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THE DEPENDENCE OF LIQUEFACTION BEHAVIOR ON
COAL CHARACTERISTICS

Part V: The Penetration of Solvent Vapor into Coal Particles

Final Technical Report for the Period March 1981–February 1984

By
Shan-Tao Hsieh
J. L. Duda

April 1984
Date Published

Work Performed Under Contract No. AC22-81PC40784

The Pennsylvania State University
University Park, Pennsylvania

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**Final Technical Report
for the Period
March 1981 to February 1984**

**Part V: The Penetration of Solvent Vapor
into Coal Particles**

**by
Shan-Tao Hsieh and J.L. Duda**

**Department of Chemical Engineering
and the Coal Research Section
The Pennsylvania State University
University Park, Pa. 16802**

Date Published - April 1984

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DEPARTMENT OF ENERGY**

under

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FOREWORD

1. Objectives and Scope

The principal objective of this program has been to deepen understanding of the ways in which yields of products and product distributions in liquefaction are determined by the chemical, petrographic, mineralogical and geochemical characteristics of coals. In particular, it is desired to provide a scientific basis for correlations previously established empirically. The following studies are included:

(i) Attempts to induce coals to generate their own hydrogen donor solvent during a repeated series of batch runs. It is very desirable to be able to characterize and compare coals in terms of the quality of the solvent they can generate. A possible way to achieve this ability is to use the products of one run to provide part of the solvent for the next run with the same coal, and repeat this until coal product has replaced the initial tetralin.

(ii) Tests for synergistic effects when mixtures of coals are liquefied. Effects could be due to superior donor solvent or catalytic minerals contributed by one component of the mixture. Quantitative analyses of mineral distributions and some degree of product analysis are obtained when effects are found.

(iii) Aspects of the phenomenology of liquefaction, and in particular rates of loss of O and S functions in the early stages. Can thioether cleavage be an efficient chain initiator in coals of high organic sulfur content?

(iv) The relevance to liquefaction behavior of recent literature concepts of coal as a macromolecular network containing physically trapped molecules. Does liquefaction consist to a significant extent merely of the release of molecules already present inside imperfections in the network? What is the structural character of the network?

(v) An in-depth study of product yields and distributions in the liquefaction of a homogeneous, selected, set of 25 high sulfur, medium rank coals, whose organic chemical structure has been well characterized by means of FTIR, ^{13}C nmr, and analyses of product distributions from oxidation with pertrifluoroacetic acid (Deno reaction). The mass of data is to be examined statistically.

(vi) Exploit the pertrifluoroacetic acid oxidation to characterize asphaltenes and compare them with their parent coals. Asphaltenes are difficult to fractionate chromatographically, and so, like others, we seek average information for unfractionated material.

(vii) Compare the liquefaction behavior of sets of maceral concentrates, including vitrinites, liptinites and semifusinites. Detailed product analyses have been made.

(viii) Exploit computerized GC/MS techniques, particularly regeneration of single ion chromatograms, for identifying key characteristics of the distribution of products in the hexane-soluble oil from a set of coals. Single ion chromatography is specially valuable for detecting and identifying structural types all of which give a common ion under electron impact; alkanes and many homologous series of alkyl aromatics have this feature.

2. Some Comments on this Phase of the Research

It is generally agreed that the presence of a hydrogen donor solvent is of great importance in coal liquefaction, both as a source of hydrogen and as a solvent for products. It is by no means clear how molecules of solvent succeed in penetrating to the loci inside coal particles where their hydrogen is needed. It seems likely that the pore system in coals investigated by, for example, CO₂ adsorption, is of little relevance, because the system may not even exist under liquefaction conditions, and, even if it does, one would not expect rapid penetration of very small pores by bulky solvent molecules. This study was therefore planned to address such questions as, how does solvent penetrate, and at what rate?

In brief the answer seems to be that solvent enters by direct dissolution, or imbibition, into the coal structural matrix; diffusion of solvent and relaxation of the coal structure then follows. The interaction of, for example, toluene vapor at 110° with coal turns out to be surprisingly complex. Perhaps the most important contributions of this study, as it turned out, are the light it throws on the macromolecular network structure of coals, and the demonstration that surface areas determined by gas adsorption are of little value in predicting uptake of condensable vapors.

The study described herein was supported partly by DOE funds and partly by industrial funds from Penn State's Cooperative Program in Coal Research.

ABSTRACT

The investigation of the sorption of solvent vapor into high volatile bituminous coal (PSOC-375) at temperatures up to 175°C indicates that the solvent weight gain by a coal particle involves a complex coupling of several phenomena including adsorption, sorption into the coal matrix, capillary condensation and extraction into the condensed vapor phase. The acceptor number (AN), which indicates the electrophilic property of the solvent, and the donor number (DN), which indicates the nucleophilic property of the solvent, correlate the sorption behavior quite well. A similar correlation has been used for coal extraction measurements. It appears that the sorption in untreated coal is dominated by the capillary condensation induced by solvent extraction. As a result, an equilibrium state is not attainable for the sorption in untreated coal. This extraction mechanism can be eliminated by the preextraction of the coal particles with pyridine. Vapor sorption experiments conducted on pyridine-extracted coal can be used to obtain information concerning the adsorption process and the process associated with the diffusion of the solvent molecules into the coal matrix.

Vapor sorption studies conducted on pyridine-extracted coal particles indicate that the sorption process involves a coupling of adsorption, molecular diffusion and a relaxation of the coal structure to a new state. Similar behavior is commonly observed for vapor sorption into glassy polymers. The coal sorption measurements have been accurately described by use of two models, one by Berens and Hopfenberg, the other by Long and Richman. Both models were derived to describe coupling of molecular diffusion and polymer chain relaxation in glassy polymers.

Thermodynamic equilibrium data as a function of solvent activity have been employed to evaluate the Flory model. This model was derived to describe the sorption of solvent vapors into crosslinked polymers. Although the Flory model fits the coal sorption data quite well, the physical significance of the resulting parameters in this model is open to question. The same thermodynamic equilibrium data were used to test two other models, one by Lucht and Peppas and the other by Kovac. Both models fit the sorption data well, but the parameters obtained by these two models are not reasonable. The thermodynamics of solvent sorption into coal particles is further complicated by the presence of severe hysteresis effects. The amount of solvent sorbed by a coal particle is not only a function of solvent activity but depends upon the past history of the sorption process which influences the structure of coal.

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LIST OF SYMBOLS

a	Radius of the sphere
a_1	Activity of solvent at T and P
AN	Acceptor number
C	Concentration of solvent
C_1	Concentration of solvent
C^*	Equilibrium concentration of solvent
C_s	Surface concentration
C_o	Initial surface concentration of solvent
C_{eq}	Equilibrium concentration of solvent
D	Binary mutual effective diffusion coefficient
D	Donor solvent
DN	Donor number
ΔE	Cohesive energy
ΔE_d	Nonpolar interaction
ΔE_H	Hydrogen bonding interaction
ΔE_p	Permanent-dipole-permanent-dipole interaction
f_1	Fugacity of the solvent in the swollen polymer at T and P
f_1^o	Fugacity of pure solvent at T and P
ΔG_1	Chemical potential change of the solvent due to mixing
ΔG_{1e}	Chemical potential change of the solvent due to elastic network
K	Relaxation-rate constant
M_c	Average molecular weight of chain between crosslinks
$M_{t,D}$	Amount of solvent sorbed in the sphere at time t
$M_{\infty,D}$	Equilibrium solvent gain

LIST OF SYMBOLS (contiuned)

$M_{t,R}$	Amount of sorption due to relaxation at time t
$M_{\infty,R}$	Ultimate amount of sorption due to relaxation
M_t	Amount of sorption due to Fickian diffusion and relaxation
M_{coal}	Coal sample mass
N	Number of repeating units between crosslinks
P	Partial pressure of pure solvent
R	Gas constant per mole
r	Radial coordinate
t	Time
T	Temperature
T_1	Temperature of sorption column
T_2	Boiler temperature
u	Quantity defined as $u = Cr$
V_m	Molar volume of solvent
$\hat{V}_1$	Molar volume of solvent
$\bar{V}$	Specific volume of coal
Z	Compressibility factor for the gas phase

Greek Letters

β	Relaxation parameter
δ	Solubility parameter defined by equation (1)
δ_D	Dispersion component of the solubility parameter
δ_H	Hydrogen bonding component of the solubility parameter
δ_P	Polar component of the solubility parameter
μ_I	Chemical potential of component I in solution per mole
μ_I^o	Chemical potential of pure component I per mole

LIST OF SYMBOLS (Continued)

ρ_c	Density of coal sample
ρ_s	Density of solvent
θ_1	Quantity defined by equation (41a)
θ_2	Quantity defined by equation (41b)
ϕ_I	Volume fraction of component I
χ	Flory interaction parameter
ω_s	Mass fraction of solvent

Subscripts

1	Solvent
2	Coal

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I. INTRODUCTION

The interaction of solvents with coal is very important in several coal utilization processes. For example, during coal liquefaction, it is commonly accepted (13) that the first step in the reaction is the breaking of covalent bonds in coal particles, and then free radicals are generated. If there is a donor solvent, such as tetralin, which is able to donate hydrogen to these free radicals, liquid products may be obtained. On the other hand, if there is no donor solvent available, solid products may be produced by retrogressive reactions and they are not desirable in coal liquefaction processes. Therefore, from these reaction steps, it is possible that the migration of the donor solvent is related to the rates of coal liquefaction.

Several investigators have attempted to elucidate the significance of mass transfer and diffusion limitations by determining the influence of particle size on liquefaction. A recent survey of the literature indicates that the results are inconclusive (56). It may be argued that if conversion in coal liquefaction is independent of the particle size, the intraparticle mass transfer limitations are not significant. In fact, the critical diffusion length is not the overall dimensions of the particle, but the distance between pores. Furthermore, the characteristic diffusion length may not be altered by reducing the overall size of the coal. Also, it could be argued that under the severe conditions of liquefaction, the particles are broken down into characteristic sizes which are dictated by the temperature history and solvent interactions; and the characteristic length of the particle in the reactor may not be related to the initial input particle size.

