate does not penetrate the coal bulk during the IGC experiment.^{2,5} If measurements are made at infinite dilution surface coverage, adsorbate-adsorbate interactions are not involved. This enables direct determination of adsorbate-coal surface interaction energies.

Many workers have recognized the importance of determining interaction strengths for molecules with coal surfaces.^{4,6-11} Larsen et al. and Arnett et al. used IGC to measure adsorption enthalpies of molecules on bituminous and anthracite coals, respectively.^{6,7} Fowkes et al. and Jones used flow calorimetry to measure

interaction enthalpies of pyridines and other polar molecules with bituminous coals.^{4,8} Parekh and Aplan, Good et al., and Ramesh and Somasundaran determined coal surface tensions with polar and nonpolar liquids.⁹⁻¹¹

In the present work, IGC was used to determine adsorption enthalpies for basic and acidic adsorbates on original and demineralized Illinois No. 6 coals. Data for nonpolar adsorbates demonstrate that a graphitized carbon surface is a good model for the non-specific component of the Illinois No. 6 coal surface.² It has been possible to separate non-specific (van der Waals) adsorption enthalpies from those due to "specific" interactions such as hydrogen-bonding.

Experimental

The experimental apparatus and procedure for IGC of coal surfaces have been described in a previous paper.²

Illinois No. 6 coal obtained from the Argonne sample bank was used as the stationary phase. The original coal was sieved to 40/60 mesh particle size. Extracted coal was prepared by extracting coal of 40/60 mesh particle size in tetrahydrofuran (THF) in a Soxhlet extractor for several days. Citric acid washed (CAW) coal was prepared by refluxing coal of 40/60 mesh particle size in citric acid solution under N₂ atmosphere for 15 hours.¹² The coal was washed exhaustively with distilled water in a Soxhlet extractor until the pH of the wash water was the same as that of the distilled water. HF-HCl demineralized coal was prepared by

heating (55-60°C) coal of 40/60 mesh particle size in 49% aqueous HF for 24 hours under N₂ atmosphere.¹² The coal was washed exhaustively with distilled water, heated at 55-60°C in 5N HCl overnight under N₂, and washed until the pH of the wash water was neutral. Chemical analysis gave 16.7% ash for the original, 9.2% ash for the CAW, and 2.0% ash for the HF-HCl demineralized coals (Galbraith Laboratories, Inc.). The THF-extracted, CAW, and HF-HCl coals were dried in a vacuum oven at 110°C overnight. All four coals, original, THF-extracted, CAW, and HF-HCl, were packed into separate 1/8 inch O.D., 2.1 mm I.D. stainless steel columns about 150 cm in length. The original and THF-extracted coals were heated at either 150°C or 250°C in helium for 2 weeks. The CAW and HF-HCl demineralized coals were heated at 250°C for 2 weeks before chromatograms were acquired.

All of the reagents were obtained from Aldrich at the highest purities available. They were admitted to the vacuum line for injection without further purification after three freeze-pump-thaw cycles.

Chromatograms were obtained in the range 30 to 250°C, depending on the interaction strength of a given probe with the coal surface. The carrier gas was helium. Injector and detector temperatures were kept at 180°C for hydrocarbons and at 250°C for injections of polar adsorbates. Flowrates for experiments with hydrocarbon adsorbates ranged from 3 to 40 ml/min. and flowrates for experiments with polar adsorbates ranged from 20 to 42 ml/min except for experiments with carbon dioxide for which flowrates of

about 10 ml/min. were used. The pressure drop across the column was about 1 to 2 atm for hydrocarbons and about 3 atm for polar adsorbates. A flame ionization detector was used to obtain chromatograms for all adsorbates except carbon dioxide and carbon disulfide for which a thermal conductivity detector was used. Retention volumes were determined from the first moments of the peaks as described previously.² Peak areas for several of the adsorbates on coal and on glass bead columns were compared to make sure that 100% of the probes were eluting and that none were retained in the column.

Results

Table I lists isosteric adsorption heats, q_{st} , for acidic and basic adsorbates interacting with the surface of original and demineralized Illinois No. 6 coals. Adsorption heats were determined from plots of the uncorrected retention volumes (V_R) over column temperature ($\ln V_R/T$) vs. one over the column temperature ($1/T$; van't Hoff plots). Typical plots are shown in Figure 1. Results for hydrocarbons were published earlier.² For all polar adsorbates except CO_2 , van't Hoff plots were constructed from retention volumes determined over the temperature range 150 to 250°C. Retention volumes for CO_2 were determined over the range 50 to 100°C. Injections were made every 5 to 10°C. The van't Hoff plots were constructed using at least three injections at each temperature over a temperature range of at least 40°C except for pyridine on original Illinois No. 6 for which the temperature range

was 230 to 250°C.

Because the coals were heated at 250°C before polar adsorbates were injected, the adsorption heats may differ from those which would be obtained for Illinois No. 6 coal not so heated. Thermogravimetric studies show no effects of heating coal to 250°C, but extraction studies demonstrate that heating coal at this temperature causes bond breaking in bulk coal.^{13,14} In the present work, no attempt was made to determine the effect(s) of heating on the measured adsorption heats for polar adsorbates.

Errors in the adsorption heats reported in Table I are the errors in the slopes of the linear regression fits for the van't Hoff plots. The errors represent less than 6% of the measured values for the hydrocarbons (not shown).² The errors are $\pm 10\%$ for all of the polar adsorbates on all three coals. The errors for the more strongly interacting adsorbates (pyridine and amines) are larger for original compared to demineralized coals. This is probably because the peaks for adsorbates on original coal were broader than peaks for adsorbates on demineralized coal, leading to more inaccurate first moments.¹⁵ The 10% error in the adsorption heat for pyridine on the original coal may reflect the effect of tailing on the first moment, or the small temperature range which had to be used. Because a column temperature range of only 230 to 250°C was used to determine the adsorption heat for this system, this datum is significantly uncertain. Pyridine did not elute as an observable peak on original coal at column temperatures lower than 230°C.

Some other alcohol and amine adsorbates also did not elute as observable peaks during the experiments (see Table I). Instead, the GC baseline began to slope after these adsorbates were injected onto the columns. When the column temperature was increased above the temperature at which the injection had been made, very broad peaks with widths on the order of hours were often observed. Heating at 250°C overnight was required for the baseline to stabilize before an experiment could be attempted with another adsorbate. It is surmised that alcohol and amine adsorbates which did not elute as reasonable peaks gave peaks that were so broad as to be indistinguishable from the baseline. Alternatively (or additionally), these adsorbates may have adsorbed on very strong sites or equivalently, diffused into the coal and desorbed from it very slowly. Adsorption thermodynamics could not be obtained for these molecules. This situation is a real limitation in the inverse gas chromatography technique for coal surfaces. By going to higher column temperatures it might be possible to obtain adsorption heats for these adsorbates, but heating above 250°C could modify the coal surface so that the adsorption heats would represent interactions of the adsorbates with different (modified) coal functional groups. A detailed study of the effects of temperature on adsorption heats of polar adsorbates is worth pursuing.

All of the experiments for polar adsorbates were performed on Illinois No. 6 coal which had been heated at 250°C for at least 2 weeks. This was done because it was necessary to run the

experiments at column temperatures up to 250°C in order to elute some of the more strongly adsorbed probes (pyridine, methylamine, *t*-butylamine, and methanol). This was especially the case for the non-demineralized coal which had higher adsorption heats for these adsorbates. In order to provide a means for comparison of the thermodynamic data on original, demineralized, and extracted coals, all of the coals were pretreated by heating at 250°C before any IGC experiments were performed. The effect of incremental increases in pretreatment temperature on the measured adsorption heats for polar adsorbates was not determined and would make an interesting subject for future study.

Discussion

Separation of Acid-Base and van der Waals Interactions at the Surface of Illinois No. 6 Coal

Most polar molecules, unlike hydrocarbons, are capable of interacting with the coal surface by specific acid-base interactions. Figure 2 is a plot of isosteric adsorption heat vs. polarizability for sixteen polar adsorbates on HF-HCl demineralized Illinois No. 6 coal which are listed in Table I. Molecular polarizability is a good measure of a molecule's non-specific, van der Waals interactions.¹⁶ Also plotted are isosteric adsorption heats for eight hydrocarbons on Illinois No. 6 coal which had been extracted in tetrahydrofuran and heated at 250°C.² The line is drawn through the points for the hydrocarbon adsorbates. The

hydrocarbons cannot undergo specific acid-base interactions with the surface so this line represents the non-specific (van der Waals) contribution to the total adsorption enthalpy. The points for the polar adsorbates fall above the line. The vertical distance between the point for a particular polar adsorbate and the line is an estimate of the specific component of the isosteric adsorption enthalpy, $Q_{st,specific}$.

In order to calculate the specific components of the adsorption enthalpies for the polar adsorbates, the non-specific or van der Waals component is subtracted from the total isosteric adsorption heat (q_{st}). That non-specific component cannot be directly measured. Two methods were used to estimate non-specific adsorption enthalpies for the polar adsorbates: 1) the hydrocarbon line in Figure 1 and the polarizability of the polar adsorbate were used to estimate the non-specific contribution, or 2) they were set equal to the enthalpy of interaction of these adsorbates with a carbon black surface containing no polar (heteroatom) functional groups.

In the first method, non-specific adsorption heats were calculated from the adsorbate's polarizability and the plot of isosteric adsorption heat vs. polarizability for hydrocarbon adsorbates.² We demonstrated previously that the isosteric adsorption heats for hydrocarbons on Illinois No. 6 coal became more exothermic with increasing adsorbate polarizability.² These adsorbates have no polar groups and can interact with the surface by van der Waals forces only. The polarizabilities of the polar

adsorbates were calculated from the formula $\alpha = [3M/\rho N] * [(n^2 - 1)/(n^2 + 2)]$ where M is the molecular mass, ρ is the density, N is Avogadro's number, and n is the refractive index using refractive indices and densities from reference 17.¹⁶

In the second method, non-specific adsorption heats for the polar adsorbates were set equal to isosteric adsorption heats for the polar adsorbates on graphitized carbon black (Q_0).¹⁸ We demonstrated previously that adsorption enthalpies of non-polar molecules (hydrocarbons) are the same on Illinois No. 6 coal and graphitized carbon black (Kiselev's data).^{2,18} Because carbon black has no polar (heteroatom) functional groups, specific interactions with the polar adsorbates cannot occur. The graphitized carbon black surface is a good model for interactions of hydrocarbons with the Illinois No. 6 coal surface.

We prefer the second method for estimating the non-specific contribution because it accounts for non-specific interactions absent from the first. Using hydrocarbons and the coal surface (method 1), induced dipole-induced dipole (dispersion) interactions and coal dipole-hydrocarbon induced dipole are the only interactions included. Using the carbon surface and polar molecules (method 2) includes these interactions and all others except those involving polar (heteroatom) groups on the coal surface. For hydrocarbons, both methods should give the same results. This has been demonstrated.² For polar molecules, method 2 (carbon) should give more exothermic heats than method 1 (polarizability). This is demonstrated by the data in Figure 3.

Whenever possible, method 2 is used. When not possible, we fall back on method 1.

The specific component of the isosteric adsorption heat is useful as a measure of the coal surface's ability to participate in acidic and basic interactions. Other workers have determined specific interaction enthalpies for acids and bases on solids including silica, carbon, and glassy polymers.¹⁹⁻²⁹ Basic adsorbates provide the simplest type of interaction because they can only accept a hydrogen (donate an unshared electron pair), while hydrogen acids can both donate and accept hydrogen bonds with the surface.

Adsorption Heats for Aprotic Organic Bases on Illinois No. 6 Coal

Organic bases can participate in specific interactions with a surface by donating an unshared pair of electrons. The specific adsorption heats for these types of molecules with Illinois No. 6 coal provide strong evidence for hydrogen-bonding with the coal surface.

Figure 4 is a plot of specific isosteric adsorption enthalpy ($Q_{st,specific}$) on HF-HCl demineralized Illinois No. 6 coal vs. enthalpies of hydrogen-bond formation with p-fluorophenol, $\Delta H_{f, PFP}$, for seven aprotic organic bases.³⁰ The specific adsorption heats for all of the bases in Figure 3 are identical to their hydrogen-bond heats with phenol. This remarkable coincidence strongly suggests that these bases interact with pendant phenol groups on the coal surface. The base-phenol interaction is a good model for

the base-coal surface interaction.

As seen from Table I, the adsorption heats for the bases are the same on original and demineralized coals. At low coverage, the bases are preferentially associated with phenols on the organic coal surface. Because the *p*-fluorophenol data were obtained in such a way as to preclude the self-association of *p*-fluorophenol, the data also provide evidence that the hydroxyl groups which are involved in hydrogen-bonding on the coal surface are not self-associated.³⁰ If they were, additional energy would be required to break coal-coal hydrogen-bonds, and the specific adsorption heats of the bases would be less exothermic than hydrogen-bond interaction heats with the phenol.

The exothermicities of the specific adsorption heats for the bases on Illinois No. 6 coal in Figure 3 increase in the same order as bulk swelling ratios for several bituminous coals in these solvents.³¹ In addition, the adsorption heats for the bases pyridine, dimethyl sulfoxide, THF, diethyl ether, and acetone decrease in the same order as the swelling ratios for acetylated vs. original Illinois No. 6 coal in these solvents.³² These observations support the view that coals contain internal hydrogen-bonds and that coal-coal hydrogen-bonds are broken during swelling of coals in these solvents.^{32,33}

The adsorption heat for acetonitrile (not shown), a weak hydrogen-bond acceptor, does not fit on the line with the other organic bases, being more exothermic than predicted. The dipole moment of acetonitrile is larger than that of the other polar

adsorbates studied ($\mu \sim 4D$ for acetonitrile vs. $\sim 3D$ or less for the other polar adsorbates, except dimethyl sulfoxide, which also has $\mu \sim 4D$).¹⁷ The reason for the large aspecific adsorption heat of acetonitrile is not known. It may be that dipole-dipole forces make a significant contribution to acetonitrile's interaction with the coal surface. These forces are not taken into account by either of the methods for estimating the non-specific component of the adsorption heats.

Adsorption Heats for Amphoteric Adsorbates on Illinois No. 6 Coal

Compared to the interactions of organic bases, the specific interactions of alcohols and amines with the coal surface are more complex because these latter adsorbates may act as either acids, bases, or both. For example, alcohols and amines have both an unshared electron pair(s) and a hydrogen atom to donate in interactions with a surface. These adsorbates may hydrogen-bond to the surface by accepting or donating a hydrogen atom, making it more difficult to characterize the nature of their interactions with coal.

Some of the adsorbates interact preferentially and strongly with coal mineral matter. The specific adsorption heats for pyridine, methylamine, methanol, and t-butylamine on original Illinois No. 6 coal are much more exothermic than the specific adsorption heats of the organic bases THF, acetone, and diethyl ether on this coal. The specific adsorption heats of pyridine, methylamine, methanol, n-propanol, and 2-propanol on the

demineralized coal are of similar magnitude as the specific adsorption heats of the other organic bases with this coal. These observations suggest that pyridine, alcohols, and amines have an additional interaction with the original, mineral matter-containing coal which is not experienced by the aprotic oxygen bases. Since the main difference between the coal samples is the presence of some types of mineral matter, we ascribe the difference in adsorption enthalpies to strong interactions of pyridine, methylamine, methanol, and *t*-butylamine with mineral matter.

Other workers have obtained thermodynamic data for alcohols, pyridines, and amines on original and demineralized coals.^{4,34,35} Ramesh et al. measured an isosteric adsorption heat of 10.5 kcal/mol for a surface coverage of 0.25 mmol of methanol per gram of a low ash bituminous coal using a calorimetric method.³⁴ This value is closer to the isosteric adsorption heat of methanol on the demineralized coal, 12.2 kcal/mol, than on the original coal, 20.5 kcal/mol (Table I). Fowkes et al. reported that *t*-butylphenols and *t*-butylpyridines had more exothermic adsorption heats on high compared to low ash bituminous coals.⁴ Green and West found that the same molar amount of four different primary linear amines was absorbed by original (non-demineralized) Illinois No. 6 coal and that the amount absorbed was larger than needed to saturate all of the hydroxyl sites in the coal.³⁵ They concluded that amines interact with specific (non-hydroxyl) sites in the coal. The data in Table I provide evidence that non-phenolic (mineral matter) sites for amine adsorption exist on the original coal.

The bulky adsorbates t-butylamine and t-butanol have less exothermic specific adsorption heats compared to methylamine, methanol, n-propanol, and 2-propanol on both the original and demineralized coals. These observations suggest that the branched geometries of the t-butyl-substituted adsorbates may prevent them from interacting as strongly with coal surface groups as do the linear alcohols and amines. Fowkes et al. reported less exothermic flow calorimetric adsorption heats for t-butyl-substituted pyridines and phenols compared to the unsubstituted molecules on bituminous coals.⁴

As seen from Table I, all of the adsorbates including the oxygen bases, pyridine, alcohols, and amines have similar adsorption heats on citric acid washed and HF-HCl treated demineralized coals. Citric acid washing removes carbonate and ion-exchangeable minerals from the coal.¹² This treatment caused the coal's ash analysis to decrease from 16.7% to 7.2%. HCl also removes carbonate and ion-exchangeable minerals, while HF removes silicates and clay minerals from the coal.¹² The HCl-HF treatment caused the coal's ash analysis to decrease to 2.0%. The IGC data provide evidence that pyridine, alcohols, and amines interact more strongly with carbonate and/or ion-exchangeable minerals than with silicate or clay minerals on the original coal surface. It is also possible that clay and silicate minerals are not present at the coal surface and so cannot contribute to the measured adsorption heats. Others have found evidence that clay minerals promote chemical reactions in coals.^{36,37} The IGC data neither refute nor

support this conclusion.

Alcohol and amine adsorbates could act as either hydrogen-bond acceptors or donors to the coal surface. These adsorbates have similar specific adsorption heats as the oxygen bases on the demineralized coal, suggesting that they may hydrogen-bond to the organic portion of the coal surface. Their specific interactions with the original coal are much more exothermic than with the demineralized coal. The specific interactions of methanol, methylamine, and *t*-butylamine with the original coal account for an additional 3-7 kcal/mol above their interactions with the demineralized coal, suggesting that mineral matter sites which are 3-7 kcal/mol stronger than organic sites exist on this coal for interactions with these adsorbates.

Adsorption Heats for Carbon Dioxide and Carbon Disulfide on Illinois No. 6 Coal

Carbon dioxide and carbon disulfide are important adsorbates. Although both of these molecules are capable of swelling coals, the nature of their interactions with coal remain unknown. Carbon dioxide is widely used for determining coal surface areas and a controversy exists over whether this surface is part of a pore network or consists of isolated pores accessible to CO₂ because it specifically interacts and diffuses rapidly into coal.³⁸⁻⁴⁰ CS₂ is a uniquely effective co-solvent and a component of the best coal extracting solvent mixture known.⁴¹ Carbon disulfide has lower swelling ratios for coals compared to hydrogen-bonding solvents.³¹

Typical swelling ratios are about 1.5 for bituminous coals in CS₂ and 2.0 or higher for bituminous coals in pyridine.³¹ Neither CO₂ nor CS₂ has a molecular dipole moment. CO₂ may act as a hard acid in its interactions.⁴² It has been speculated that the quadrupole moment of CO₂ is responsible for its interactions with coals.³⁸

Specific adsorption heats for CO₂ and CS₂ on Illinois No. 6 coal are 1.5 to 2.5 and 2.5 to 3.5 kcal/mol, respectively (Table I). These data confirm the suggestion that CO₂ interacts specifically with coals.¹ They are neutral on the question of whether this interaction enables a rapid diffusion of CO₂ through coals.³⁸ The specific adsorption heat of CS₂ provides evidence that its unique swelling properties are in part the result of specific interactions with coal.⁴¹

Dispersive Surface Tensions for Original and Extracted Illinois No. 6 Coal

The dispersive surface tension of a solid is the van der Waals component of the force that a molecule of a liquid experiences when it occupies a given area at the solid-liquid interface.⁴³ Dispersive solid surface tensions are typically determined from contact angle measurements.^{43,44} It can be shown that, for a hydrocarbon liquid on a solid surface, the contact angle is a function of the dispersive component of the surface tension of the pure liquid (calculated from the polarizability, ionization potential, intermolecular distance, and molar volume of the liquid) and the dispersive surface tension of the solid, resulting in an

equation with only one unknown which can be solved for the dispersive solid surface tension, γ_s^d .⁴³

The dispersive surface tension of a solid stationary phase can be determined from retention volumes for hydrocarbons obtained by inverse gas chromatography.^{27,45} Coal surface tensions are relevant to processes such as coal cleaning in which the hydrophobic nature of the coal surface (related to the van der Waals component of the surface interaction) determines how successful different liquids are in separating mineral matter from organic coal components.⁴⁶ In the present work, it is shown that when Illinois No. 6 coal is heated at 250°C or extracted, its dispersive surface tension decreases. This could be the result of changes in porosity, surface structure, or polarizability of the surface.⁴⁷ The adsorption heats for bulky hydrocarbons are used to determine which of these processes is responsible for the decrease.

Dispersive solid surface tensions for hydrocarbons on Illinois No. 6 coal were determined from the retention volumes (V_N) using the relationship between the free energy of adsorption, ΔG_{ads}^d , and the work of adhesion, W_A^d , as described below.^{27,45} The superscript d indicates dispersive interactions. The free energy of adsorption for dispersive interactions is obtained from the IGC retention volume from the relation $\Delta G_{ads}^d = -RT \ln V_N^d$. The work of adhesion for dispersive interactions is defined in terms of the dispersive solid surface tension, γ_s^d , and the dispersive liquid surface tension, γ_L^d ; $W_A^d = 2(\gamma_s^d \gamma_L^d)^{1/2}$. This relation is based on the mean value approximation which says that the van der Waals interaction between

two phases may be separated into van der Waals interactions for each of the pure phases.⁴³ Equating ΔG_{ads}^d obtained from the IGC retention volume with W_A^d (where N is Avogadro's number and a is the area occupied by the adsorbate molecule at the surface),^{27,45}

$$\begin{aligned} -\Delta G_{ads}^d &= NaW_A^d \\ RT \ln V_N &= 2Na(\gamma_s^d \gamma_L^d)^{1/2} \end{aligned} \quad (1)$$

The slope of a plot of $RT \ln V_N$ vs. $2a(\gamma_L^d)^{1/2}$ for adsorbates that interact with the surface by dispersive forces only (eg., hydrocarbons) gives the dispersive component of the solid surface tension (γ_s^d).

Figure 5 is a plot of equation 1 for Illinois No. 6 coal heated at 150°C and for extracted Illinois No. 6 coal heated at 150 and at 250°C. Retention volumes at 90°C were used in calculating the dispersive surface tensions from equation 1. Liquid dispersive surface tensions (γ_L^d) for n-pentane and n-hexane used in the plot were 17.0 and 18.4 mJ/m², respectively.⁴⁸ Liquid surface tensions for the other n-alkanes were derived by assuming that the increment between the dispersive surface tension for successive alkanes was 1.4 mJ/m².⁴⁸ Values of a were determined using the formula $a = (B/N)^{2/3}$ where B is the molar volume of the adsorbate using values of B from reference 17.⁴⁹ Others have calculated a from contact angle measurements.⁴⁸ Because the value of γ_s^d is determined from the slope of a plot of equation 1, different a values could result in values of dispersive surface tensions for a given solid which vary by up to ~5%.

From the slope of the plot in Figure 5, the dispersive component of the surface tension for Illinois No. 6 coal heated at 150°C is 104 mJ/m². This is similar to surface tensions reported for activated and porous carbons and for graphite.^{24,26,50} Extracting the coal in THF or heating to 250°C caused the surface tension to decrease to 49 mJ/m². This is larger than surface tensions reported for polymers (~10 to 40 mJ/m²) but is similar to surface tensions reported for nonporous carbons.^{23,48,44,51} Others have found critical surface tensions similar to this value for coals of varying rank.⁹⁻¹¹ Using iodomethane, glycerol, and water, Good et al. reported critical surface tensions of about 50 mJ/m² from receding contact angles and ~40 mJ/m² from advancing contact angles for coals ranging from 62 to 94% carbon.¹⁰ Ramesh and Somasundaran reported an average critical surface tension of 44 mJ/m² for a Bruceton coal.¹¹ Parekh and Aplan found critical surface tensions of ~47 mJ/m² for coals of 46 to 95% carbon from contact angles in polar and nonpolar liquids.⁹ Lopez-Garzon et al. found that when surface tensions for microporous carbons were corrected for surface curvature (microporosity), the surface tensions decreased from about 400 to 550 mJ/m² to about 35 to 50 mJ/m².⁵² These results suggest that a dispersive surface tension of 35 to 50 mJ/m² is typical of a flat, uncurved carbonaceous surface. The dispersive surface tension of the extracted coal is characteristic of such a carbonaceous surface.