From the physical state of coal during liquefaction, it appears that the thermodynamic interaction of solvent with coal and the mass transfer of solvent molecules in the presence of the coal molecules are important factors for the conversion of coal into liquids. Therefore, a better fundamental understanding of the interaction of solvents with coal is needed to improve the coal liquefaction process.

The sorption of organic vapors, including benzene and tetralin, in untreated coal at temperatures up to 70°C has been studied by Nelson (40). Efforts have been made by him to determine the diffusivity of solvent in coal from sorption data. However, due to the limitation of his experimental apparatus, sorption operations could not last for a long period. Therefore, the amount of solvent gain in coal after 24 h was taken in his study as the final true equilibrium value to determine the diffusivity of solvent in coal. However, this approach may cause an uncertainty in the value of the diffusivity, because the final true equilibrium value plays an important role in determining the diffusivity.

For many years, solvents have been utilized as molecular probes to elucidate the structure and morphology of polymeric materials (46). Both the thermodynamics and transport characteristics of solvents in polymers can be interpreted in terms of molecular models which are related to the morphological characteristics of the material such as crystal structure, the presence of molecular aggregates and the distribution of free-volume. In a similar fashion, studies of diffusion and sorption of solvents into coal can be used as a means of elucidating aspects of the molecular structure of coal and physical state of coal such as glassy state or rubbery state. A better understanding of the molecular structure and physical state of coal will enhance the utilization of coal.

Studies of coal structure (30,31,34) indicate that coals have a three-dimensional crosslinked macromolecular structure. Furthermore, interspersed within this polymeric structure are small molecules which are attached to the network by weak bonds such as hydrogen bonding. The recent work of Jurkiewicz and coworkers (25,37) using pulse NMR shows that electron-donor-acceptor interactions in coal can be destroyed by some solvents such as pyridine and part of the mobile phase can be removed. Therefore, it is reasonable to consider that after pyridine extraction the residue can be treated as a three-dimensional cross-linked macromolecular structure.

Many investigators have attempted to elucidate the network structure of coal by the study of solvent swelling. Sanada and Honda (47), and Kirov and coworkers (28) investigated the swelling equilibrium by exposing coal samples to liquid solvent, and the molecular weight between cross-links was estimated by use of the Flory-Rehner equation. The major problem of this approach is that there are two unknown parameters, χ and M_c , in the Flory-Rehner equation, where χ is the interaction parameter for the coal-solvent system and M_c is the molecular weight between cross-links. In order to determine these two unknown parameters, at least two sets of sorption data are needed. If the sorption is conducted only at solvent activity 1.0 which represents liquid solvent, one of these two parameters χ must be estimated from other measurements. For instance, assuming that the extract and the residue have a basic similarity, Sanada and Honda (47) estimated the value of χ from the concentration dependence of osmotic pressure in pyridine solutions of coal extract. However, the value of M_c obtained from this approach is not consistent with the value of M_c determined from mechanical measurements on the

elasticity of the coal. There is a large discrepancy in M_c , as pointed out by Larsen and Kovac (31).

Two models other than the Flory-Rehner model have been proposed by Lucht and Peppas (34) and Larsen and Kovac (29,31). They have convincingly argued that the distribution of crosslinks in coal does not obey the Gaussian model which was assumed in the derivation of the Flory-Rehner model. Consequently, more parameters have been introduced in their models; but they cannot be uniquely determined from the swelling data of coal in pure solvents.

By restricting measurements to the solvent swelling in liquid solvents, all previous investigators have unnecessarily constrained the amount of relevant data that can be obtained. In fact, the Flory-Rehner equation is a limiting case of a general equation. In his original work, Flory considered the interaction of a solvent vapor in a crosslinked elastic polymer network, and the chemical potential change of the solvent due to the mixing and the elastic reaction of the network structure was derived at different values of solvent activity. Therefore, if the sorption of solvent in coal is conducted at various values of solvent activity, as shown in this study, a plot of solvent uptake and solvent activity is then obtained. If the general equation of the Flory model is used to correlate the sorption data, these two unknown parameters χ and M_c can be determined simultaneously. This approach represents the first unambiguous method to test the Flory model. A similar approach can be employed to evaluate the models of Lucht and Peppas, and Larsen and Kovac.

II. OBJECTIVES

The objectives of this research were as follows:

1. Elucidate the mechanism of sorption of solvent in coal.
2. Test the effects of temperature and concentration on the diffusion coefficient.
3. Establish the relationship between the solvent activity and thermodynamic equilibria.
4. Use solvent swelling as a means to study the structure of coal.

III. THEORIES OF SOLUBILITY AND DIFFUSION IN COAL

In order to investigate solubility and diffusion of solvent in coal, it is very important to understand some properties of coal first.

A. Characteristics of Coal

The investigation of physical and chemical composition of coal indicates that coal is composed of organic macerals and inorganic minerals, and coal is highly heterogeneous (6).

Coal is a porous medium and it has high surface area (12,54). The pore size distribution in coals ranges from micropores, through transitional pores, to macropores. The nature of the porosity in coals varies in rank from anthracite to lignite.

Coal has some polymeric characteristics. When a piece of cross-linked polymer is brought in contact with a solvent, it swells. Coal demonstrates similar behavior (28,34,47). Coal also behaves like a piece of rubber: if a piece of rubber is subjected to a stress, it will deform until it reaches the limit set by the crosslinks. After the stress is removed, the rubber returns to its original dimensions. A similar relationship between the stress and the strain has been observed for coal (31,36,39).

B. The Sorption of Solvents in Coal

Since coal has some polymeric characteristics, the concepts of the solubility parameter, which have been widely used to interpret the interaction of solvents with polymer, have been employed by many investigators (21,28,47,48,55) to study the solubility of solvents in coal.

The original work by Hilderbrand on the solubility parameter (20) has been modified to provide a better explanation of the interaction between the solvent and the solute in terms of three major forces: dispersion force, dipole moment and hydrogen-bonding interaction (18,19, 49,50).

The definition of the solubility parameter δ is given by

$$\delta = (\Delta E/V_m)^{0.5} \quad (1)$$

where ΔE is the cohesive energy arising from contributions from nonpolar interactions ΔE_d , permanent-dipole permanent-dipole interactions E_p , and hydrogen bonding ΔE_H . Therefore, the following equation can be written:

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_H \quad (2)$$

Dividing this equation by the molar volume of a solvent V_m gives

$$\frac{\Delta E}{V_m} = \frac{\Delta E_d}{V_m} + \frac{\Delta E_p}{V_m} + \frac{\Delta E_H}{V_m} \quad (3)$$

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2 \quad (4)$$

where

$$\delta_d = (\Delta E_d/V_m)^{0.5} \quad (5)$$

is the dispersion component of the solubility parameter,

$$\delta_p = (\Delta E_p/V_m)^{0.5} \quad (6)$$

is the polar component of the solubility parameter, and

$$\delta_H = (\Delta E_H/V_m)^{0.5} \quad (7)$$

is the hydrogen-bonding component of the solubility parameter.

The determination of these three partial solubility parameters δ_d , δ_p , and δ_H for solvents has been reported by many authors including Hansen (16,17), Blanks (7) and others (2,3,19).

When a piece of crosslinked polymer is brought in contact with a solvent, the polymer will not be dissolved in the solvent, but will be swollen by the solvent. If a series of solvents with solubility parameters ranging from $7.0 \text{ (cal/cm}^3)^{0.5}$ to $24 \text{ (cal/cm}^3)^{0.5}$ are chosen to swell the crosslinked polymer, the plot of solvent solubility parameter δ vs. the degree of swelling of the polymer usually shows a single-mode curve, and the solubility parameter of the solvent that causes the maximum swelling is assigned as the solubility parameter of the crosslinked polymer.

Studies of the solubility parameter of coal have been conducted by many investigators (21,28,47,48,55), but the results are not conclusive. For example, Honda (47) exposed pyridine-extracted coal to several solvents with different solubility parameters at 25°C. His results indicated that a single-mode curve was obtained by plotting the solubility parameter vs. the volume ratio of swelling. The maximum swelling occurred at the solubility parameter $\delta=11.0 \text{ (cal/cm}^3)^{0.5}$, which is the solubility parameter of pyridine. In Yen's work (32), two miscible liquids were used to form binary mixtures with effective solubility parameters ranging from 7.0 to $23.4 \text{ (cal/cm}^3)^{0.5}$. His results indicated that the plot of solubility parameter vs. swelling of pyridine-extracted and untreated coals did not yield such a single-mode curve; instead, two sharp peaks were found in his swelling spectra.

1. The Sorption of Solvent in Untreated Coal

The sorption process is strongly related to the molecular and physical structure of the coal. Therefore, when the untreated coal is exposed to a solvent vapor, the mechanisms of the sorption are better elucidated by a physical picture of coal structure, shown in Figure 1. From this picture, it is realized that there are three mechanisms occurring simultaneously in the course of the sorption:

- a. The solvent vapor is adsorbed on the surface of the coal and pore walls, and the capillary condensation occurs in the small pores.
- b. The solvent vapor diffuses into the coal matrix.
- c. The mobile phase in the coal matrix is extracted out by the condensed penetrant to form a mixture in these small pores, and this mixture lowers the chemical potential of the penetrant; therefore, more solvent is driven into this mixture until an equilibrium state is obtained.