We previously reported that the adsorption heats for hydrocarbons and inert gases on Illinois No. 6 coal heated at 150°C

were more exothermic than isosteric adsorption heats on extracted and 250°C heated coal, i.e., extracting or heating the coal decreased its surface energy.² Large dispersive surface tensions and more exothermic isosteric adsorption heats for hydrocarbons may result if micropores (pores with diameters less than about 10 Å) are present at the surface.^{47,52} When an adsorbate is adsorbed in a micropore, it is adjacent to two surfaces, which is effectively the same as being twice as close to a single surface.⁵³ Since van der Waals interaction strengths increase with the sixth power of increasing distance to the surface, adsorption in a micropore enhances the adsorption heat compared to its value on a flat surface. Enhanced adsorption heats may also result from the presence of highly polarizable atoms at the surface or from a high surface atom concentration.⁴⁷

Microporosity is not responsible for the large dispersive surface tension and exothermic adsorption heats of hydrocarbons on original Illinois No. 6 coal. This can be shown by considering the dependence of these quantities on molecular size. When the adsorbed molecules become too large to fit into the micropores, both surface tension and adsorption heat change suddenly. This behavior is shown for microporous carbons in Figure 6.⁵² In contrast, our adsorption enthalpies for bulky molecules on original Illinois No. 6 coal show no break with molecular diameter. See Table II. Given the size of the molecules used (Table II), no micropores with diameters ≤ 6 Å are present at the coal surface. The large dispersive surface tension of the coal, 104 mJ/m²,

probably does not result from microporosity.

We do not know what causes the change in dispersive surface tension when the coal is heated to 250°C or extracted with THF. Clearly, the structure of the coal surface is changed by these treatments. It has been established that swelling/extracting coals causes structural rearrangements which change many properties.⁵⁵ We can now add dispersive surface tension to the list. But the structure changes have not been characterized on a molecular level. It is not known whether polar groups move to the surface. It is known that the fractal dimensionality of the surface is decreased and that the rearranged coal is stabilized by greater non-covalent interactions.⁵⁶

It is not certain that heating to 250°C and THF extraction even cause the same structure changes. Both processes result in new structures with the same dispersive surface tension and adsorption enthalpies for hydrocarbons and it is reasonable to assume that this indicates similar structures. But it does not prove it.

IGC provides a new and convenient method for measuring dispersive surface tensions for liquids on coal surfaces. It permits such measurements at conditions not otherwise accessible. Contact angle methods report similar dispersive surface tensions for a wide range of unmodified coals.⁹⁻¹¹ This may be because these methods are not sensitive to low coverage coal surface sites while IGC has been shown to be sensitive to low coverage sites.² IGC surface tensions and adsorption heats have revealed interesting

changes in coal structure which will require investigation by other techniques for their characterization.

Summary

The inverse GC technique is useful for determining acid-base interactions at coal surfaces. The data provide insight into the specific acid-base interactions of adsorbates with coal surfaces. Interactions with organic coal surface groups as well as with mineral matter can be studied. This technique has potential for characterizing the surface energetics of a wide range of molecules and coals.

Acknowledgement

We are grateful to the U.S. Department of Energy for support of this work through grant number DE-FG22 89PC9757. We thank Bob Hunsicker for preparing the citric acid washed coal and Shang Li for preparing the HF-HCl demineralized coal.

Table I Isosteric adsorption heats, $-q_{st}$, and specific isosteric adsorption heats, $-q_{st,specific}$, for acid and base adsorbates on original, citric acid washed (CAW), and HF-HCl demineralized Illinois No. 6 coals heated at 250°C. Also listed are non-specific isosteric adsorption heats, $-q_{st,non-specific}$, on graphitized carbon black (reference 18) or on Illinois No. 6 coal (reference 2).

Adsorbate	$-q_{st}$ (kcal/mol)			$-q_{st,specific}$ (kcal/mol)			$-q_{st,non-specific}$ (kcal/mol)
	<u>Coal,</u> <u>Exptl. Value</u>			<u>Coal,</u> <u>Calc. Value</u>			<u>Carbon,</u> <u>Lit. Value^{a)}</u>
	Orig.	CAW	HF-HCl	Orig.	CAW	HF-HCl	
THF	14.1± 0.3	14.7±0.2	13.3± 0.2	6.6	7.2	5.8	7.5 ^{b)}
diethyl ether	12.3± 0.3	15.6±0.5	14.3± 0.3	3.7	6.9	5.7	8.6
acetone	14.3± 0.3	15.4±0.6	13.5± 0.6	6.3	7.4	5.5	8.0
acetonitrile	15.7± 0.6	17.0±0.6	16.9± 0.3	10.5	11.8	11.7	5.2
pyridine	30.8± 2.8	19.3±0.6	18.1± 0.5	20.0	8.5	7.3	10.8
ethyl acetate			16.2± 0.3			4.8	11.4 ^{b)}
tetrahydrothiophene			12.4± 0.3			3.4	9.0 ^{c)}

dimethyl sulfoxide			14.5± 0.5			7.1	7.4 ^{b)}
<u>t</u> -butylamine	19.1± 1.6		11.6± 0.4	9.8		2.3	9.3
methylamine	18.2± 0.9	d)	14.4± 0.3	14.6	d)	10.8	3.6 ^{b)}
<u>t</u> -butanol	d)	10.9±0.3	10.9± 0.6	d)	2.6	2.6	8.3
methanol	20.5± 0.7	d)	12.2± 0.7	15.2	d)	6.9	5.3
<u>n</u> -propanol		13.1±0.3	14.4± 0.4	d)	5.0	6.3	8.1
2-propanol			13.4± 0.3			6.3	7.1
carbon disulfide	11.9± 0.3	11.8±0.3	10.5± 0.3	3.7	3.6	2.3	8.2 ^{b)}
carbon dioxide	6.6 ±0.2	6.4±0.2	5.8± 0.2	2.5	2.3	1.5	4.3

^{a)}values are isosteric adsorption heats on graphitized carbon black from reference 18.

^{b)}values were calculated from adsorbate polarizabilities and the slope and intercept of a plot of polarizability vs. isosteric adsorption heat for hydrocarbon adsorbates.²

^{c)}value is the isosteric adsorption heat for thiophene on graphitized carbon black from reference 18.

^{d)}adsorbates did not elute from the column as observable peaks (see Results section for explanation).

Table II. Adsorption heats for bulky adsorbates on original Illinois No. 6 coal heated at 150°C

Adsorbate	molecular diameter (nm)	$-q_{st}$ (kcal/mol)
benzene	.52 ^{a)}	9.6
neopentane	.58 ^{b)}	8.9
neohexane	.60 ^{a)}	10.2

^{a)}values from ref. 52

^{b)}value from ref. 54

References

1. Larsen, J. W.; Wernett, P. C. Energy Fuels 1988, 2, 719-20.
2. Glass, A. S.; Larsen, J. W. Energy Fuels, 1993, 7, 994-1000.
3. Hsieh, S.-T.; Duda, J. L. Fuel 1987, 66, 170.
4. Fowkes, F. M.; Jones, K. L.; Li., G.; Lloyd, T. B. Energy Fuels 1989, 3, 97-105.
5. Glass, A. S.; Larsen, J. W. Macromolecules, 1993, 96, 6354-6358.
6. Larsen, J. W.; Kennard, L.; Kuemmerle, E. W. Fuel 1978, 57, 309-13.
7. Arnett, E. M.; Hutchinson, B. J.; Healy, M. H. J. Am. Chem. Soc. 1988, 110, 5255-60.
8. Jones, K. L. Coal Prep. 1992, 10, 47-57.
9. Parekh, B. K.; Aplan, F. F. In Recent Developments in Separation Science, vol. 4; Li, N. N., Ed.; CRC: West Palm Beach, Florida, 1978, pp. 107-13.
10. Good, R. J.; Srivasta, N. R.; Islam, M.; Huang, H. T. L.; Van Oss, C. J. J. Adhesion Sci. Technol. 1990, 4, 607-17.
11. Ramesh, R.; Somasundaran, P. Coal Prep. 1990, 9, 121-30.
12. Larsen, J. W.; Pan, C.-S.; Shawver, S. Energy Fuels 1989, 3, 557-61.
13. Solomon, P. R.; Serio, M. A.; Carangelo, R. M.; Bassilakis, R.; Gravel, D.; Baillargeon, M.; Baudais, F.; Vail, G. Energy Fuels 1990, 4, 319-333.
14. Nishioka, M.; Larsen, J. W. Energy Fuels 1988, 2, 351-355.

15. Conder, J. R.; Young, C. L. *Physicochemical Measurement by Gas Chromatography*; Wiley & Sons: New York, 1979; Chapter 2.
16. Kauzmann, W. *Quantum Chemistry*; Academic: New York, 1957.
17. Weast, R. C., Ed. *Handbook of Chemistry and Physics*; CRC: Boca Raton, Florida, 1979.
18. Avgul, N. N.; Kiselev, A. V. In *Chemistry and Physics of Carbon*, vol. 6; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1970; pp. 1-124.
19. Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. *New Solid Acids and Bases*, Stud. Surf. Sci. Catal. vol. 51; Elsevier: Amsterdam, 1989.
20. Cusumano, J. A.; Low, M. J. D. *J. Catal.* 1971, 23, 214-27.
21. Fowkes, F. M.; *J. Adhes. Sci. Technol.* 1987, 1, 7-27.
22. Saint Flour, C.; Papirer, E. J. *Coll. Int. Sci.* 1983, 91, 69-75.
23. Schultz, J.; Lavielle, L.; Martin, C. J. *Adhesion* 1987, 23, 45-60.
24. Nardin, M.; Balard, H.; Papirer, E. *Carbon* 1990, 28, 43-48.
25. Panzer, U. *Colloids Surf.* 1991, 57, 369-74.
26. Donnet, J.-B.; Park, S.-J. *Carbon* 1991, 29, 955-61.
27. Panzer, U.; Schreiber, H. P. *Macromolecules* 1992, 25, 3633-37.
28. Briscoe, B. J.; Roach, S.; Williams, D. R. In *Interfacial Phenomena in Composite Materials*; Jones, F.,

Ed.; Butterworths: Guildford, 1989, pp. 132-37.

29. Deng, Z.; Schreiber, H. P. In Contemporary Topics in Polymer Science, vol. 6 (Int. Symp. Multiphase Macromolecular Systems (1988)); Culbertson, B. M., Ed.; Plenum: New York, 1989, pp. 385-400.
30. Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. J. Am. Chem. Soc. 1974, 96, 3875-91.
31. Quinga, E. M. Y.; Larsen, J. W. In New Trends in Coal Science, NATO ASI Series vol. 244, Yürüm, Y., Ed.; Kluwer: Netherlands, 1988, pp. 85-116.
32. Larsen, J. W.; Green, T. K.; Kovac, J. J. Org. Chem. 1985, 50, 4729-35.
33. Fujiwara, M.; Ohsuga, H.; Takanohashi, T.; Iino, M. Energy Fuels 1992, 6, 859-862. See, however, Painter, P. C. Energy Fuels 1992, 6, 863-864.
34. Ramesh, R.; Francois, M.; Somasundaran, P.; Cases, J. M. Energy Fuels 1992, 6, 239-41.
35. Green, T. K.; West, T. A. Fuel 1986, 65, 298-99.
36. Ross, D. S.; Hirschon, A. S.; Green, T. K. Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 1988, 33, 283-91.
37. Sharma, D. K.; Zulfikar, B. M. Fuel 1983, 62, 916-17.
38. Mahajan, O. P. Carbon 1991, 29, 735-42.
39. Marsh, H. Carbon 1987, 25, 49-58.
40. Larsen, J. W.; Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 1992, 37, 849-855.
41. Iino, M.; Takanohashi, T.; Ohsuga, H.; Toda, K. Fuel

- 1988, 67, 1639-1647 .
42. Huheey, J. E. Inorganic Chemistry, 2nd ed.; Harper & Row: New York, 1978; p. 279.
 43. Fowkes, F. M. Ind. Eng. Chem. 1964, 56, 40-52.
 44. Zisman, W. A. In Contact Angle, Wettability, and Adhesion, ACS Adv. Chem. Series 43; ACS: Washington, D.C., 1964, pp. 1-73.
 45. Doris, G. M.; Gray, D. G. J. Coll. Int. Sci. 1980, 77, 353-362.
 46. Good, R. J.; Islam, M. Langmuir 1991, 7, 3219-21.
 47. Kiselev, A. V.; Yashin, Ya. I. Gas-Adsorption Chromatography; Plenum: New York, 1969.
 48. Schultz, J.; Lavielle, L.; Martin, C. J. chim. phys. 1987, 84, 231-37.
 49. Emmett, P. H.; Brunauer, S. J. Am. Chem. Soc. 1937, 59, 1553.
 50. Fowkes, F. M. In Contact Angle, Wettability, and Adhesion, ACS Adv. Chem. Series 43; ACS: Washington, D.C., 1964, pp. 99-111.
 51. Good, R. J.; Van Oss, C. J. In Modern Approaches to Wettability; Schrader, M. E.; Loeb, G., Eds.; Plenum: New York, 1992, pp. 1-27.
 52. Lopez-Garzon, F. J.; Pyda, M.; Domingo-Garcia, M. Langmuir 1993, 9, 531-36.
 53. Denoyel, B.; Fernandez-Colinas, J.; Grillet, Y.; Rouquerol, J. Langmuir 1993, 9, 515-18.

Figure Captions

Figure 1. Van't Hoff plots for acetone on original Illinois No. 6 coal (o), t-butanol on citric acid washed Illinois No. 6 coal ($\square$), and CO₂ on HF/HCl demineralized Illinois No. 6 coal (Δ). All coals heated at 250°C.

Figure 2. Plot of isosteric adsorption heat ($-q_{st}$) vs. polarizability (α) for hydrocarbons and polar adsorbates on Illinois No. 6 coal. $\bullet$ =hydrocarbons on Illinois No. 6 coal extracted in THF and heated at 250°C; $\blacktriangle$ =polar adsorbates on HF-HCl demineralized Illinois No. 6 coal heated at 250°C. Hydrocarbons in order from left to right (increasing exothermicity) are: methane, ethane, cyclopropane, propane, n-propene, n-butane, 1-butene, and n-hexane.

Figure 3. Plot of non-specific component of q_{st} ($q_{st,non-specific}$) for polar adsorbates on Illinois No. 6 coal vs. their adsorption heats on graphitized carbon (Q_0) from reference 18. Adsorbates are: 1, CO₂; 2, methanol; 3, acetonitrile; 4, 2-propanol; 5, acetone; 6, n-propanol; 7, t-butanol; 8, diethyl ether; 9, pyridine.

Figure 4. Specific adsorption enthalpy, $-q_{st,specific}$, on HF-HCl demineralized Illinois No. 6 coal, vs. heat of hydrogen-bond formation in p-fluorophenol, $-\Delta H_{f,PPF}$, for seven bases. p-fluorophenol adsorption heats from reference 30.

Figure 5. Plot of equation 1 for hydrocarbons on Illinois No. 6 coal. o=original coal heated at 150°C; Δ=coal extracted in THF and heated at 250°C; □=coal extracted in THF and heated at 150°C. Adsorbates in order from left to right are: methane, ethane, propane, n-butane, n-pentane, and n-hexane.

Figure 6. Plot of adsorption heat vs. molecular diameter for bulky adsorbates on active carbons determined by IGC. Figure reproduced from reference 52. Different active carbons are indicated in the figure by P1-P4. P1, total volume of pores=0.366 ml/g. of which 0.119 ml/g. had diameters $\leq 36 \text{ \AA}$; P2, total volume of pores=0.134 ml/g. of which 0.093 ml/g. had diameters $\leq 36 \text{ \AA}$; P3, total volume of pores=0.422 ml/g. of which 0.163 ml/g. had diameters $\leq 36 \text{ \AA}$; P4, total volume of pores=0.346 ml/g. of which 0.105 ml/g. had diameters $\leq 36 \text{ \AA}$.

Back-up
Blank

PART 3

Surface Structure Determination by ^{13}C NMR

Back of
L. H. H. H.

INTRODUCTION:

Background

An understanding of the surface structure and chemistry of coals is necessary for a true understanding and optimization of coal cleaning and other surface interactions. In all chemical reactions of solid coal, the reagent first encounters the coal surface. The extent of surface which is available to a molecule and the interactions which occur during the molecule/surface encounter are critical to understanding the chemistry of the interaction of coals with various solvents. These studies were undertaken with the objective of understanding these complex interactions. Our present scientific understanding of coal structure and interactions are rudimentary and inadequate to develop new processes or explain existing technology, much of which was developed on a trial-and-error basis. To the best of our knowledge, NMR has not previously been applied to surface studies of coal. In contrast, solid state NMR has been applied extensively to coal and related systems. It is a powerful technique because line positions and intensities are indicative of geometry, bonding hybridization and population of distinct functionalities as well as local environment effects. The NMR spectrum can be influenced by many factors including dipolar through-space coupling between an unpaired electron spin and the spin of the carbon atom. The unpaired electron can act as a relaxation sink, significantly shortening the spin-lattice relaxation time (T_1) of the coupled carbon-13 atom. This shortening of the T_1 can theoretically broaden the signal to the point where it disappears. The effective range of interaction is proportional to the inverse sixth power of the separation of the electron and ^{13}C nuclear spins (r^{-6}).¹ In this system the effective range is a relatively short distance, on the order of approximately one nanometer. Assuming that the paramagnetic centers are deposited on the surface of our sample, an effective range of approximately one nanometer would limit the paramagnetic effects to surface functionalities.

When NMR relaxation agents are deposited on the surface of coals, the dipolar coupling of the unpaired electron spin of the relaxation agent and the carbon atom should significantly shorten the carbon T_1 which should broaden the resonance away. By obtaining the NMR spectrum of a coal sample before and after relaxation agent deposition and subtracting the spectra, the difference spectrum represents the

functionalities within approximately one nanometer of the surface and thus represents the surface composition of the coal.

Two NMR relaxation agents were used in this work. Copper(II) ions with one unpaired electrons were used initially because some background work had already been completed using this relaxation agent on model systems.² The second NMR relaxation agent evaluated was dysprosium (I) because it is a better relaxation agent than copper(II). Dysprosium (I) ions are in the +1 oxidation state having five unpaired electrons. When compared to the other lanthanides, dysprosium exhibits the largest downfield shifting behavior³ (see Figure 1.) We chose a downfield shifting lanthanide so that if carbonyl resonances shift, they would not move into the highly congested aromatic region. We evaluated various concentrations of these relaxation agents by monitoring the spin lattice relaxation times of various carbons and protons in the spectra. The relaxation times were measured using several NMR protocols described below. Proton spin lattice relaxation times were monitored indirectly using the carbon spectra.

Figure 1: Observed isotropic shifts for the most shifted resonances of 0.8M solutions of n-hexyl alcohol (H-1), 4-picoline N-oxide (H-2), and 4-vinylpyridine (H-2), in the presence of $\text{Ln}(\text{dpm})_3$ with the mole ratio of shift reagent / substrate = 0.125 measured at 30° in deuteriochloroform solutions.³

Cross Polarization vs. Bloch Decay

Several of the NMR protocols involve a technique commonly used in solid state NMR known as cross polarization (CP) in which magnetization is transferred from an abundant spin systems to a dilute systems.

This provides an enhancement in the signal to noise ratio on the order of the gyromagnetic ratios for the two nuclei. For carbon-13 there is a theoretical enhancement of approximately 4. Several issues need to be considered before CP is used to study coal and related systems. Cross polarization depends on the relaxation behavior found for the abundant nuclei. Since protons tend to relax faster than carbon atoms, this phenomenon allows faster experiment recycling, and thus an even greater signal to noise enhancement through signal averaging.⁴ Problems can occur using cross polarization due to the complex, time-dependent evolution of the carbon magnetization. The efficiency of cross polarization is controlled by the proton-carbon-13 dipolar coupling.⁴ Therefore, for magnetically inequivalent carbons, CP is dependent on their individual polarization transfer times (T_{CH}) and on the behavior of the proton reservoirs with respect to the rotating frame ($T_{1\rho}H$). Carbon nuclei particularly susceptible to inefficient polarization transfer are those subject to weak proton-dipolar interactions, either as a result of large C-H internuclear distances (i.e. nonprotonated carbons) or by motional averaging of the dipolar interaction due to molecular motion or by magic angle sample spinning (MASS).⁵ The differential rate of polarization transfer is not the only problem with CP. The presence of unpaired electrons, for example, free radicals and paramagnetic metal ions, can 1) shorten the $T_{1\rho}H$, causing the 1H spins to relax before complete polarization transfer to the ^{13}C can be achieved, and 2) cause loss of signal from carbons in close proximity due to shielding and relaxation effects.⁶ This leads to a condition in which there is no longer one optimal Hartmann-Hahn matching condition suitable for the ensemble of nuclei in the coal sample. The uncompromising nature of the Hartmann-Hahn matching condition required for optimal transfer of magnetization may lead to distortions in signal intensities for any given match time. An advantage of this behavior is that signals from the rotor and stator are greatly reduced using CP techniques since they do not contain protons. This differential behavior is a significant disadvantage if quantitative spectra are required for a particular application.

A single pulse or Bloch decay experiment⁷ does not experience distortion problems as described for the CP experiments⁴, however, Bloch decay experiments often incur sensitivity problems. A Bloch decay does not have any enhancement in the signal to noise ratio as observed in CP experiments. Since the relaxation in a Bloch decay experiment is dependent only on the ^{13}C nuclei which usually have longer T_1 's than

protons, the amount of time between acquisitions is usually longer. These two factors significantly increase the overall experimental time if a Bloch decay spectrum is to be obtained with a signal-to-noise ratio comparable to that in a CP experiment.

Operating at high magnetic field strengths another problem becomes evident. In order to average out chemical shift anisotropies magic angle sample spinning (MASS) is often employed. Magic angle sample spinning is a technique in which the sample is spun at $54^{\circ} 44'$, the magic angle. Spinning at moderate to low speed (1-6 kHz) at high static magnetic field strengths often yields large rotational side bands at intervals related to the spinning speed. These rotational sidebands can be minimized by spinning at higher speeds. High speed spinning, however, interferes with the ^1H - ^{13}C dipolar coupling and thus the cross polarization process.⁶

Coal spectra are complicated by numerous problems making them difficult to interpret quantitatively. These include the natural occurrence of unpaired electrons in the form of both organic free radicals and paramagnetic metal ions, which tend to broaden and/or relax away signals, and the overall complexity of the spectra due to the inherent heterogeneous nature of the coal. The question of whether cross-polarization can lead to additional distortions in coal spectra is therefore very important.

Principal Component Analysis

For some time the quantitative reliability of cross polarization nuclear magnetic resonance spectroscopy (CP-NMR) experiments of coal has been questioned.^{5,6} The problems associated with obtaining coal spectra using either CP or Bloch (single pulse) experiments were described above. In order to draw reliable conclusions from the data regarding the structure of the coal, the spectra must be as quantitative as possible. Since a completely quantitative spectrum of coal using our high field instrument is difficult to obtain due to the inherent nature of the coal and the field strength of the NMR, we used principal component analysis (PCA) to determine if differences other than the overall increase in the signal to noise ratio exist in coal spectra when CP techniques are used. Principal component analysis determines what the differences are.

Principal component analysis is a method of analyzing large quantities of data using matrix algebra based on correlations between variables. Principal component analysis attempts to gather together

variables or features that are highly correlated into a new variable called a principal component (PC). Features are variables that have been manipulated or "pretreated" in some manner. This is done graphically by rotating the feature axes in such a way as to create new axes, which are linear combinations of the old axes. The new axes are selected such that the first axis passes through the middle of the points in a direction to maximize variance along the axis. The second axis is chosen orthogonal to the first, again passing through as much variance as possible. Additional axes are chosen the same way, orthogonal to the earlier ones passing through the maximum variance possible. Mathematically, PCA can be performed in a number of ways. We used singular value decomposition (SVD). Singular value decomposition manipulates the data such that the original data matrix can be decomposed into the product of three matrices,

$$X = USV^T$$

where V is the loadings matrix and U is the scores matrix autoscaled to unit length. S is a diagonal matrix which contains the standard deviations or singular values of each of the new principal components (PC). The loadings represent how much of the original features were used to make the new axes. If the scores of two PC's are plotted against each other, this often leads to clustering of related features. These plots are often used in the technique called pattern recognition. Pattern recognition is a technique in which the data are simplified so that recognizable patterns and correlations are observed. Comparison of the scores plots with a loadings plot can yield information on how these clusters are related.⁹

Data are often pretreated prior to the SVD process. Pretreatment includes such operations as scaling and centering. Preprocessing makes it easier for the mathematics to handle the data in meaningful ways. The content and interpretation of the results are greatly influenced by how the data are pretreated. The data in this work were mean-centered. This means that the origin was moved to the mean value of each variable. Since the signal to noise ratio is very different in the CP experiments compared to the Bloch decay experiments, the data were also normalized. Normalization makes the length of all the data vectors for each sample the same.⁹ A multiplicative scatter correction was also used. The multiplicative scatter

correction adjusts the data by doing a least squares plot of a spectrum versus the mean of all spectra in the learning set. It then adjusts the former to give a slope of one and an intercept of zero. It should correct for differences in sample size.¹⁰

Relaxation Protocols

Relaxation times are very sensitive to exposure to unpaired electrons. Therefore, the effect of a paramagnetic center in close proximity to an atom should have a profound effect on its spin-lattice relaxation time (T_1), shortening it significantly. The relative changes in the various T_1 's should serve as a distance profile of different atoms from the paramagnetic center, as well as a monitor of the efficiency of the paramagnetic center.