When coal sample is exposed to solvent vapor, it is easier for solvent molecules to diffuse into the pores than into coal matrix. This has been proved by Nelson et al. (41) using gravimetric and pycnometric techniques. Hence, the first mechanism, the adsorption and capillary condensation, is a fast process and will reach an equilibrium in a very short period. The second mechanism, the diffusion of solvent into coal matrix, is suppressed by the extraction process because the diffusion in coal matrix is in an opposite direction to the extraction process, as

Figure 1. The diffusion, capillary condensation and extraction in untreated coal

shown by the arrows in Figure 1. The third mechanism, the extraction, will not reach an equilibrium state because the chemical potential of the penetrant in the condensed mixture is always lower than that in the pure solvent vapor. As a result, the extraction process may be dominant during the sorption of solvent in untreated coal and the sorption will not reach an equilibrium state even after a long period of operation. Since the extraction process may predominate in the sorption of solvent in untreated coal, the concept of a donor and acceptor number, which has been used to correlate the results of coal extraction by Marzec et al. (38), may be employed to interpret the interaction of solvents with untreated coal. The donor number and the acceptor number defined by Gutmann (14,15) are used to measure the nucleophilic and the electrophilic properties of the solvent, respectively. According to Gutmann's scale, the donor number of a solvent (DN) is defined as the negative ΔH -value in $\text{Kcal} \cdot \text{mol}^{-1}$ for the interaction of the nucleophilic solvent (Lewis base) with SbCl_5 in a highly diluted solution of dichloroethane:

The acceptor number (AN) is used to measure the electrophilic behavior of a solvent. Gutmann uses Et_3PO as the reference base and correlates the AN of a given solvent with the relative ^{31}P chemical shift induced by dissolving the reference base in the pure solvent

AN values are scaled to an arbitrarily chosen value of 0 for the shift produced by hexane and 100 for the shift produced by the 1:1 $\text{Et}_3\text{PO-SbCl}_5$ adduct in 1,2-dichloroethane (15).

Values for 53 solvents with DN ranging from 0.1 Kcal/mole to 61 Kcal/mole and 34 solvents with AN value ranging from 0 to 100 have been measured and published by Gutmann (14,15).

In order to interpret the interaction of solvents with coal, a two-parameter approach has been used by Marzec et al. (37) to correlate the results of coal extraction. As a result, a correlation has been established between the extraction yield and the parameter DN minus AN. The correlation indicates that any solvent with DN minus AN less than 0 shows a low extraction yield. But, when the DN-AN value of the solvent is greater than zero, the larger the value of the difference, the greater the solvent's ability to extract material from coal.

2. The Sorption of Solvent in Pyridine-Extracted Coal

Results of coal extraction studies by Marzec et al. (38) and the subsequent studies of the molecular structure of coal (28,37) may lead to an important concept. This concept is that when the pyridine-extracted coal is exposed to a solvent which has a lower extraction capability than pyridine, such as benzene or toluene, extraction will not occur because substances extractable by these weak agents have been extracted out by pyridine. As a result, the sorption of solvent in the pyridine-extracted coal is attributed to the following two simultaneous mechanisms:

- a. Adsorption on pore walls and capillary condensation in the small pores.

b. Diffusion of solvent into the coal matrix.

Since the extraction process does not occur when the pyridine-extracted coal is brought in contact with a solvent weaker than pyridine, the pyridine-extracted coal and solvent should reach an equilibrium state. Furthermore, because the structure of the pyridine-extracted coal is treated as a three-dimensional polymeric network, the theory of the solubility parameter and the Flory model which is used to elucidate the network structure of coal can be tested by the solvent swelling data.

C. The Relationship Between Thermodynamic Equilibria and Coal Structure

The solvent can be used as a probe for elucidating the network structure of the crosslinked polymer. For instance, if a piece of cross-linked polymer has many crosslinks, it is very hard for a solvent to swell such a polymer. On the other hand, if the polymer only has a few crosslinks, it will swell to a significant extent in a good solvent. Since the pyridine-extracted coal is treated as a three-dimensional cross-linked polymer, the Flory model, which considers the interaction of a solvent vapor with a crosslinked elastic polymer network, is used not only to establish the relationship between thermodynamic equilibria and the solvent activity but also to determine the molecular weight between crosslinks. For the Flory theory (11), the chemical potential of the solvent in the swollen polymer (coal) is given by

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \left(\frac{\hat{v}_1}{\bar{v}_{M_c}}\right)\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right) \quad (8)$$

$$\omega_s = \frac{M_s}{M_s + M_{\text{coal}}} \quad (8a)$$

$$\phi_1 = \frac{\omega_s / \rho_s}{\omega_s / \rho_s + (1 - \omega_s) / \rho_c} \quad (8b)$$

where

μ_1 = chemical potential of solvent in the swollen polymer at T and P,

μ_1^0 = chemical potential of pure solvent at T and P,

ϕ_1 = volume fraction of sorbed vapor,

ϕ_2 = volume fraction of coal = $1 - \phi_1$,

χ = Flory interaction parameter,

$\hat{V}_1$ = molar volume of solvent at T and P,

$\bar{V}$ = specific volume of coal,

M_c = average molecular weight of chain between crosslinks,

M_s = solvent mass,

M_c = coal sample mass,

ρ_c = density of coal = $1/\bar{V}$,

ρ_s = density of solvent, and

ω_s = mass fraction of solvent.

In order to determine the volume fraction of solvent ϕ_1 , two assumptions are made. The first is that the density of coal is assumed to be equal to 1.3 g/cm^3 (31). The second is that there is no volume change due to mixing of pure solvent with coal. Hence, the volume fraction of solvent ϕ_1 can be determined by equation (8b).

The Flory model was derived for isotropic crosslinked polymer. Since coal is anisotropic, this makes the application of the Flory model difficult. However, the Flory model may provide a useful information about the structure of coal.

The first three terms on the right-hand side of equation (8) represent the chemical potential change of the solvent due to the mixing of pure solvent with non-crosslinked polymer. The last term introduces the modification of the chemical potential change due to the elastic reaction of the network structure (11).

According to the thermodynamic definition, the left-hand term of equation (8) can be expressed as follows:

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln \frac{f_1}{f_1^0} = \ln a_1 \quad (9)$$

where

f_1 = the fugacity of the solvent in the swollen polymer at T and P,

f_1^0 = the fugacity of the pure solvent at T and P, and

a_1 = the activity of the solvent at T and P.

Substitution of equation (9) into equation (8) gives

$$\ln \frac{f_1}{f_1^0} = \ln a_1 = \ln (1 - \phi_2) + \phi_2 + \chi \phi_2^2 + \left(\frac{\hat{V}_1}{\bar{V}M_c} \right) \left(\phi_2^{1/3} - \frac{\phi_2}{2} \right) \quad (10)$$

At equilibrium, the fugacity of the solvent in the swollen gel is equal to the fugacity of the solvent in the vapor phase. Since the vapor pressure of coal is almost zero, the concentration of coal in the vapor phase is zero as well; therefore, the vapor phase only contains the solvent, and the fugacity of the solvent which is simply a function of temperature and pressure, then can be determined.

It is easy to show that the term $\ln f_1/f_1^0$ in equation (10) can be expressed in terms of measurable properties as follows (52):

$$\ln \frac{f_1}{f_1^0} = \ln \left(\frac{P}{P_s} \right) + \int_{P_s}^P \frac{Z - 1}{P'} dP' + \frac{\hat{V}_1}{RT} (P_s - P) \quad (11)$$

where

Z = compressibility factor for the gas phase,

$\hat{V}_1$ = molar volume of the solvent at T ,

R = gas constant per mole,

T = temperature, and

P_s = vapor pressure of pure solvent at T .

The last two terms of equation (11) include the correction for the deviation from the ideal gas behavior and pressure effects in the liquid phase.

The vapor pressures of the solvent as a function of temperature are calculated by use of the Antoine equation. The Antoine equation coefficients for each solvent are given by Reid et al. (44).

The Flory-Rehner equation is a limiting case of the Flory model. For the Flory-Rehner equation, the coal sample is exposed to a liquid solvent and the activity of the solvent becomes 1.0; therefore, the term on the left-hand side of the equation (10) is zero, and the expression for the Flory-Rehner equation is given by

$$\ln \phi_1 + \phi_2 + \chi \phi_2^2 = - \left(\frac{\hat{V}_1}{\bar{V}_c} \right) \left(\phi_2^{1/3} - \frac{\phi_2}{2} \right) \quad (12)$$

To test the relationship between the thermodynamic data and coal structure by use of equation (10), an experiment is designed. The details of the design and experimental procedures will be shown in the section of experiments.

Models other than the Flory model have been proposed by Lucht and Peppas (34,35) and Larsen and Kovac (29,31). They convincingly argued that since the chains in coal are probably to be thought of as short and stiff, the Gaussian theory which was assumed in the derivation of the Flory model is not applicable to the determination of the structure of coal. Therefore, they used the modified Gaussian model to derive the chemical potential change of the solvent in coal. Results of their derivations are described as follows.

The Kovac model (29) postulates that the chemical potential change of the solvent due to mixing, ΔG_1 , can be expressed by the Flory-Huggins equation

$$\Delta G_1 = RT \{ \ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2 \} \quad (13)$$

and the chemical potential change of the solvent due to the elastic network ΔG_{1e} is given by

$$\begin{aligned} \Delta G_{1e} = & \frac{RT \hat{V}_1 \phi_2^{1/3}}{\bar{V} M_c} \left(1 + \frac{2}{N} \phi_2^{-2/3} + \frac{1}{N^2} \phi_2^{2/3} \right) \\ & \times \left(1 - \frac{3}{N} \phi_2^{-2/3} + \frac{3}{N^2} \phi_2^{-4/3} - \frac{1}{N^3} \phi_2^{-2} \right) \end{aligned} \quad (14)$$

The total chemical potential change of the solvent in the coal is the sum of equations (13) and (14). Hence

$$\begin{aligned} \frac{\mu_1 - \mu_1^0}{RT} &= \ln \frac{f_1}{f_1^0} = \ln a_1 \\ &= \{ \ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2 \} \end{aligned}$$

$$\begin{aligned}
& + \frac{\hat{V}_1 \phi_2^{1/3}}{\bar{V}M_c} \left(1 + \frac{2}{N} \phi_2^{-2/3} + \frac{1}{N^2} \phi_2^{2/3}\right) \\
& \times \left(1 - \frac{3}{N} \phi_2^{-2/3} + \frac{3}{N^2} \phi_2^{-4/3} - \frac{1}{N^3} \phi_2^{-2}\right)
\end{aligned} \tag{15}$$

The Lucht-Peppas model (34,35) was derived in a similar fashion and is given by

$$\begin{aligned}
\frac{\mu_1 - \mu_1^0}{RT} &= \ln \frac{f_1}{f_1^0} = \ln a_1 \\
&= \{\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2\} \\
&+ \frac{\hat{V}_1}{\bar{V}M_c} \frac{(\phi_2^{1/3} - \phi_2/2)(1 + \phi_2^{1/3}/N)^2}{(1 - 1/N \phi_2^{2/3})^3}
\end{aligned} \tag{16}$$

Equation (16) indicates that the chemical potential change due to mixing, which is the first term of this equation, is given by the Flory-Huggins theory, and the second term represents the chemical potential change resulting from the elastic reaction. As the number of repeating units between crosslinks N becomes greater than 50, the two terms related to N in equation (16) become much less than 1.0 and the Lucht-Peppas model, equation (16) is almost identical to the Flory model expressed by equation (10).

In equations (15) and (16), M_c is the number average molecular weight between crosslinks, $\hat{V}_1$ and $\bar{V}$ are the molar volume of the swelling agent and the specific volume of the macromolecule, ϕ_2 is the volume fraction of the coal, and χ is the Flory interaction parameter.

Both equation (15) and equation (16) are the general expressions of the Kovac model and the Lucht-Peppas model. However, in their papers

(29,34,35) only the limiting case where the activity of the solvent is equal to 1.0 was reported.

D. The Classification of Diffusion in Coal

Since the structure of coal is very complex, the diffusion of the solvent into coal is the combination of several mechanisms, which include the diffusion into macropores, transitional pores, micropores, and, particularly, coal matrix. The diffusion of solvent into coal matrix can be proved by the swelling of coal sample in contact with solvents (28,34,47).

The types of diffusion in pores depend upon the pore radius and the mean free path of molecules between intermolecular collisions. If the radius of the pore is much greater than the mean free path, bulk diffusion is taking place. As the pore size becomes smaller than 1000 Å, transport of molecules in pores is the so-called Knudsen diffusion. When the size of diffusing species closely approaches the size of the aperture through which it passes, the interaction between the solid walls and the species becomes important. This type of molecular transport falls into the class of activated diffusion (53).

As mentioned earlier, the pyridine-extracted coal may be treated as a three-dimensional crosslinked polymer. Thus, the diffusion of solvent into pyridine-extracted coal may be classified as diffusion in a polymer.

In order to investigate diffusion in a polymer, it is useful to classify the types of diffusion in a polymer first. Alfrey et al. (1) was the first investigator to propose a useful classification for characterizing the types of diffusion in a polymer. In his classification, the glass transition temperature of a polymer is the focal point.

If a sorption occurs at a temperature well above the glass transition temperature of a polymer, the polymer is in a rubbery state and polymer chains adjust very fast to accommodate themselves to the sorption. In other words, the time to relax the stress caused by the diffusion of solvent into the polymer is very short. Hence, the rate of relaxation is much faster than the rate of diffusion. This kind of sorption behavior is referred to as Fickian diffusion or Case I diffusion.

If a sorption temperature is below the glass transition temperature of a polymer, the polymer is in a glassy state and the rearrangement of polymer chains responding to the sorption of solvent is very slow. Hence, the rate of relaxation and the rate of diffusion become comparable. This kind of sorption behavior is classified as non-Fickian or anomalous diffusion.

E. Calculation of the Mutual Diffusion Coefficient for Fickian Diffusion

If the diffusion behavior obeys Fick's law, the mutual diffusion coefficient can be obtained by setting up a mass balance equation plus boundary conditions and making the following assumptions:

1. The temperature change associated with the sorption of penetrant is negligible.
2. The diffusivity is constant.
3. Diffusion occurs in only one direction.
4. No chemical reactions occur in the course of diffusion.
5. The surface of the particle is always in equilibrium with the vapor pressure of the solvent.
6. No volume change takes place.

When the coal particle is considered as a sphere, the diffusion equation with an initial condition (I.C.) and boundary conditions (B.C.) inserted can be set out as follows (8):

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (17)$$

$$\text{I.C.} \quad C = 0, \quad t = 0, \quad 0 < r < a \quad (18)$$

$$\text{B.C.} \quad C = C^*, \quad r = a, \quad t > 0 \quad (19)$$

$$\frac{\partial C}{\partial r} = 0, \quad r = 0, \quad t > 0 \quad (20)$$

Initial condition indicates that there is no solvent in the sphere before the sphere is exposed to the solvent vapor. The first boundary condition which is equation (19) indicates that the surface concentration is at its equilibrium value C^* . This boundary condition is valid for Fickian diffusion in which the rate of relaxation is much faster than the rate of diffusion. The second boundary condition expressed by equation (20) shows that the concentration profile at the center of the sphere is symmetrical.

In order to solve this partial differential equation easily, the form of equation (17) should be simplified. This can be achieved by a proper transformation of variables. If a variable u is defined as $u = Cr$, equations (17)-(20) then become

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \quad (21)$$

$$\text{I.C.} \quad u = 0, \quad t = 0, \quad 0 < r < a \quad (22)$$

$$\text{B.C.} \quad u = aC^*, \quad r = a, \quad t > 0 \quad (23)$$

$$u = 0, \quad r = 0, \quad t > 0 \quad (24)$$

This partial differential equation with such initial condition and boundary conditions can be solved by means of the Laplace transformation (18). The solution to equations (21)-(24) is given by

$$\frac{M_{t,D}}{M_{\infty,D}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \quad (25)$$

where $M_{t,D}$ is the amount of solvent sorbed in the sphere at time t , and $M_{\infty,D}$ is the equilibrium solvent gain.

When t is very small, equation (25) can be simplified as follows (8):

$$\frac{M_{t,D}}{M_{\infty,D}} = 6 \left(\frac{D}{\pi a^2} \right)^{0.5} \cdot \sqrt{t} \quad (26)$$

Sorption described by Fickian diffusion is usually expressed by the plot of $M_{t,D}$ vs. $\sqrt{t}$. From equation (26), it is realized that the amount of solvent gain $M_{t,D}$ is proportional to the square root of time at the early stage of the sorption, and the slope of this straight line is equal to $6(D/\pi a^2)^{0.5} \cdot M_{\infty,D}$. If the equilibrium solvent gain $M_{\infty,D}$ is obtained from the sorption experiment, the diffusion coefficient D is then determined.

A plot of $M_{t,D}$ vs. $\sqrt{t}$, constructed from equations (25) and (26), exhibits the features of Fickian diffusion. At the early stage of the sorption, $M_{t,D}$ is proportional to $\sqrt{t}$. As time goes on, the sorption curve will level off and reach an equilibrium value. Therefore, it is very convenient to classify the diffusion behavior just from the plot of M_t vs. $\sqrt{t}$. If the sorption curve follows the features of Fickian diffusion, sorption is classified as the Case I diffusion. Otherwise,

the sorption falls into either Case II diffusion or non-Fickian diffusion.

The diffusion coefficient determined in this study is called the effective diffusion coefficient, because the particle size of the coal is used in equation (26) to determine the value for D . Since coal is a porous medium, the characteristic diffusion length is the distance between pores. However, this distance is unknown. The value of the effective diffusivity is greater than that of diffusion coefficient calculated by using the distance between pores as the diffusion length. However, the effective diffusion coefficient provides an upper bound of the true diffusion coefficient.

F. Calculation of the Mutual Diffusion Coefficient for Non-Fickian Diffusion

As the diffusion and relaxation rates become comparable, sorption is a combination of these two processes and does not follow the typical Fickian diffusion. This non-Fickian sorption behavior has been observed in many cases for the penetration of solvents into glassy poly (methyl methacrylate) (PMMA) spheres at 90°C (5), as shown in Figure 3, is classified as a non-Fickian sorption. The plot of M_t vs. $\sqrt{t}$ exhibits a linear relationship at the early stage of sorption, but sorption does not level off as shown in a typical Fickian diffusion. Instead, sorption still continues at a slow rate. This slow, long sorption process is attributed to a relaxation process in which rearrangement of the polymer structure occurs.

To simulate non-Fickian diffusion, several mathematical models have been proposed. However, since the relaxation process is very complex, no single model is able to explain mechanism completely. In this study,

$$P_{\text{rel}} = 0 \rightarrow 0.01$$

Figure 2. Sorption of CCl_4 in $0.134 \mu\text{m}$ PMMA sphere at 90°C

Source: Berens and Hopfenberg, J. Membrane Science, 10, 283 (1982).

two mathematical models have been employed to interpret the sorption data in coal: one was postulated by Berens and Hopfenberg (4); the other was proposed by Long and Richman (33). Both models are discussed in the following sections, respectively.

1. Mathematical Model by Berens and Hopfenberg

The mathematical model proposed by Berens and Hopfenberg (4) is composed of two independent mechanisms. One is the ideal Fickian diffusion. The other is the relaxation mechanism and the rate of the relaxation is assumed to be first order in the concentration difference that drives the relaxation. The differential equation for the relaxation is therefore given by

$$\frac{dM_{t,R}}{dt} = K(M_{\infty,R} - M_{t,R}) \quad (27)$$

where K is the relaxation-rate constant, $M_{\infty,R}$ is the ultimate amount of sorption due to relaxation, and $M_{t,R}$ is the amount of sorption due to relaxation. Integration of equation (27) leads to

$$M_{t,R} = M_{\infty,R} \{1 - \exp(-Kt)\} \quad (28)$$

The total amount of sorption per unit weight of sample M_t is the amount of sorption due to Fickian diffusion $M_{t,D}$ and the amount of sorption due to relaxation $M_{t,R}$. Hence,

$$M_t = M_{t,D} + M_{t,R} \quad (29)$$

Substitution of equations (25) and (28) into equation (29) yields

$$M_t = M_{\infty,D} \left\{ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{a^2}\right) \right\}$$

$$+ M_{\infty,R} \{1 - \exp(-Kt)\} \quad (30)$$

Equation (30) represents the analytical expression for the non-Fickian diffusion. There are four parameters in this equation, $M_{\infty,D}$, D , $M_{\infty,R}$ and K , and they can be determined empirically from the experimental sorption data by use of a nonlinear regression analysis (SAS Nonlinear Regression Analysis Package at The Pennsylvania State University Computer Center).