There are a number of ways to measure T_1 values. Due to the possibility of distortions in spectral intensity as described above, relaxation experiments were compared using protocols utilizing CP and also ones that did not. Diagrams of the pulse sequences can be found in the appendix. One category of experiments is called inversion recovery based on a $180-\tau-90$ pulse sequence. In the inversion recovery sequence the magnetization is flipped 180° so that it is in a nonequilibrium state along the $-z$ axis. During the time period τ , the magnetization begins to relax back along the z axis to its original state. After the time τ , the magnetization is then pulsed 90° into the $x-y$ plane so that it can be measured. By doing the experiment with varying τ lengths, the different amounts of magnetization at each τ time can be compared. We use a modified sequence which we call T_1CP1H in which the magnetization is transferred to the carbons from the protons following the τ period to determine the proton T_1 values. A typical exponential plot used in the determination of the proton T_1 's can be seen in Figure 2a. The T_1 's are calculated using the following variation of the Bloch equation:⁸

$$y = M_0 \{1 - 2 \exp(-\tau/T_1)\}$$

where:

y = peak area (intensity)

τ = relaxation time (tau)

M_0 = amplitude at $x \gg T_1$

a)

b)

Figure 2: a) A theoretical exponential plot of signal intensity (M_τ) versus relaxation delay (τ) for typical inversion-recovery data for a resonance with $T_1 = 1$ sec. b) The same data normalized to the Bloch equation to view it in a linear format.

The T_1 is determined by plotting ΔM as a function of τ assuming a perfect 180° pulse. This data is then normalized to a linear format by plotting the $\ln (M_0 - M_\tau)$ Vs. τ giving a straight line (see Figure 2b.) These points are then fit to a linear regression using a Lotus 123 spreadsheet. The data are very sensitive to the value chosen for M_0 , so an equilibrium value for the M_0 must be established at long τ values. If the T_1 values are very long this can increase the experiment time considerably.

Another pulse sequence called T1SR is for the measurement of carbon T_1 's without the use of cross polarization. This pulse sequence employs a saturation comb followed by a normal Bloch or one pulse decay^{7,8}. A disadvantage of this experiment is that the peaks often appear on top of a broad background signal. This signal arises from plastic parts in the probe and is lost when cross polarization is used because the KEL-F plastic in the probe does not have very many protons needed to cross polarize. Cross polarization is not always efficient when paramagnetic centers are deposited on the substrate, due to the presence of the unpaired electrons. An advantage of this method is that it is not cross polarization dependent. Therefore, this method becomes useful even though it may take long times to acquire the data. Since we are interested in the nuclei that are directly influenced by the addition of paramagnetic relaxation agents, this pulse sequence is especially useful because the fastest relaxing nuclei are observed at the shortest relaxation times. We call this experiment T1SR. We analyzed the data in two ways. We used the data reduction program found on the General Electric GN-300 NMR spectrometer. The data reduction program exponentially fits the data to the Bloch equation:¹¹

$$y = A * [1 - \exp(-t/T_1)]$$

where

A = amplitude at $x \gg T$

T_1 = T_1 relaxation time (sec)

t = relaxation time delay in the pulse sequence

We also processed the data using the initial slope method of analysis where the first several points are used to plot the line. This method represents data at very short times, before most of the nuclei have begun to relax, so it represents the ensemble average of the nuclei in the sample. The data points that are dropped

out are those occurring at longer tau times. We wrote a spreadsheet using Lotus 123 software for this analysis. This analysis fits the data to a linear regression of the Bloch equation:⁸

$$I_{\infty} - I_t = I_{\infty} [1 - \exp(-t/T_1)]$$

where

t = relaxation time delay in the pulse sequence

I_t = measured intensity at t

I_{∞} = measured intensity after complete recovery of the magnetization and is proportional to the equilibrium magnetization M_0

T_1 = relaxation time (sec)

The I_{∞} value was determined by taking at least 2 points after the magnetization reached equilibrium and averaging them. The magnetization generally reaches equilibrium after $5T_1$'s so this can be very time consuming if the T_1 is very long.

There are two pulse sequences using cross polarization employed in our laboratory for the determination carbon T_1 's. These sequences are similar. We call these T1CP¹² and T1NOE¹³. In both cases the experiment involves cross polarization followed by a 90- τ -90 pulse sequence on the carbons. In these experiments, the cross polarization and first 90° pulse set up a non-equilibrium magnetization along the z axis. This relaxes back to M_0 during the tau period. The second 90° pulse flips the magnetization into the x-y plane so that it can be measured. Phase cycling cancels out M_0 . The T1NOE sequence also includes a series of proton pulses between the 90° pulses during the tau period. The purpose of these pulses is to saturate the protons and suppress any transient nuclear Overhauser effects. The advantage of these two experiments is that the magnetization decays exponentially to zero, so the tedious establishment of the equilibrium M_0 required for the inversion recovery or saturation recovery experiments is not necessary. A theoretical exponential decay -to- zero plot can be observed in Figure 3a. This data can be plotted in a semilog format to make it linear (see Figure 3b.) The major disadvantage of these techniques is their dependence on cross polarization. If we are observing materials that have difficulty cross polarizing due to lack of protons or an abundance of unpaired electrons, these methods would be difficult or impossible. These data were processed using the following equation:⁸

Figure 3: A) A theoretical exponential decay-to-zero plot obtained with the T1CP experiment. B) A theoretical semilog plot of the signal intensity (M_τ) versus relaxation delay (τ) of the same data set. The T_1 for the data set was 1 sec.

$$y=A*\{1-\exp(-x/T_1)\}$$

where

A= amplitude at x=0

and then using the same linear fit described above on the Lotus 123 spreadsheet and the Freelance graphics software. The ^{13}C decay pattern is often non-linear, a common phenomenon with solids.¹⁴ This non-linearity arising from varying T_1 's for different molecular orientations. Because of this non-linearity, the data were fit using the initial slope method of analysis.

Each experiment has its own advantages and disadvantages. One must consider relative relaxation times and why the experiment is being done to determine which experiment is best in each case. In general, the experiments that require the shortest tau times allow for the greatest number of acquisitions and thus the greatest signal-to-noise ratio. We must therefore balance time and ability to cross polarize when selecting experiments.

Microscopy Studies

Once we ascertained that the paramagnetic ions were having an effect on the relaxation behavior of samples, we then needed to develop a method to determine whether the paramagnetic ions were on the surface of the sample. We used three surface sensitive techniques: x-ray photoelectron spectroscopy (XPS or ESCA), electron probe microanalysis (EPMA) and scanning transmission electron microscopy (STEM). There is an inherent problem in using any of these instruments for the analysis of coal particles, because EPMA, STEM and XPS were all designed to analyze substrates that can be polished flat and that are dense and conducting. They were not designed for analyzing particulate, non-conducting materials like coal.

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is a surface technique that can be used for the elucidation of chemical structure. The binding energy for each electron in each element is unique. The measurement of the binding energy in XPS allows the identification of the element and its oxidation state. The relative atomic concentrations of each element can also be determined.¹⁵

There are advantages and disadvantages for using either EPMA or STEM to analyze coal samples. EPMA samples are prepared by polishing away part of the particle (see cartoon in Figure 4). Mapping the

Figure 4 Cartoon of Particle Shapes After SEM Sample Preparation
(Grinding and Polishing)

a) Lines Represent 1 μm Depth

A

B

C

b) Each Box Represents the Spatial Resolution of 1 Mapping Step

A

B

C

particle should yield a concentration profile for dysprosium if it is on the surface. EPMA has a spatial resolution of approximately 1 μm measuring dysprosium located up to 1 μm depth.¹⁶ Advantages for using EPMA are: it has a better minimum mass fraction (detection limit) than STEM; a significantly easier sample preparation; and has both energy dispersive (EDS) and wavelength dispersive (WDS) or crystal spectrometers. The STEM has only EDS detectors. The advantage of the WDS is that it has much greater sensitivity than the EDS. The WDS is "peaked" or focused on a single wavelength, and it only detects x-rays from a single element. The EDS is useful because it can collect and simultaneously display x-ray data over a wide energy range for several elements simultaneously, however, the sensitivity for a particular element is not as good as is that of WDS.¹⁷ One problem with EPMA can occur if particles are polished to thin slivers ($< 1 \mu\text{m}$ thick). The instrument will then record all the dysprosium across the particle (see particle b in Figure 4a). This should not be a problem with our analysis since all the particles selected for analysis are at least 100 μm across. Assuming the particles are somewhat spherical, they must have a depth significantly larger than 1 μm . There is also the possibility that only a small fraction of the surface edge of a particle may be present in the active volume. If the amount of dysprosium is below the minimum mass fraction in the volume sampled, it will not be detected. The first box in Figure 4b particle A illustrates this situation. The spatial resolution of EPMA is not as good as in STEM, but for our purposes it was adequate. Normal EPMA maps are 128 X 128 pixels. In order to get a quick overview of the particles, we ran 32 X 32 maps. This decreased our resolution to about 6 μm , but it decreased instrument time from 6 hours to about 0.5 hours per map. Once again we had to balance time versus resolution opting for shorter times.

In order to improve resolution STEM can be used on particles which are sliced to thin films. The resolution for STEM is approximately 20 nm.¹⁷ This improvement in resolution is obtained by using a smaller probe (on the order of 20 nm across), thin films, and higher beam energy. These factors produce fewer interactions within the film and thus a smaller active volume.¹⁸ An advantage of STEM is that the sample slices are of uniform thickness. Problems with this technique are that higher concentrations of dysprosium are required for detection than for EPMA because the sample volume is smaller and there are only EDS detectors available on the instrument. Sample preparation is significantly more complicated and

time consuming, often taking several days to obtain an appropriate slice because coal is brittle and it breaks up when microtomed. Since very high resolution is not necessary for this work, we concentrated our time developing the EPMA technique.

NMR Standards and Spin Counting

Tetrakis(trimethylsilyl)silane (TKS) has been used as a qualitative chemical shift standard and as a quantitative internal standard for ^{13}C NMR spectroscopy of coals.¹⁹ Since this work is dependent on accurate subtraction of two spectra, we used TKS as a standard for determining spectral subtraction parameters. The two spectra were acquired at different times. Although every effort was made to reproduce acquisition parameters exactly, there are small changes that occur, such as slight differences in probe orientation, radiofrequency field strength, etc. The RF feedback control circuit was used to minimize changes in field strength, and the presence of TKS was used to standardize the spectra so that they could be appropriately compared. We also used TKS in our preliminary attempts at spin counting, a method of determining the weight percent observable carbon in a sample. It involves measuring the spectrum of a weighed sample blended with a known quantity of standard. Integrated intensities corrected for spectral overlaps provide a measure of the weight percent of NMR observable carbon in the sample.²⁰

EXPERIMENTAL METHODS AND MATERIALS:

All chemicals were obtained from Aldrich unless otherwise noted. Dysprosium nitrate and dysprosium metal were obtained from Johnson-Matthey Alfa. Aryl sulfonate silica gel chromatography packing was obtained from J.T. Baker, Phillipsberg, N.J. Beulah Zap lignite and Pittsburgh No. 8 coal, in nitrogen filled vials, ground to 100 mesh (US.) was obtained from the Argonne Premium Coal Series, Argonne National Laboratory.²¹ All dry manipulations of the coal were performed in a nitrogen filled dry box. During drying steps, vacuum ovens were filled with nitrogen prior to opening. All reactions were performed under nitrogen to minimize oxidation.

All solid state NMR spectra of the coal were obtained using a General Electric GN 300 solid state NMR spectrometer operating at 75.4 MHz for carbon utilizing either a Doty Scientific, Inc. 7mm or 5mm probe and an RF feedback control circuit. The 7mm and 5mm rotors hold about 300 mg and 175 mg of sample respectively. Specific sample sizes will be discussed under the individual experiment descriptions.

Samples were examined under magic angle sample spinning (MASS) and high power proton decoupling. All coal samples were spun at 5-5.6KHz. The silica gel samples were spun at about 4 -5 KHz. Sapphire rotors with Kel-F endcaps (Doty Scientific) were used. Spectra were acquired with 1 -2 K data points and 10.24 msec acquisition times at ambient temperatures. All spectra were processed with a background correction, experimental multiplication of 100 - 200 Hz linebroadening for coal and 50 Hz linebroadening for the model samples, a zero fill, Fourier transform and then manual phasing or an autophase, background fix, autophase and finally a minimal amount of manual phasing. Cross polarization generally had 3000 - 5000 transients. Bloch decay spectra generally had approximately 500.

Model Studies

The effectiveness of both copper (II) and dysprosium (I) ions were evaluated using an aryl sulfonate silica gel chromatography packing. Varying amounts of copper (II) and dysprosium (I) were deposited on the silica gel surface. Percent surface coverage was determined on a charge equivalence basis. Samples of 0, 5, 10, 30, and > 90% copper (II) were made. The silica gel was prepared by soaking it in a pH 9 sodium carbonate/sodium bicarbonate buffer, to convert all the sulfonate groups to the sodium form. Deposition was carried out by dissolving known amounts of copper (II) chloride in water and titrating into a slurry of silica gel gently stirring. The samples were then filtered and dried at RT under vacuum. The filtrate of the >90% loaded sample was analyzed for residual copper using atomic adsorption spectroscopy and it was found to be minimal. Dysprosium samples of 0, 1, 2, 3, 4, 8, and 16% loadings were made by titrating the silica gel with known amounts of dysprosium nitrate dissolved in water. These samples were then dried as with the copper and evaluated by measuring the T_1 's of various carbons and protons.