2. Mathematical Model by Long and Richman

Long and Richman (33) proposed a mathematical model to explain the diffusion of vapor into glassy polymers. In their model, when the glassy polymer is exposed to the solvent vapor, the surface concentration is not immediately in equilibrium with the solvent vapor. Instead, the surface concentration is below the equilibrium value. But after the solvent diffuses into the glassy polymer, the surface concentration gradually approaches the equilibrium value, varying with time according to the equation

$$C_s = C_o + (C_{eq} - C_o) \{1 - \exp(-\beta t)\} \quad (31)$$

where C_s is the surface concentration, C_o is the initial surface concentration, C_{eq} is the equilibrium concentration, and β is the relaxation parameter.

This model was originally derived for a film. Since the coal particle is treated as a sphere, Long and Richman's model has been adapted for a sphere and is given by

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (32)$$

$$\text{I.C.} \quad C = 0, \quad t = 0, \quad 0 < r < a \quad (33)$$

$$\text{B.C.} \quad C_s = C_o + (C_{eq} - C_o)\{1 - \exp(-\beta t)\} \quad (34)$$

$$C = \text{finite}, \quad r = 0 \quad (35)$$

On putting

$$u = Cr, \quad (36)$$

equations for C become

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \quad (37)$$

$$\text{I.C.} \quad u = 0, \quad t = 0, \quad 0 < r < a \quad (38)$$

$$\text{B.C.} \quad u = u_o + (u_{eq} - u_o)\{1 - \exp(-\beta t)\} \quad (39)$$

$$u = 0, \quad r = 0 \quad (40)$$

This parabolic partial differential equation (PDE) with such initial condition and boundary conditions can be solved by the method of the Laplace transformation (8). The solution to this PDE is given as follows:

$$\begin{aligned} M_t = & \left(\frac{4}{3} \pi a^3 C_o\right) \left\{1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D n^2 \pi^2 t / a^2)\right\} \\ & + \left(\frac{4}{3} \pi a^3\right) (C_{eq} - C_o) \left\{1 - \frac{3D}{\beta a^2} \exp(-\beta t)\right\} \\ & \times \left(1 - \left(\frac{\beta a^2}{D}\right)^{0.5} \text{Cot}\left(\frac{\beta a^2}{D}\right)^{0.5}\right) \\ & + \frac{6\beta a^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{\exp(-D n^2 \pi^2 t / a^2)}{n^2 (n^2 \pi^2 - \beta a^2 / D)} \} \end{aligned} \quad (41)$$

where

C_o = initial surface concentration,

C_{eq} = equilibrium concentration,

a = radius of the sphere,

M_t = solvent gain in coal,

D = diffusivity, and

β = relaxation parameter.

If the following two expressions

$$\theta_1 = (4/3) \pi a^3 C_o \quad (41a)$$

and

$$\theta_2 = (4/3) \pi a^3 (C_{eq} - C_o) \quad (41b)$$

are substituted into equation (41), equation (41) becomes

$$\begin{aligned} M_t = & \theta_1 \left\{ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \right\} \\ & + \theta_2 \left\{ 1 - \frac{3n}{\beta a} \exp(-\beta t) \left(1 - \left(\frac{\beta a^2}{D} \right)^{0.5} \text{Cot} \left(\frac{\beta a^2}{D} \right)^{0.5} \right) \right. \\ & \left. + \frac{6\beta a^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{\exp(-Dn^2\pi^2 t/a^2)}{n^2(n^2\pi^2 - \beta a^2/D)} \right\} \end{aligned} \quad (41c)$$

The solvent gain is composed of two parts. The first part is due to diffusion into the sample under an initial surface concentration C_o . The second part results from the time dependence of the surface concentration.

The value of the relaxation parameter β is an indication to show the rate of the relaxation process. If the value of β approaches ∞ , the rate of relaxation is very fast; the surface concentration is always in equilibrium with the solvent vapor and is equal to C_{eq} . As a result, this anomalous diffusion becomes the classical Fickian diffusion.

There are four unknown parameters, C_o , D , C_{eq} and β , in this model. In order to determine the optional values for these four parameters, this model is used to fit the sorption data and these four parameters are determined simultaneously by use of a nonlinear regression analysis.

A procedure for running the sorption experiments is called the incremental sorption method. This procedure consists of a series of experiments in which the sample is first exposed to a low solvent activity until an equilibrium is attained, and then the same sample is exposed to a high solvent activity until a new equilibrium is reached and so on. Therefore, the presence of vapor in the sample due to the previous equilibrium should be taken into account. The boundary conditions corresponding to this sorption procedure are given as follows:

$$C = C_1, \quad t = 0, \quad 0 < r < a \quad (42)$$

$$C = C_o + (C_{eq} - C_o)(1 - \exp(-\beta t)), \quad r = a, \quad t > 0 \quad (43)$$

$$C = \text{finite}, \quad r = 0 \quad (44)$$

The solution to equations (32) and (42) to (44) is given by

$$\begin{aligned} M_t = & \left(\frac{4}{3} \pi a^3\right) (C_o - C_1) \left\{ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-D n^2 \pi^2 t / a^2) \right\} \\ & + \left(\frac{4}{3} \pi a^3\right) (C_{eq} - C_o) \left\{ 1 - \frac{3D}{\beta a^2} \exp(-\beta t) \right. \\ & \times \left(1 - \left(\frac{\beta a^2}{D}\right)^{0.5} \coth\left(\frac{\beta a^2}{D}\right)^{0.5} \right) \\ & \left. + \frac{6\beta a^2}{\pi^2 D} \sum_{n=1}^{\infty} \frac{\exp(-D n^2 \pi^2 t / a^2)}{n^2 (n^2 \pi^2 - \beta a^2 / D)} \right\} \end{aligned} \quad (45)$$

Equations (41) and (45) are very similar. The only difference is that C_o in the first term of equation (41) is replaced by $C_o - C_1$ in equation (45).

To determine the four unknown parameters $(C_o - C_1)$, D , $(C_{eq} - C_o)$ and β in equation (45), a nonlinear regression analysis is used to correlate the experimental sorption data.

IV. EXPERIMENTAL

A. Measurements of Solubility of Solvents in Coal

1. Sample Preparation

The coal samples were provided by The Pennsylvania State University Coal Bank. After the coal is taken from the can, the following procedures are used to prepare samples for further use.

- a. Riffle the coal with a riffle splitter several times.
- b. Spread the coal on a flat area and divide the layer into several even parts with a spatula.
- c. Pick up a small amount of coal from each part of the layer to obtain a representative coal sample.
- d. Repeat procedure c until the desired amount is obtained.

The particle size of the coal sample from the can is about -20 mesh. In order to obtain smaller sizes, two kinds of mill have been employed to grind coal sample in this study. One is the Spex Freezer/Mill and the other is the Bleuler Rotary Mill.

The Spex Freezer/Mill is used to grind a small amount of coal sample. Approximately 0.5 gram of coal is placed in a vial with magnetic end-caps and rod-pestle. The whole vial is then immersed in liquid N_2 prior to and during the entire grinding operation. Coils at the ends of vial are energized alternately to attract the rod-pestle back and forth between them. Since the whole vial is in liquid N_2 , no local heat accumulates to damage delicate samples. After one or two minutes, most substances are reduced to powder. The coal sample is then taken out and sifted by a No. 400 sieve. To obtain a representative sample, the whole

coal sample must be reduced to -400 mesh. If any coal particle does not pass the No. 400 sieve, it must be ground again until its size is less than 400 mesh (0.0037 cm).

For a large amount of coal sample, the Bleuler Rotary Mill is used to reduce the size of the coal particles and the sieve analysis is also employed to make sure that the size of the coal sample meets the desired requirement.

In this study the particle size of the coal sample is determined by the sieve analysis. If the coal particles are able to pass the No. 400 sieve, the particle size of this sample is termed -400 mesh (0.0037 cm).

After the sieve analysis, the coal sample is dried in a vacuum oven at 120°C for 24 hours and then taken out of the oven. The next step is to put this dry coal sample in a bottle, purge the bottle with N₂ or argon, seal it with a cap, and, finally, place it in a desiccator. The sample up to this stage is termed untreated coal. If pyridine-extracted coal is needed, this untreated coal sample will be extracted by pyridine.

Pyridine extraction is a common method to pretreat coal samples. The extraction technique used in this study was investigated by Raymond (1). The experimental apparatus for pyridine extraction is shown in Figure 3. The apparatus consists of Soxhlet extraction vessel, a thimble and a condenser. The experimental procedures for pyridine extraction are described as follows:

- a. A layer of dry potassium chloride is placed at the bottom of the thimble to prevent bursting of the thimble due to the swelling of coal in the course of extraction.

Figure 3. Soxhlet extraction apparatus for coal sample

- b. Approximately 10 grams of coal is mixed well with 15 grams of dry potassium chloride, and then this mixture is put in the thimble.
- c. A glass pedestal is placed below the thimble to keep the thimble out of the region where drainage is incomplete.
- d. Cooling water enters from the bottom of the condenser, through the condenser, and then leaves from the top of the condenser, as shown in Figure 4.
- e. Nitrogen is passed over the system during the extraction to prevent any excess of oxygen and consequent oxidation.
- f. 250 ml of pyridine are placed in a round-bottom flask and boiling chips are added to this flask to eliminate bumping.
- g. A heating mantle is used to supply heat to the flask and is controlled by a variable transformer so that pyridine drips from the condenser at the rate of two drops per second.
- h. The pyridine is changed several times during the extraction process and the experiment is continued until liquid around the thimble is almost clear.
- i. After the pyridine is removed from the thimble area, the thimble is washed by 0.1 N HCl to remove excess pyridine left in the coal.
- j. To remove potassium chloride from coal, the coal and potassium chloride mixture is extracted by water at the normal boiling point.
- k. Water in the flask is changed several times until there is no chloride ion in the water. To test this, AgNO_3 is added to the

Figure 4. Diffusion chamber

water. If there is no precipitate, the removal of potassium chloride is complete and the water extraction is then terminated.

1. The coal sample is then dried in a vacuum oven at 110°C for a few days to remove the remaining water and pyridine.
- m. The coal sample is put in a bottle. This bottle is purged by nitrogen and then sealed with a cap.
- n. Finally, the bottle is stored in a vacuum desiccator and the pyridine-extracted coal is ready to be used in this study.

2. Experimental Apparatus and Procedures

To measure the equilibrium solvent weight gain of coal in various solvents, a simple device is designed for this study as shown in Figure 5. This device consists of a weighing bottle, ceramic packing and a vial.

The solvent is put into the weighing bottle up to two-thirds of the height of the packing ceramic. About 0.1 gram of coal sample is placed in the vial and the weight of the vial plus the coal sample is measured with a Mettler balance. After the weight is recorded, the vial is placed at the top of the packing ceramic and covered with a filter paper. The diffusion chamber is then sealed by the lid and is moved to a temperature-controlled box at 25°C . The vial is taken out once a week to measure the solvent uptake. Therefore, the relationship between solvent uptake and time is obtained. When the equilibrium state is approached, the weight gain reaches a plateau.

A high-volatile A bituminous coal, PSOC-375, was used in this study. The proximate and ultimate analysis of this coal is given in Table 1.

A series of solvents was used in this study and the physical parameters for these solvents are given in Table 2.

Table 1

Analysis of High Volatile Bituminous Coal PSOC-375

Seam name: Hazard No. 9
 County: Harlan
 State: Kentucky

		dmmf, %
<u>Proximate Analysis</u>		
Volatile matter		38.92
Fixed carbon		61.02
<u>Ultimate Analysis</u>		
Dry, mineral-containing		
C	70.8	84.5
H	4.6	5.5
N	1.3	1.5
S (org.)	0.7	0.8
O (diff.)	6.4	7.7
Min. matter	16.2*	
(incl. 0.71% FeS ₂)		
Maceral composition		
Vitrinite		76
Liptinites		12
Inertinites		12

* Mineral matter calculated by modified Parr equation.

Note: dmmf = dry, mineral-matter-free.

Table 2
Physical Parameters for the Solvents Used

Solvents	DN	AN	DN-AN	δ^* (cal/cm ³) ^{0.5}	δ_H^{**} (cal/cm ³) ^{0.5}
Methanol	19.0	41.3	-22.3	14.5	10.9
Water	33.0	54.8	-21.8	23.4	20.7
Nitromethane	2.7	20.5	-17.8	12.7	2.5
Ethanol	20.5	37.1	-16.6	12.7	9.5
Isopropanol	20.0	33.5	-13.5	11.5	8.0
Nitrobenzene	4.4	14.8	-10.4	10.0	2.0
Benzene	0.1	8.2	- 8.1	9.2	1.0
Acetone	17.0	12.5	4.5	9.9	3.4
DMSO ⁺	29.8	19.3	10.5	12.0	5.0
THF ⁺⁺	20.0	8.0	12.0	9.1	3.9
Pyridine	33.1	14.2	18.9	10.7	2.9
Ethylene Diamine	55.5	20.9	24.6	12.3	8.3
Glycerol	-	-	-	16.5	14.3

* δ = solubility parameter defined by equation (1).

** δ_H = hydrogen bonding component of the solubility parameter defined by equation (7).

⁺Dimethylsulfoxide.

⁺⁺Tetrahydrofuran.

B. Kinetic and Equilibrium Measurements of Solvent System in Coal

In order to conduct the kinetic and equilibrium measurements of solvent sorption in coal, three sorption balances have been employed. Although these three sorption balances are different in appearance, the basic design of them remains the same. The details of the design and experimental procedures for each balance will be shown later, but a simplified scheme, shown by Figure 5, is presented first to demonstrate the concept of design.

A coal sample is placed in a quartz bucket which is inside the sorption chamber. The penetrant vapor is supplied from the boiler. In each experiment, the chamber temperature and the boiler temperature are controlled at T_1 and T_2 , respectively. After the sorption chamber is under vacuum, the valve between the boiler and the chamber is opened, and the penetrant vapor starts to diffuse into the coal sample driven by a difference in chemical potential until an equilibrium is attained. When an equilibrium is achieved, it means that the chemical potential of solvent in the vapor phase is equal to that in the coal sample. To achieve different values of solvent activity, the chamber temperature T_1 is fixed, but the boiler temperature T_2 is varied in each experiment. Hence, as thermodynamic data, weight gain of the coal due to uptake of solvent in equilibrium as a function of solvent activity, are obtained, the data are utilized to analyze the coal structure. In addition to these thermodynamic data, kinetic measurements, weight gain of the coal due to uptake of solvent as a function of time, are also obtained.

A high temperature sorption balance, shown in Figure 6, has been utilized successfully to measure the mutual diffusion coefficient for many polymer-solvent systems (32,42). The apparatus design and operating

Figure 5. Simplified scheme of experimental apparatus for sorption in coal

Figure 6. High temperature sorption balance

procedures for this balance were described in detail by Duda et al. (9). This balance had been used temporarily in this study to investigate the sorption of solvent into coal before the following two sorption balances were constructed.

1. The High Temperature Sorption Balance I

A high temperature sorption balance has been constructed and a schematic diagram of this apparatus is shown in Figure 7. This apparatus consists of four major components:

- a. the main sorption column,
- b. the sorption temperature control system,
- c. the penetrant vapor feed system, and
- d. the pressure measuring device.

The main sorption column, constructed of 10 cm I.D. glass pipe and 1.2 m in length, is jacketed with 15 cm I.D. glass pipe, leaving an annular gap of 2 cm width. The quartz spring and the pan with coal sample can be contained inside the sorption chamber. A calibrated non-rotating quartz spring with the sensitivity 0.25 mm/lmg and maximum load 2.1 gm was used in this study. Hemispherical pans with diameter 20 mm are employed. The quartz springs and pans were provided by Worden Quartz Products, Inc. A cathetometer (Gaertner Scientific, Chicago) with an accuracy of 0.01 mm was used to measure the spring extension. The whole sorption column is covered with fiberglass insulation to reduce the heat loss from the column to the surroundings. To evacuate the column prior to a sorption or to conduct a desorption after a sorption, a vacuum system is connected to the column as shown in Figure 7. This vacuum system is composed of a vacuum pump (Model No. 1400, Sargent Welch Scientific Co.), two traps and a McLeod gauge.

Figure 7. High temperature sorption balance I

UCON high temperature heat-transfer fluid (Blue M Electric Company) is used in the oil bath (Model No. MW-115A-1, Blue M Electric Company). Thermostatted fluid is pumped through the jacket by a vertical immersion pump (Dayton Electric Company) to maintain the whole column at a desired temperature. The column temperature is monitored by a thermometer on the divider inside the sorption chamber. To prevent any free convection, a heating mantle is placed at the top of the column and is controlled by a variable transformer to supply enough heat to keep the whole column at the same temperature.

The penetrant feed system includes an insulated boiler filled with penetrant, a stirrer and a temperature controller (Lab Monitor III, Cole Parmer). The vapor pressure of the penetrant is controlled by the temperature of the boiler. In order to prevent condensation in the vapor inlet line, this inlet line is wrapped with heating tapes and then covered with insulation. The heating tapes controlled by variable transformers are used to keep the line at a temperature above the boiler temperature; therefore, no condensation occurs during the sorption and the pressure inside the sorption chamber is equal to the vapor pressure of the penetrant at the boiler temperature.

A high-temperature strain gauge pressure transducer (T-series, Sensotec, Columbus, Ohio) is used to measure the column pressure, and an indicator (Model 450D, Sensotec) is connected to this pressure transducer to provide digital readout scaled in mmHg.

The sorption balance I is designed to conduct sorption experiments up to at least 180°C. The ultimate upper temperature limit depends upon the safe use of heat-transfer fluid and the interaction between the solvent vapor and the Viton diaphragms in valves. However, the Dow

Corning silicone fluid is serviceable up to 260°C. Moreover, a new elastomer, Kalrez, made by Du Pont, which can resist temperatures up to 290°C, may be used to make diaphragms. Therefore, it is a very promising experiment for the future to run a sorption experiment up to 260°C.

2. The Sorption Balance II

The sorption balance II, shown in Figure 8, has been constructed to study the sorption of solvent vapor in coal at temperatures below 150°C. This balance is very similar to the high-temperature balance I, but the major difference between these two is the temperature control system for the sorption column. An oil bath is used in balance I, while an air bath is employed in balance II.

In this apparatus, the whole sorption column is contained within the air bath. The temperature of this bath is controlled by a temperature controller (Series 4001, Omega Engineering, Inc.). Air is circulated from the outlet of the blower, through heating coils in the duct, then to the sorption chamber. Two thermocouples, one at the lower part and the other in the middle part of this bath, are used to check the temperature distribution of this air bath.

3. Operating Procedures for Balance I

The first step of the operating procedures is to clean the boiler and to fill it with the desired penetrant. The boiler then is connected to the sorption column by an o-ring joint. The terminals of the heating coil of the boiler are then linked to electrical cords, and the boiler is covered by fiberglass insulation to reduce heat loss.

After the quartz spring and the pan with coal sample are hung onto the hook inside the sorption chamber, a piece of stainless steel screen

Figure 8. High temperature sorption balance II

is placed at the top of the divider to eliminate any condensation drop during sorption. Then, the sorption column is covered by a cap and a vacuum seal is formed by tightening the flange of the o-ring joint. The next step is to evacuate the sorption chamber. As the pressure of the sorption chamber drops to 0.1 mmHg, shown by a McLeod gauge, the stirrer of the boiler is turned on and the vapor admission valve is opened for a short period, which is about 2 to 3 minutes, to remove air in this boiler. Afterwards, the contaminated pump oil should be replaced and the pressure of the sorption chamber is maintained below 0.1 mmHg before the sorption starts.