Relaxation times were determined using a combination of the pulse sequences described above. The sequences called T1CP, T1NOE, and T1SR were used to measure the ^{13}C spin lattice relaxation times. The pulse sequence called T1CP1H was used to measure the proton relaxation times. Sequences utilizing cross polarization were run with a 1-2 msec Hartmann-Hahn contact time and recycle delays on the order of 0.5-1 sec. These experiments were set up with varying delay lists that went from 10 μsec to 2 seconds for the CP experiments. The T1SR experiment was run with a 0.8 sec recycle delay and a delay list that

went from 10 μ sec to 45 seconds. The intensity of the various carbon peaks were then plotted as a function of delay time. The initial slope method of analysis was used as described in the Introduction.

Sample Preparation

The effectiveness of the copper (II) and dysprosium (I) ions as relaxation agents was evaluated on coal as well. Various quantities of copper (II) chloride and dysprosium nitrate were added to water slurries of 1-5 g samples of Beulah Zap lignite and Pittsburgh No. 8 coal. Coal samples were prepared several ways. The Beulah Zap lignite was stirred under nitrogen in a solution of concentrated aqueous sodium bicarbonate for a week to convert any acid groups to sodium salts. Excess sodium bicarbonate was removed by dialysis. The coal slurry was poured into a tied off Spectrapor Membrane Tubing with molecular weight cut off 12,000 - 14,000. The sealed membrane was then placed in a 2 L. beaker filled with distilled water and stirred slowly. The water was replaced every 24 hours. The pH of the water bath was checked after each dialysis period. Dialysis was discontinued when the water pH was neutral, usually requiring three days. The clean coal slurry was then poured into an 125 mL. Erlenmeyer flask and a known quantity of aqueous copper (II) chloride or dysprosium nitrate added. The slurry was stirred for a week under nitrogen and then dried using rotary evaporation. The T_1 's of these samples were determined. Location of the dysprosium was also evaluated using XPS, STEM, and EPMA (see below.)

Additional samples of Beulah Zap lignite and Pittsburgh No. 8 coal were prepared by adding an aqueous solution of dysprosium nitrate to a pristine sample of coal, swirling for a few seconds and then removing the water by either rotary evaporation followed by drying in a 60° vacuum oven or lyophilization. Lyophilized samples were considered to be dry after one day on the vacuum pump. These samples were evaluated as described above.

Microscopy Studies

The location of the dysprosium was evaluated using several surface sensitive techniques. X-ray photoelectron spectroscopy studies were conducted using a Scienta ESCA 300 spectrometer. Survey and regional spectra were taken of each of the dysprosium treated Beulah Zap samples described above and an unreacted Beulah Zap sample. The dysprosium treated samples were also sputtered with argon to a depth on the order of 10 - 50 Å, and XPS spectra taken. Dysprosium metal was also analyzed. The dysprosium

metal was scraped prior to insertion into the spectrometer and then scraped again inside the sample preparation chamber. Survey and regional spectra were then taken. The dysprosium metal was then exposed to 1×10^{-5} mbar of oxygen for ten minutes and spectra were taken of the oxide. Coal samples were prepared by pressing the coal powder onto double sticky tape with a dab of silver paint serving as a conductor of charge to the silver metal mount.

Samples for STEM analysis were prepared by imbedding a few coal particles in gelatin capsules using low viscosity hard L.R. White resin. They were first placed in the refrigerator overnight to allow the resin to wick into the particles. The capsules were then placed in a vacuum oven at room temperature for several hours to assure complete wicking, and finally they were heated at 70° under vacuum overnight to cure the resin. Once cured, the samples were trimmed and microtomed. For these preliminary studies a high concentration dysprosium/ Beulah Zap sample and a low concentration dysprosium/ Beulah Zap were used. The high concentration sample was selected to determine if dysprosium was observable using the STEM and the low concentration sample was selected as having a dysprosium concentration representative of most of the samples we wish to analyze. Analysis was performed using the Phillips 430T TEM with a Link x-ray detection system.

Samples were also prepared for EPMA analysis on the JEOL 733 Super-probe Scanning Electron Microscope with a Tracor Northern X-ray Analyzer. Sample preparation consisted of mixing about 0.25-0.5 grams of Beulah Zap lignite sample with an epoxy resin. These samples were placed in cylindrical molds of about 1" diameter. The epoxy cured overnight and then fresh epoxy was added to fill the mold. This yielded a sample mount approximately 1" high by 1" wide with the sample concentrated at the bottom of the mount. The sample mount was then ground and polished. Several grits were used for the grinding with water before the sample was polished using SiO_2 .

Additional samples were prepared by mixing a small amount of Pittsburgh No. 8 sample (a few hundred milligrams) with LR white epoxy resin in gelatin capsules. After the epoxy had hardened, the samples were removed from the capsules, placed in metal clips to distinguish one sample from another, and mounted in cylindrical molds approximately 2.5 cm in diameter using Buehler resin. This yielded a sample mount approximately 2.5 cm high by 2.5 cm wide with both coal preparations in a single sample mount.

The sample mount was then ground "smooth". Ethylene glycol was used as the grinding solvent to prevent dysprosium from washing over the face of the mount. A sample of untreated Pittsburgh #8 was also prepared using this type of mount. Another sample mount was prepared in which the rotary evaporated Pittsburgh No. 8 coal preparation was mixed with Struers Mounting Resin 2, a copper/acrylic resin mixture. This resin was set using a pressure/heat regime. The sample mount was prepared by mixing a few hundred milligrams of the coal and about 1.25 cm of resin in a 2.5 cm diameter metal cylinder. A rod that fits snugly into the cylinder is then placed over the mixture, and the cylinder heated to 150° under pressure for five minutes. When cool the mount was built up by adding Bakelite to the top of the sample and thermally treating under pressure as described above. This sample was then ground using ethylene glycol as described earlier. A sample mount using Wood's metal was also attempted, but the metal would not wet the coal and the coal rubbed out of the metal.

The LR white and the copper/acrylic mounts were then analyzed using EPMA. 32 X 32 Pixel maps were used for most analyses. This yields a resolution of about 6 μm per pixel. Three or four particles were analyzed using each preparation for statistical purposes.

Chemometric Studies

Bloch decay⁷ and cross polarization⁴ experiments were used in the chemometric analysis of these two techniques. The samples for this work were Pittsburgh No. 8 coal of the Argonne Premium Coal Series from vials 401:1700 (Sample 77) and 401:1698 (Sample 78).²¹ Coal samples were dried under vacuum at 110°C to constant mass. The samples were then packed into 7mm rotors. Cross polarization experiments were performed using a 1 msec Hartmann-Hahn contact time. All other operating parameters were identical for the various sets of experiments except for the recycle delays. The times for the recycle delays were based on the proton and carbon spin lattice relaxation times, T_1 's. For complete relaxation a time greater than or equal to five times the T_1 is usually required. Therefore from the proton (.23-.27 s.) and carbon (1.2-9.8 s.) T_1 's determined earlier for Pittsburgh No.8 coal, five relaxation delays were selected. The first selected was a delay of about five times the T_1 . The other delays were based on this time with one value slightly longer, one slightly shorter, and one much shorter than the initial time determined. For the CP experiments these times were 2, 1.25, 1, and 0.8 s (a much shorter time was not possible for the CP data

due to instrumental constraints), and for the Bloch experiments the times were 60, 50, 40, and 2 s. Experiments were set up to run in tandem, with two sets of experiments run for each delay time for each sample. Cross polarization experiments had 3072 acquisitions and the Bloch experiments had 512 acquisitions each.

The data were acquired and processed in the usual manner. Processing consisted of a baseline correction, exponential multiplication with 100 Hz linebroadening, a zero fill, and a Fourier transform. Following the Fourier transform, the autophase function was used followed by a baseline fix and another autophase to minimize subjectivity in phasing. The autophase sequence was followed by a minimal amount of manual phasing.

Inherent in Bloch decay experiments is the occurrence of a broad background signal resulting from carbon atoms in the rotor end caps and the stator. This signal is eliminated in the CP experiments because these materials do not cross polarize well. In order to remove this signal from the Bloch spectra, the spectrum of an empty rotor was taken and subtracted from each of the Bloch spectra prior to transferring the spectra from the spectrometer to the personal computer. There were over 16,000 acquisitions in the empty rotor spectrum. This was done so that the amount of noise introduced into the spectrum by the subtraction would be minimal.

The data were processed on the NMR instrument and transferred in binary format using Kermit²² to an IBM compatible personal computer. The data were then converted to ASCII format using a binary to ASCII conversion program TEFT.²² The ASCII formatted data could then be taken into MATLAB.²³

Three matrices were built using these data. A 16 X 512 matrix containing the CP data, one containing the Bloch data, and one containing both the CP and Bloch data with the 2 longest recycle times. These matrices were then pretreated and a singular value decomposition performed. Both the CP and Bloch matrices were pretreated using the multiplicative scatter correction and mean-centering. The mixed matrix was normalized to account for differences in signal to noise ratio between the two techniques, and then mean-centered. In order to determine the effect of the pretreatment techniques, the Bloch matrix was also processed with just mean-centering, and both the Bloch and mixed matrices were processed without mean-centering. The principal component loadings were then plotted for each of these SVD's. From the

loadings plots, the number of significant principal components for each SVD set was determined. Principal component scores, loadings and biplots were then plotted and compared.

Spectral Subtraction

A Pittsburgh No. 8 coal sample treated with water and dried and a sample treated with dysprosium and lyophilized were carefully weighed into the rotors so that each rotor contained the same amount of coal. Equal quantities of tetrakis(trimethylsilyl)silane (TKS), a spin counting standard, was also weighed into each rotor. Bloch decay (single pulse) spectra of these two samples were recorded with relaxation delays greater than three spin lattice relaxation times (T_1 's). The two spectra were then subtracted using the subtraction protocol on the GN 300 NMR¹¹ and the difference spectrum plotted. Loss of the TKS peak was used to adjust the subtraction weighting factor.

RESULTS AND DISCUSSION:

Model Studies

Aryl sulfonate silica gel was selected as a model system because it has a well defined structure with carbons of different chemical shifts. It also has a large enough surface area so that the surface groups are readily observable in the NMR spectra. The effectiveness of the paramagnetic agents can be monitored as a function of distance using this model since there are different types of carbons at different distances from the surface. Figure 5 is a cartoon of the structure of this silica gel. Figure 6 is a solid state NMR spectrum of the silica gel without any paramagnetic agent present.

Figure 5: Structure of the Aryl Sulfonate Silica Gel

Figure 6: Solid state NMR of Aryl Sulfonate Silica Gel

DQMA01. 701 MCS
MA001 T1CP 4KHZ

16NOV93

9599

The effect of various concentrations of copper (II) ions and dysprosium (I) was evaluated using this model system. Copper (II) concentrations ranging from 0 to >90 % were evaluated. These percentages were determined on a charge equivalence basis. This corresponds to the percentage of ions present if 100 % is enough to just neutralize the sulfonate groups present on the surface of the silica gel. Dysprosium (I) ion concentrations from 0 to 16 % were also evaluated. The filtrate from the >90 % copper (II) sample was evaluated using atomic absorption spectroscopy and the amount of residual copper in the filtrate was found to be negligible. Concentrations of dysprosium (I) ion greater than 16 % were not evaluated because at 16 % the NMR signal was completely lost. We believe this is due to complete relaxation of all the carbon atoms on the NMR time scale. Figures 7 and 8 show the relaxation rate as a function of ion concentration for copper and dysprosium respectively. In each case the rate of relaxation increases as a function of increasing ion concentration or the T_1 decreases as a function of increasing ion concentration. The observation that the signal was completely relaxed at only 16 % dysprosium indicated that the dysprosium (I) was a much more efficient relaxation agent than the copper (II). With this determination we began applying the relaxation agents to coal.

Chemometric Studies

Due to the complex nature of coal and the complex nature of the spin dynamics during the evolution of the cross polarization experiment, the differences between the coal spectra determined using cross polarization and Bloch decays were evaluated. Figure 9 shows the differences in signal to noise of the CP and Bloch spectra when they are "overlaid". In order to overcome the inherent difference in S/N between these two techniques, the data were normalized (see Figure 9.) The peaks in Figure 10 have been labeled to simplify the interpretation of the loadings. These spectra were normalized such that the area under the curves are the same. Even normalized, it is apparent that there are significant differences among these spectra. Principal component analysis, as described above, will be used in an attempt to elucidate the differences in these spectra.