The temperature controller of the oil bath is set at the desired temperature. For safety, a control for preventing overheating is employed and it is set at a temperature slightly higher than the desired temperature. If the bath temperature is over the temperature set on this protection control, the oil bath is shut down automatically. The operating procedures for this oil bath are described in detail by the operation and maintenance manual. As the oil bath is turned on, the immersion pump is also turned on to deliver oil through the jacket and heat up the sorption column gradually. In the meantime, the heating mantle over the cap is turned on and is adjusted to the desired temperature by a variable transformer. Therefore, a free convection due to a temperature difference is eliminated. Finally, the whole column reaches the desired temperature.

The next step is to turn on the temperature controller, heating coil and stirrer of the feed system. Meanwhile, heat is applied to the admission tube by heating tapes, and the temperature of the tube is usually maintained 10°C higher than the temperature of the boiler.

Hence, any condensation of penetrant vapor in this tube can be eliminated.

After the boiler temperature reaches the set temperature, the valves and the pump of the vacuum system are shut off. Then, the initial spring length is monitored by the cathetometer and recorded as a reference point. Next, the admission valve is opened slowly and the sorption starts. Thus, the relationship between solvent uptake and time is then obtained.

4. Operating Procedures for Balance II

The operating procedures for balance II is the same as those for balance I except the procedure for operating the temperature control system for the sorption column.

The heat supply to the air bath comes from two sources. One is fixed heat and the other is variable heat which is controlled by the Omega temperature controller. For the fixed heat, three selections are available and the selection depends upon the desired temperature. The selection is chosen such that the heat is enough to keep the bath temperature just below the set point. Then, the variable heat, adjusted by the temperature controller, is used to make up the heat supply and keep the bath temperature at the set point.

V. RESULTS AND DISCUSSION

An investigation of the interaction of various solvents with untreated and pyridine-extracted coal has been conducted. The solubility parameter and the donor and acceptor numbers have been employed to correlate the solvent uptake for untreated and pyridine-extracted coal. Solvent uptake used in this study represents the amount of solvent with a unit gram in one gram of coal. The results of these correlations are presented in graphs. The problems and difficulties associate with each correlation are discussed.

The sorption of solvents, including benzene, toluene and tetralin, in coal at temperatures up to 175°C has been investigated. The mathematical models by Berens and Hopfenberg (4) and by Long and Richman (33) have been applied to interpret the sorption of solvents in pyridine-extracted coal. Results of these two models are presented and comparison between these two models has been made.

The thermodynamic data of toluene in pyridine-extracted coal PSOC-375 at 110°C have been used to test the Flory model and other models. Problems of each model are presented and discussed.

Equation (11) provides a correct way to determine the solvent activity. However, for these solvents used, including tetralin and toluene, correction for the deviation from ideal gas behavior and for pressure effects in the liquid phase at the operating conditions of this study is quite small. Therefore, a good approximation for the solvent activity is the ratio of vapor pressure P/P_s . For example, the error for toluene activity caused by this approximation is less than 3%.

Finally, hysteresis of sorptions of toluene and tetralin in pyridine-extracted coal PSOC-375 have been observed.

A. The Solubility of Solvent in Coal

The untreated coal PSOC-375 of particle size -20 mesh was brought into contact with various solvents listed in Table 2, at 25°C and activity 1.0. After 61 days exposure to the liquid solvent, no equilibrium was observed in these systems. A typical example shown in Figure 9 is the sorption of Dimethylsulfoxide (DMSO) into untreated coal PSOC-375. The sorption still continued and there was no sign to show that the system would reach an equilibrium even after more than 61 days exposure. The reason why equilibrium was not attainable was mainly due to extraction process, as discussed in the theory of this study.

Attempts have been made to correlate the weight gain due to solvent by untreated coal PSOC-375 with various solvent properties. First, the solubility parameter was used to correlate the solvent uptake. Results, shown in Figure 10, indicate that there is no correlation between the solvent uptake and the solubility parameter. The data are scattered and a single-mode curve is not attainable. Second, the acid-base characteristic of the solvent, the parameter of DN-AN, was tested for its ability to correlate the solvent uptake. The value of the difference, DN-AN, seems to be a good parameter for correlating the solvent uptake in untreated coal, as shown in Figure 11. The solvent uptake is small in the region where the value of DN-AN is less than 0. But, the solvent uptake increases with an increase in the DN-AN value when these values become positive. For ethylene diamine, the coal sample became fluid and the solvent uptake is beyond the scale of this figure.

Figure 9. The sorption of DMSO into untreated coal PSOC-375 at 25°C and activity = 1.0

Figure 10. Solvent uptake for untreated coal PSOC-375 vs. solubility parameter of solvent at 25°C and at activity 1.0

Figure 11. The solubility of solvents in high volatility bituminous coal (PSOC-375) as a function of the acid-basic characteristic of the solvent, 25°C, solvent activities = 1

The reason why the value of DN minus AN is a good parameter may be due to extraction. A similar correlation has been obtained by Marzec (38), shown in Figure 12, to explain the results of coal extraction.

As the pyridine-extracted coal PSOC-375 was exposed to the same solvents as the untreated coal PSOC-375 at 25°C and at activity 1.0, an equilibrium state was achieved for those solvents whose extraction capacity is less than pyridine. In other words, the pyridine-extracted coal and the solvent with DN-AN value less than pyridine did reach an equilibrium state. On the other hand, for a solvent with DN-AN value greater than pyridine, such as ethylene diamine, extraction still occurred and an equilibrium is not achieved.

An example is given to illustrate the comparison between the sorption of tetralin into untreated and pyridine-extracted coal PSOC-375 at the same operating conditions, $T = 110^{\circ}\text{C}$ and activity = 0.44, as shown in Figure 13. Sorption data were obtained by use of the high-temperature sorption balance I. Comparison indicates that sorption in pyridine-extracted coal eventually reaches an equilibrium; in contrast, the sorption in untreated coal still continues with no sign that the system reaches equilibrium after nine days.

Attempts have been made to correlate the solvent uptake of various solvents in pyridine-extracted coal PSOC-375 with solvent parameters. Figure 14 shows the correlation of the solvent uptake by the parameter of DN-AN value. Results indicate that the DN-AN value is not systematically related to solvent uptake in pyridine-extracted coal.

The solubility parameter δ and the hydrogen parameter δ_H have been used to correlate the solvent uptake in the pyridine-extracted coal, as shown in Figures 15 and 16. A single-mode curve has been drawn in

Figure 12. Coal extract yields vs. DN-AN of solvents

Source: Marzec, A. et al., Fuel Processing Technology 2 (1979), 35-44.

Figure 13. Sorption of tetralin in untreated and pyridine-extracted coal PSOC-375

Figure 14. The solubility of solvents in pyridine-extracted high volatility bituminous coal (PSOC-375) as a function of the acid-basic characteristic of the solvent, 25°C, solvent activities = 1

Figure 15. The solubility of solvent in coal vs. δ

Figure 16. The solubility of solvent in coal vs. δ_H .

each figure to try to represent the variation in solvent uptake. However, there is a great deal of scatter and the correlation with these single parameters is poor.

The results of swelling in this study have been compared with those in recent studies by Reucroft and Patel (45), and Szeliga and Marzec (51). Reucroft and Patel (45) conducted solvent swelling experiments at room temperature and at various relative pressures by using a Cahn balance. Eight solvents were used in their studies. Sorption data were correlated by the solubility parameter of the solvent. A single-mode curve was obtained and the curve passed through a maximum at a value of $21.9 \text{ Mpa}^{1/2}$ (pyridine, $\delta = 21.9 \text{ Mpa}^{1/2}$). Szeliga and Marzec (51) studied the swelling of a hvB coal by exposing this coal to twenty solvents. They found that the correlation of solvent uptake by the solubility parameter was poor. The results of solvent swelling in this study are not in accord with those by Reucroft and Patel (45), but are in good agreement with those by Szeliga and Marzec (51).

B. The Sorption of Benzene in Coal

The sorption of benzene in untreated coal PSOC-375 with particle size 0.0037 cm (-400 mesh) was conducted at 175°C by use of the McBain balance. Results of sorption are presented as a plot of solvent uptake versus time in Figure 17. Results clearly indicate that the sorption still increases even after 30 days operation and no equilibrium has been achieved. This confirms the sorption model for the untreated coal proposed in the theory. Therefore, the determination of equilibrium solvent gain and the diffusion coefficient for the sorption of benzene in untreated coal is not attainable.

Figure 17. Sorption of benzene in untreated coal PSOC-375 at 175°C

Since benzene has less extraction capacity than pyridine, the benzene-soluble material in coal should be removed by pyridine extraction. Hence, extraction should not occur in the sorption of benzene by pyridine-extracted coal, and an equilibrium should be achieved in this sorption. In order to support this point, the sorption of benzene in pyridine-extracted coal PSOC-375 with particle size 0.0037 cm was conducted at 175°C and at activity 0.1. Results of this sorption are shown in Figure 18. A fast solvent uptake due to adsorption is followed by a slow sorption process. This slow sorption process is attributed to molecular diffusion into the coal matrix. A linear relationship between solvent uptake and $\sqrt{t}$ is obtained in the early stage of this slow sorption process. Then, this sorption gradually levels out and approaches a final equilibrium value.

Weight gain due to adsorption can be determined by extrapolation of the straight line PQ to the coordinate and the intercept AO is the amount of adsorption.

If the equilibrium state is assumed to be achieved at $\sqrt{t} = 1000 \text{ sec}^{0.5}$, the final true equilibrium value due to the molecular diffusion in the coal matrix is then obtained. The amount is AM, indicated in Figure 18. Hence, a plot of fractional uptake M_t/M_∞ vs. $\sqrt{t}$ can be derived and is shown in Figure 19, where M_∞ is the final true equilibrium value and M_t is the solvent uptake due to the diffusion at time t . This plot is very useful in determining the diffusion coefficient. The circles in Figure 19 represent the sorption data. In the early stage of the sorption, fractional uptake M_t/M_∞ is proportional to the square root of time and, hence, a straight line can be drawn through these data points. The slope of this straight line can be used

Figure 18. Sorption of benzene in pyridine-extracted coal sample PSOC-375

Figure 19. Comparison of diffusion data for benzene in pyridine-extracted coal PSOC-375 with Fickian diffusion

to determine the value of the diffusion coefficient. From equation (26), the slope of this straight line is equal to $(D/\pi a^2)^{0.5}$. Since the radius of the coal particle a is known, the diffusion coefficient D is then determined from equation (26).