Figures 11a and b are loadings plots for the mean-centered CP, Bloch data. Figure 11a shows the loadings plot for PC1. It shows a loadings plot with the signal really apparent. Figure 11b, the loadings plot for PC6 is almost all noise, therefore we do not need to consider any principal components higher than

Figure 7:

Carbon and Proton T1 Relaxation Rate vs. Cu Conc

Figure 8:

Carbon and Proton T1 Relaxation Rate vs. Dy Conc

Figure 9: Non-Normalized NMR data plots for both CP and Bloch decay experiments

Figure 10: Normalized data sets for the same data as above

Figure 11a: Loadings Plot for PC1 for Meancentered Bloch Vs CP Data Matrix

Figure 11b: Loadings Plot for PC6 for Meancentered Bloch Vs CP Data Matrix. Notice it is mostly noise

PC6. Figure 12a is the biplot for PC1 vs. PC2. From this plot, PC1 separates the Bloch from the CP experiments. PC2 seems to be fitting sample 2. By looking at the loadings and biplots for PC1 vs. PC2 (Figures 12a and b), it appears that the points most associated with the CP data are in the region of 297-298, this corresponds to a chemical shift of about 30 ppm, the aliphatic region of the coal spectrum. The loadings most associated with the Bloch data are in the region of 237-238 and 198-203, or about 100 ppm and 150 ppm, and these correspond to aromatic bridgehead carbons and oxygenated aromatics respectively. Since differences do exist in the Bloch and CP spectral intensities, Bloch decay experiments were used for most of this work.

NMR of Beulah Zap Lignite

We selected Beulah Zap for this initial work because it is a hydrophilic coal with a high oxygen content and we expected the metal ions to coordinate with carbonyl functionalities on the surface of the coal. Initially we ion exchanged this coal with a concentrated sodium bicarbonate buffer. This was to convert all the carbonyl functionalities into the sodium form. We could then ion exchange the sodium with either copper (II) or dysprosium (I). Initial copper (II) studies showed a decrease in T_1 with the addition of copper ions. The dysprosium (I) studies, however, were not as clear. The T_1 's for the dysprosium treated samples did not follow any particular trend. Large quantities of dysprosium caused loss of the entire coal signal. Figures 13 and 14 show ^{13}C NMR spectra of Beulah Zap lignite treated with buffer and copper (II), and Beulah Zap lignite treated with buffer and with a high concentration of dysprosium, respectively. The copper treated sample spectrum shows loss of the carbonyl resonance. Complete loss of the NMR signal with the high dysprosium concentration indicated that either the dysprosium was diffusing throughout the coal affecting all the coal nuclei, or the large number of paramagnetic ions present was disrupting the dipolar interactions and the cross polarization was ineffective. If the loss of signal was CP dependent, a Bloch decay experiment should yield signal. The experiments were repeated using Bloch decay experiments and no signal was observed. This indicates that the dysprosium was diffusing through the coal. The location of the dysprosium was now a crucial question. Two Beulah Zap samples were evaluated. One sample was soaked for a week in buffer and then a week in dysprosium nitrate. The other sample was soaked with dysprosium nitrate for half an hour without buffer treatment and the water

PC1 separates CP from Bloch

Figure 12a: Biplot of both loadings and scores for PC1 Vs. PC2 for the meancentered Bloch and Cp data

matrix

Figure 12b: The loadings plot for the same data as in 12 a.

^{13}C NMR OF COAL

Figure 13: NMR spectra for Beulah Zap lignite buffer treated and treated with a high concentration of Cu^{2+} ions. Notice the loss of the carbonyl peak in the Cu^{2+} treated sample.

^{13}C NMR OF COAL

Figure 14: NMR spectra for Beulah Zap lignite buffer treated and treated with a high concentration of Dy^{3+} ions. Notice the loss of signal in the Dy^{3+} treated sample.

removed using rotary evaporation. NMR analysis of these samples showed the buffered sample (Figure 15) to have slightly shorter T_1 values and a signal to noise ratio of about half that of the unbuffered sample (Figure 16) when the spectra were processed identically. See Table 1 and Figures 15 and 16. This indicates that the dysprosium is located in different parts of the coal. The loss of signal in the buffered sample indicates that the dysprosium is probably dispersed throughout the coal matrix and is not confined to the coal surface. This would explain why at very high concentrations there is essentially no NMR signal. If the dysprosium is confined to the surface it should only broaden away the surface functionalities. These T_1 values were determined using the T1NOE and T1CP1H protocols to determine the ^{13}C and ^1H T_1 's respectively.

Table 1: T_1 Values (Seconds) for Beulah Zap Lignite Untreated and Treated with Dysprosium With and Without NaHCO_3 Buffer Treatment

	^{13}C T_1 Untreated	^{13}C T_1 With Buffer	^{13}C T_1 Without Buffer	^1H T_1 Untreated	^1H T_1 With Buffer	^1H T_1 Without Buffer
30 ppm	0.39 (0.08)	0.298 (0.001)	0.433 (0.002)	0.04 (0.02)	0.035 (0.004)	0.046 (0.003)
128 ppm	0.5 (0.1)	0.164 (0.002)	0.517 (0.006)	0.024 (0.006)	0.018 (0.001)	0.025 (0.001)
142 ppm	0.4 (0.1)		0.402 (0.004)	0.025 (0.001)		0.023 (0.001)
205 ppm	0.3 (0.1)	0.163 (0.008)	0.566 (0.003)	0.03 (0.01)	0.021 (0.001)	0.018 (0.001)

Errors are shown in parentheses.

Microscopy Studies

The two samples described above were also surveyed using XPS. A survey spectrum of dysprosium metal and dysprosium metal exposed to oxygen to produce dysprosium oxide were completed to determine

Figure 15: NMR spectrum of Beulah Zap lignite treated with buffer and dysprosium nitrate.

DQ032 . 110 DMQ 12DEC91
DQ032 BZ DY #8 NAHCO3 ROTOVAP T1CP1H 5.6KHZ

Figure 16: NMR spectrum of Beulah Zap lignite treated with just dysprosium nitrate.

DQ033 . 110 DMQ 17DEC91
DQ033 T1CP1H BZ DY #8 NO NAHCO3 ROTOVAP 5.6KHZ

the binding energies for the various valences of dysprosium. Figure 17 consists of two survey spectra that show the comparison between pristine Beulah Zap and a dysprosium treated sample. These survey spectra appeared similar. Since the dysprosium concentrations are so low, the spectra are very similar. Regional spectra were also taken in order to determine relative concentrations. The samples were then sputtered with argon in order to determine the concentration within the sample. The sputtering depth is on the order of 10 - 50 Å. Figure 18 is the dysprosium 4d regions sputtered and unsputtered. The sputtered spectra show significant differences from the unsputtered. The sputtered spectra show the emergence of a doublet perhaps indicative of a difference in the oxidation states between the surface and bulk dysprosium, or it could indicate that there is sputtering damage to the dysprosium. The XPS spectra of dysprosium metal was taken and then pure oxygen was added to the spectrometer preparation chamber to oxidize the sample. The dysprosium 4d peaks in the coal are similar to those seen in the oxidized spectra. The XPS spectra for the dysprosium metal with and without oxygen are Figures 19 and 20. The area values under the carbon, oxygen and dysprosium peaks for each of the coal spectra are presented in Table 2. The atomic percents for each of these elements are presented in Table 3. The areas are probably a better indicator of relative quantities since the atomic percents are based solely on the three elements. Since coal is a complex substrate and since the sodium bicarbonate treated sample also has an increased concentration of sodium, relationships between the area ratios are probably more meaningful, than ratios between atomic percentages. The sodium Auger peak can be observed in the survey spectrum in Figure 17 at about 500 eV. There is no significant sodium peak in the dysprosium treated spectrum without buffer. When the carbon/dysprosium area ratios are computed for both the sputtered and unsputtered spectra, the ratios of the two samples are similar. The unsputtered ratios are 100 C atoms :3.1 Dy atoms and 100 C atoms :3.2 Dy atoms for the buffer treated and no buffer samples respectively. The sputtered ratios are 100 C atoms :5.3 Dy atoms and 100 C atoms :4.7 Dy atoms respectively. This appears to indicate that there is a higher dysprosium concentration below the surface. Since the sputtering efficiency was not determined and since we could not determine whether one element was sputtered preferentially, more work was needed to interpret these values. When these values are compared to those computed from the amount of coal and dysprosium nitrate used to prepare the samples, the surface and sub-surface concentrations of dysprosium

Figure 17: XPS survey spectra of Beulah Zap lignite out of the bottle and treated with dysprosium.

Figure 18: XPS spectra of the Dy 4d region of a Dy treated Beulah Zap sample before and after sputtering

90, 1.1 BZ with NaHCO₃ Buffer Before and After
Sputtering BZDY-3.003 DY4D LEHIGH 1991-11-19 14:

Pass energy
150 eV

Slit width
1.1 mm

Energy step
0.10 eV

Det. height
70 %

Lens mode
TRANSMISSION

X-ray power
2.3 kW

Rec. time
00:07:59

Figure 19: XPS spectrum of Dy metal

90, 0.8, scrape, 0 check
DYMET.015 DY4D LEHIGH 1991-12-20 13:11

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.07 eV

Det. height
70 %

Lens mode
TRANSMISSION

X-ray power
5.6 kW

Rec. time
00:08:48

Figure 20: XPS spectrum of Dy metal after exposure to oxygen. Notice the doublet is similar to that in the sputtered coal spectrum.

90, 0.8, 02 10 min 1x10-5mbar ave 1.2
 DYMET.017 DY4D LEHIGH 1991-12-20 15:12

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.07 eV

Det. height
70 %

Lens mode
TRANSMISSION

X-ray power
5.6 kW

Rec. time
00:05:57

appear higher than the values computed for uniform distribution of the dysprosium in the coal, 100 C:0.542 Dy and 100 C:0.290 Dy atoms for the buffered and unbuffered samples respectively. When the atomic percents of these three elements are compared to each other (Table 3), the relative percents are essentially the same for each sample sputtered and unsputtered. The C: Dy ratio determined from the atomic percents are very different from those determined from the areas. The values 100 C:0.25 Dy and 100 C:0.47 Dy for the unsputtered and sputtered buffer treated samples and the values 100 C:0.25 Dy and 100 C:0.35 Dy for the "no buffer" sample are closer to the values calculated for a uniform distribution of dysprosium in the coal. As indicated above, this method only takes into account the relative quantities of carbon, oxygen and dysprosium and is probably an over simplification of the system. The ratios calculated are probably useful for comparisons between the buffer and "no buffer" samples, but interpretation of the ratios in terms of overall concentrations should be made with great reservation.

Table 2: Area under XPS Peaks for Carbon, Oxygen and Dysprosium

	With Buffer Unsputtered	With Buffer Sputtered	Without Buffer Unsputtered	Without Buffer Sputtered
Dy 4d	218	5118	207	341
O 1s 1/2	4242	3996	3535	3208
C 1s 1/2	6974	9730	6392	7195
C/Dy Ratio	100 C / 3.1 Dy	100 C / 5.3 Dy	100 C / 3.2 Dy	100 C / 4.7 Dy

Areas of the peaks were determined by regional scans of each peak taken under identical conditions.

Table 3: Atomic Percents for Carbon, Oxygen and Dysprosium from XPS

	With Buffer Unspattered	With Buffer Sputtered	Without Buffer Unspattered	Without Buffer Sputtered
Dy 4d	0.2	0.4	0.2	0.3
O 1s 1/2	20.1	14.5	18.6	15.5
C 1s 1/2	79.7	85.1	81.2	84.1
C/Dy Ratio	100 C / 0.25 Dy	100 C / 0.47 Dy	100 C / 0.25 Dy	100 C / 0.35 Dy

C/Dy ratios are based on the percentages determined by the XPS experiment. Atomic percentages were determined from regional scans of the peaks taken under identical conditions.

The "no buffer" sample was also analyzed using the STEM and EPMA. In both cases dysprosium was observed throughout the particles. Figures 21 and 22 are the STEM spectrum and EPMA map respectively. Since it appeared from all three methods that the dysprosium was diffusing through the coal particles, several changes were made. The coal used for analysis was switched from Beulah Zap to Pittsburgh #8 because it is a hydrophobic coal; therefore, the water is less likely to diffuse into the coal pores. We shortened the contact time between the coal and dysprosium solution from 30 minutes to 30 seconds. We also prepared one sample by freeze drying instead of rotary evaporating and drying in a vacuum oven. Each of these modifications was intended to increase the probability of the dysprosium remaining on the surface of the particles.

There was a slight chance that the dysprosium may have been carried across the face of the particle during grinding since dysprosium nitrate is water-soluble. Therefore, the grinding solvent was switched from water to ethylene glycol.

Initial EPMA analysis of the coal samples mounted in the LR White Resin showed that the dysprosium was located on the surface for both coal preparations. However, a strong dysprosium signal was observed throughout the resin. This signal did not drop off to background even at distances greater than 100 μm

Figure 21: STEM spectrum of the dysprosium treated Beulah Zap lignite. Dy peak at 6.48 keV.

Figure 22: An EPMA map of a Beulah Zap lignite particle. The dysprosium appears to have diffused throughout the particle. Dysprosium appears white in the image.

Figure 23: EPMA of a Dy treated particle of Beulah Zap lignite in epoxy. The Dy appears to have diffused into the epoxy. DY appears white in the image.

Figure 24: EPMA map of a Dy treated particle of Pittsburgh No. 8 coal in acrylic/copper resin. The Dy appears to be located on the surface of the coal. Dy appears white in the image.

away from the particle (see Figure 23.) Concern that the LR White resin might cause an interference at the wavelength monitored for dysprosium prompted us to run a blank sample of Pittsburgh #8 using the LR White resin. There was no "dysprosium" signal observed. We concluded the dysprosium signal observed in the earlier analysis was real. The LR White is an epoxy based resin. The dysprosium was apparently dissolving and dispersing throughout the epoxy.

We then tried to make a sample mount using Wood's metal. The metal did not wet the coal and the coal brushed out of the mount. Next we used the copper/acrylic resin to prepare a sample mount using the rotary evaporated coal sample. Advantages of this mount were that the copper could serve as a conductor, with the aim of decreasing the amount of beam damage sustained during the analysis, and the acrylic was less likely to dissolve the dysprosium nitrate. This analysis showed significantly less diffusion of the dysprosium into the resin. There was still significant beam damage. Figure 24 is a map of a particle mounted in this resin. It appears from these analyses that dysprosium is on the surface of the particle, but it appears it is in globules.

NMR of Pittsburgh No. 8 Coal

The T_1 values for the dysprosium treated and untreated Pittsburgh No. 8 samples were determined. These were determined using both the T1NOE protocol used above with the Beulah Zap samples and the T1SR protocol. The T1SR experiment has the advantages that is not dependent on cross polarization dynamics and that rapidly relaxing nuclei are the first data sampled. Table 4 lists the T_1 values for the Pittsburgh No. 8 samples. The T_1 values for the T1SR experiment are about the same or shorter than those calculated from the T1NOE experiment. The shorter values are probably due to the addition of rapidly relaxing nuclei to the ensemble average.

Table 4: T_1 Values (Seconds) for the Pittsburgh No. 8 Samples

	H ₂ O	H ₂ O	H ₂ O	Dy Treated	Dy Treated	Dy Treated
	Treated ¹³ C	Treated ¹³ C	Treated ¹ H	¹³ C T1NOE	¹³ C T1SR	¹ H T1CP1H
	T1NOE	T1SR	T1CP1H			

18 ppm	1.2	1.1	0.25	1.4	1.5	
30 ppm	1.3	1.4	0.26	1.1	2.2	0.21
128 ppm	9.8	5.5	0.24	9.5	4.6	0.21
204 ppm		4.5	0.24	1.8		0.19

Errors on T_1 measurements are $\pm 5\%$.

Once the sample preparation in which the dysprosium remained on the surface of the coal was developed, this sample was used for the spectral subtraction. Equal quantities of the dysprosium treated sample of Pittsburgh No. 8 coal and a water treated sample were then packed into rotors with TKS. Sample mass was determined based on equal quantities of coal not sample. That is, the since the dysprosium treated samples contained coal and dysprosium, the sample size was determined by calculating how much of the sample weight was due to the coal. Bloch decay spectra of these samples were acquired and processed identically. Figures 25 and 26 are the NMR spectra of these samples. The Bloch decay experiment was selected so that the spectra would be as quantitative as possible. The problems associated with CP have been discussed extensively above. The spectra were then subtracted using the subtraction protocol on the GN 300 spectrometer. The features of the treated and untreated samples appear different, and the difference spectrum (Figure 27) is different from either of the parent spectra. This would indicate that the difference spectrum is real and appears to have both an aromatic and aliphatic component; features indicative of oxygenated functionalities both aromatic at about 150 ppm and aliphatic at about 50 ppm.

CONCLUSIONS:

The primary objective of this work was to develop an NMR technique that would distinguish the surface functionalities of a coal sample. The difference spectrum obtained is different from either of the spectra from which it was derived. This indicates that our objective has been met. The difference spectrum has significant intensity at about 130 - 150 ppm corresponding to aromatic groups with oxygen and 50-80 ppm corresponding to aliphatic groups with oxygen. This indicates that while the surface and bulk are quite similar, the surface may have additional oxygen functionalities. This could be due to a natural orientation of oxygen groups on the surface of the coal, or it could be due to oxidation of the coal surface. All manipulations of the coal were done under nitrogen to minimize oxidation due to atmospheric oxygen, but some exposure to the air is probable.

Figure 25: The Bloch decay spectrum of Pittsburgh No. 8 coal treated with water and lyophilized. TKS

was used as a subtraction standard,

DQ055 . 501

DQ055 PITT#8//H2O TKS BLOCH 5.6KHZ 1U P2 40S

Figure 26: The Bloch decay spectrum of Pittsburgh No. 8 coal treated with aqueous dysprosium nitrate and

lyophilized. TKS was used as a subtraction standard.

DQ054 . 501
DQ054 PITT#8/DY ROTO TKS BLOCH 5.6KHZ 1U P2 40S

Figure 27: The difference spectrum from Figure 25 - Figure 26.

DQSUB . 001
DQ055-DQ054

Validation of this technique has proven elusive, however. The primary problem in validating the technique has been finding a well defined model system in which the surface is significantly different from the bulk so as to have a different characteristic NMR chemical shift and for the sample to have a high enough surface area such that there are enough surface functionalities for the surface to be visible in the NMR. Until such a sample can be found proof of our objective will not be complete.

This work also involved the evaluation of the two primary methods of obtaining solid state NMR spectra. Cross polarization as described above is often used to enhance the signal to noise ratios of spectra involving dilute nuclei. There are however, many issues that need to be considered before one used CP for acquiring spectra of substrates as complicated as coal. We used principal component analysis to determine how much difference other than the signal to noise ratio enhancement there was if CP was used to obtain coal spectra. We found that CP discriminated against bridgehead and oxygenated carbons. These are the same carbons that appear to be preferentially distributed on the surface of the coal. Because of the discriminatory nature of the CP experiment, we chose to acquire all our spectra using Bloch decay experiments. This experimental protocol requires longer instrumental times, but we were confident that we would not be introducing distortions due to complications arising from the magnetization transfer used in the CP experiments, especially since some of the spectra would be acquired in the presence of paramagnetic ions which might cause further distortions.

We also developed a technique using EPMA to determine the location of dysprosium (I) ions in the coal and we are confident that the dysprosium (I) ion is on the surface of the coal. By going to larger pixel maps, we could increase the resolution of the EPMA, however, since we were most concerned with the general location of the dysprosium (I) ion, the work we did was sufficient.

Appendix:

Pulse programs for the NMR experiments.

1. Cross Polarization

2. T1SR

3. T1CP

4. Inversion Recovery

Figure 1. A) The pulse sequence for a simple cross polarization experiment. B) A vector diagram illustrating the behavior of the abundant spin (I) and rare spin (S) magnetizations (in this case ^1H and ^{13}C respectively). 1) The proton magnetization is rotated to the y axis by a 90° pulse; 2) The protons are spin-locked along the y axis by the applied field $B_{1(\text{H})}$, while the carbons are spin-locked along the same axis by the applied field $B_{1(\text{C})}$; 3) The spin-locking fields are removed. The carbon Free Induction Decay is acquired while high-powered decoupling is applied along the proton channel; 4) A delay time allowing for regrowth of I spin magnetization along the z axis.

Figure 2. A) The pulse sequence for the saturation-recovery experiment for the measurement of spin-lattice relaxation time (T_1) of dilute nuclei. B) A vector diagram illustrating the behavior of dilute nucleus (S) magnetization during the 90- τ -90 experiment when the relaxation delay (τ) is short. 1) A train of 90° pulses destroys both longitudinal and transverse magnetization; 2) Magnetization will begin longitudinal regrowth along +z during τ ; 3) A 90° pulse rotates the magnetization to the +y axis; 4) the FID is sampled with high-powered decoupling at the proton resonance frequency and a Fourier transform (FT) results in a positive signal. C) A vector diagram showing the change of S magnetization when the relaxation delay (τ) is long. During τ the magnetization relaxes back to its equilibrium value in the static field. The resulting Fourier-transformed signal will represent the equilibrium magnetization intensity.

Figure 4. A) The pulse sequence for the inversion-recovery experiment for the measurement of spin-lattice relaxation times (T_1) of dilute nuclei. B) A vector diagram illustrating the behavior of dilute nucleus (S) magnetization during the 180- τ -90 experiment when the relaxation delay (τ) is short. 1) The 180° pulse rotates the S magnetization to the negative z axis; 2) During the delay time the magnetization begins longitudinal regrowth toward +z; 3) A 90° pulse rotates the magnetization from -z to the -y axis; 4) the Free Induction Decay (FID) is sampled with high-powered decoupling at the proton resonance frequency and a Fourier transform (FT) results in a negative signal. C) A vector diagram showing the change of S magnetization when the delay is long. During τ the magnetization relaxes from -z to +z. The 90° pulse in step 3 will rotate the magnetization to the +y axis. Fourier transformation of the FID in step 4 results in a positive signal.

Figure 2. A) The pulse sequence for the T1CP experiment for measuring the spin-lattice relaxation rates of dilute nuclei in solids. B) A vector diagram illustrating the behavior of the dilute nucleus (S) magnetization during the T1CP experiment when τ is short. The cross polarization sequence places the magnetization along the +y axis. 1) A 90° pulse rotates the magnetization to the +z axis; 2) During τ the cross polarization-enhanced magnetization will decay toward its static equilibrium value; 3) The residual magnetization is rotated from +z to +y with a second 90° pulse; 4) The signal is collected and processed to yield a CP-enhanced peak. C) When τ is long the longitudinal magnetization along +z loses even more intensity during step 2 and the result is decreased signal intensity when the magnetization is sampled. Note: The movement of magnetization in Figure 11 applies to Equation 20.

REFERENCES:

1. Sternlicht, H. *J. Chem. Phys.* 1965, 42, 2250.
2. Alaimo, M. ; Roberts, J. Unpublished work.
3. Horrocks, W.D. Jr.; Sipe, J.P. III. *J. Am. Chem. Soc.* 1971, 93, 6800-6804.
4. Fyfe, C.A. in *Solid State NMR for Chemists*; C.F.C. Press: Ontario, (1984).
5. Botto, R.E.; Wilson, R. ; Winans, R.E. *Energy and Fuels*, 1987, 1, 173-181.
6. Snape, C.E.; Axelson, D.E.; Botto, R.E.; Delpuech, J.J.; Tekely, P. ; Gerstein, B.C.; Pruski, M.; Maciel, G.E.; Wilson, M.A. *Fuel*, 1989, 68, 547-560.
7. Bloch, F. *Phys. Rev.* 1946, 70, 460.
8. Martin, M.L.; Delpuech, J.-J.; Martin, G.L. in *Practical NMR Spectroscopy*; Heyden and Son, Ltd.: London, (1980).
9. Dahlberg, D.B. Chemistry 590: Chemometrics Notes, 1992.
10. Dahlberg, D.B. Personal Communication. 3/93.
11. General Electric Company Instruments, *NMR Instruments GN Series Manual*, Fremont, (1988).
12. Torcia, D.A. *J. Mag. Res.*, 1978, 30, 613.
13. Naito, A.; Ganapathy, S.; Akasaka, K.; and McDowell, C.A.; *J. Mag. Res.*, 1983, 54, 226.
14. Torchia, D.A. ; Szabo, A. J.; *J. Mag. Res.*, 1982, 49, 107.
15. Skoog, D.A.; West, D.M.; in *Principles of Instrumental Analysis*, Saunders College/Holt, Rinehart and Winston: Philadelphia, (1980), 453-455.
16. Goldstein, J.I.; Newbury, D.E.; Echlin, P.; Joy, D.C.; Fiori, C.; Lifshin, E. *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press: New York, (1981).
17. Newbury, D.E.; Joy, D.C.; Echlin, P.; Fiori, C.E.; Goldstein, J.I.; *Advanced Scanning Electron Microscopy and X-Ray Microanalysis*, Plenum Press: New York, (1986).
18. Joy, D.C.; Romig, A.D. Jr.; Goldstein, J.I.; *Principles of Analytical Electron Microscopy*, Plenum Press: New York (1986).
19. Stock, L.M.; Muntean, J.V.; Botto, R.E.; *New Trends in Coal Science*, 1988, 244, 159-167.
20. Hagaman, E.W.; Chambers, R.R. Jr.; Woody, M.C.; *Anal. Chem.*, 1986, 58, 387-394.

21. Vorres, K. S. *Energy and Fuels*, 1990, 4, 420-426.
22. KERMIT, Columbia University.
23. Early, T. *TEFT*, General Electric Corporate Center (1993).
24. *PC-MATLAB*, The MathWorks, Inc.