If the diffusion coefficient is assumed to be constant, a sorption curve with a constant diffusivity is established by the substitution of $D = 1.31 \times 10^{-12}$ cm²/sec into equation (25). This curve is shown in Figure 19 and is compared with the sorption data. The comparison indicates that the sorption of benzene into pyridine-extracted coal at 175°C follows the sorption curve with a constant diffusivity quite well.

After the sorption of benzene into pyridine-extracted coal reached an equilibrium, a desorption was conducted. The result of the desorption is presented by the circles in Figure 20. The ratio of M_t to M_∞ represents the fraction of penetrant remaining in the coal. If the diffusion coefficient obtained from the sorption is employed to predict desorption behavior, a desorption curve with a constant diffusivity is then established. This curve is shown in Figure 20. Figure 20 provides two pieces of information. First of all, the experimental desorption data do not follow the curve predicted by a constant diffusion coefficient. Secondly, some solvent is trapped inside the coal. This solvent trapping may result from a structure change associated with the swelling sorption process.

After desorption, the coal sample was again exposed to benzene vapor at activity 0.1. The result of the resorption, shown in Figure 21, indicates the resorption is a faster sorption process than the first exposure. Solvent uptake at equilibrium returned to the value before desorption in a very short period. The diffusion coefficient for the

Figure 20. Comparison of desorption data for benzene-coal system with Fickian desorption

Figure 21. The sorption of benzene into pyridine-extracted coal after desorption

resorption can be determined if the following two assumptions are made. First of all, the total solvent uptake for the resorption is assumed to be the difference between the weight due to trapping and the final solvent uptake for the resorption. Second, the resorption obeys Fick's law. Based on these two assumptions, the value of the diffusivity for the resorption is $3.873 \times 10^{-9} \text{ cm}^2/\text{sec}$. This result indicates that the diffusion for the resorption is faster than the diffusion for the first exposure by three orders of magnitude.

Sorption of benzene in coal is a exploratory study and it provides a comparison between the sorption in untreated and pyridine-extracted coal, the magnitude of the diffusion coefficient, and the characteristics of desorption and resorption.

The sorption balance cannot be used at pressures above atmospheric. Due to this limit, the sorption of benzene can only be conducted up to an activity of 0.1 at 175°C. In order to test the Flory model and investigate the dependence of diffusivity on concentration, an ideal solvent should have a higher normal boiling point than benzene; therefore, toluene was selected as the penetrant in the following sorption experiments.

C. The Sorption of Toluene in Pyridine-Extracted Coal

The sorption of toluene in pyridine-extracted coal has been conducted at 110°C by use of sorption balance II. Two approaches have been employed in this study. One is the integral sorption. The other is the incremental sorption.

Integral sorption as studied in this work represents a sorption in which only a single change in solvent activity is involved. Before sorption there was no toluene in the pyridine-extracted coal. When the

integral sorption began, this coal sample was exposed to toluene at a constant solvent activity. After the toluene-coal system had reached an equilibrium state, the integral sorption was terminated. The coal sample was taken out of the sorption chamber and discarded. When the next integral sorption began, fresh coal sample was used. In this study, the integral sorption was conducted at toluene activities of 0.10, 0.28, 0.50 and 0.80.

For incremental sorption, the fresh pyridine-extracted coal was first exposed to toluene at a low solvent activity. When the toluene-coal system had reached an equilibrium state, the same coal sample was exposed to a higher solvent activity until another equilibrium state was obtained. The increment in solvent activity could be adjusted so that the following two effects could be investigated. First of all, the dependence of diffusion coefficient on solvent concentration could be investigated. The diffusion coefficient in a polymer-solvent system is usually a strong function of solvent concentration. It is not unusual that a small amount of solvent in polymer may enhance the diffusion substantially. In order to investigate the dependence of diffusion coefficient on solvent concentration, a polymer sample is first exposed to solvent vapor at a low solvent activity. After the polymer-solvent system reaching an equilibrium, a certain amount of solvent is in the polymer sample and then this polymer sample is exposed to solvent vapor at a higher solvent activity; therefore, the effect of solvent concentration on diffusion coefficient can be studied. Secondly, hysteresis effects could be looked for. The incremental sorption and desorption can be used to study the reversibility of the sorption. In this study, three steps were included in the incremental sorption. The pyridine-

extracted coal was first exposed to toluene at solvent activity 0.28, then 0.55, and, finally, 0.85.

1. Results of Integral Sorption

Integral sorption of toluene in pyridine-extracted coal was conducted at 110°C and at the four solvent activities stated above. Sorption results at four activities indicate a common feature. Sorption data at activity 0.28, shown in Figure 22, is used as an example to demonstrate it. Sorption data at other three solvent activities are presented in Appendix A and shown in Figures 41 to 43.

Figure 22 indicates that a fast solvent uptake due to adsorption is followed by a slow sorption process. This slow sorption is attributed to diffusion into the coal matrix. A linear relationship between the solvent uptake and $\sqrt{t}$ has been obtained in the early stage of this slow sorption process and it exhibits one of the features of Fickian diffusion. However, this sorption does not level off as shown in Fickian diffusion. Instead, sorption continues at a very slow rate over a long period of time. This slow increase in sorption may result from a relaxation process in which the structure of coal is changing.

The mathematical models by Berens and Hopfenberg (4) and by Long and Richman (33) had been employed to interpret the sorption results at these four toluene activities. It was found that both models fit the experimental data quite well at these four solvent activities. A comparison between experimental data and a theoretical curve calculated by Berens and Hopfenberg's model is presented first. Long and Richman's model will be shown later.

Figure 22. Sorption of toluene in pyridine-extracted coal PSOC-375 at 110°C

a. Berens and Hopfenberg's Model

There are four parameters in Berens and Hopfenberg's model. If sorption data are substituted into Berens and Hopfenberg's equation, these four parameters $M_{\infty,D}$, $M_{\infty,R}$, D and K are determined by a nonlinear regression analysis. After the substitution of these four parameters into this model, a theoretical sorption curve is then established. This theoretical sorption curve is composed of two sorption curves. One is attributed to Fickian diffusion. The other is due to a relaxation process. To illustrate the physical significance of Berens and Hopfenberg's model, the sorption curve due to Fickian diffusion is presented first. The curve shown in Figure 23 is calculated from the first term of the right-hand side of equation (30). This curve fits the sorption data in the early stages quite well and this indicates that the amount of sorption is mainly attributed to Fickian diffusion. Further, a linear relationship between solvent uptake and $\sqrt{t}$ as t is small is another evidence to support the idea that the sorption mechanism at the beginning is dominated by Fickian diffusion.

Solvent uptake due to a relaxation process is calculated from the second term of the right-hand side of equation (30). As $\sqrt{t}$ is smaller than $100 \text{ sec}^{0.5}$, solvent uptake due to the relaxation is negligible. However, as $\sqrt{t}$ is greater than $100 \text{ sec}^{0.5}$, solvent uptake is mainly attributed to the relaxation. If solvent uptake due to the relaxation is added to solvent uptake due to Fickian diffusion, the theoretical sorption curve for Berens and Hopfenberg's model is obtained and is shown in Figure 24. This resulting curve fits the experimental points remarkably well and the final equilibrium value at activity 0.28 which is equal to $M_{\infty,D}$ plus $M_{\infty,R}$ is then determined.

Figure 23. Sorption of toluene in pyridine-extracted coal PSOC-375 at 110°C

Figure 24. Sorption of toluene in pyridine-extracted coal PS02-375 at 110°C

Comparisons of experimental data at activities 0.1, 0.50 and 0.80 with theoretical curves calculated from Berens and Hopfenberg's model are presented by Figures 44 to 46 in Appendix A. The four parameters $M_{\infty,D}$, D , $M_{\infty,R}$ and K for sorption at each activity are determined and summarized in Table 3.

Table 3 indicates that the diffusion coefficient D increases with the increase in the concentration of the solvent, which is expressed in terms of the mass fraction of solvent ω_s at equilibrium. Figure 25 shows the dependence of diffusivity on mass fraction of solvent ω_s . It appears that the diffusion coefficient D is roughly proportional to the mass fraction of toluene within the range, $\omega_s = 0.047$ to $\omega_s = 0.117$. However, the dependence of diffusivity on concentration is weak, compared to the dependence of diffusivity in some polymer-solvent systems (32,42). The diffusion coefficient varies from $1.08 \times 10^{-10} \text{ cm}^2/\text{sec}$ to $8.09 \times 10^{-10} \text{ cm}^2/\text{sec}$ as the weight fraction changes from 0.047 to 0.117.

The relaxation rate-constant, K , also rises with the increase of the concentration. The value of K increases from $0.471 \times 10^{-5} \text{ sec}^{-1}$ to $5.343 \times 10^{-5} \text{ sec}^{-1}$ as the mass fraction varies from 0.047 to 0.117.

The values of $M_{\infty,D}$ and $M_{\infty,R}$ are plotted against the solvent activity in Figure 26. The amount of sorption due to the diffusion $M_{\infty,D}$ increases as the solvent activity is raised; however, no strong relationship is found between the solvent activity and the amount of solvent uptake due to relaxation $M_{\infty,R}$.

b. Long and Richman's Model

Long and Richman's model is also employed to interpret the integral sorption data for toluene at these four solvent activities. As

Table 3

Summarized Results of Berens and Hopfenberg's Model at Four Solvent
Activities and at 110°C

Activity*			$M_{\infty,D}$ g/g	$M_{\infty,R}$ g/g	M_{∞} g/g	ω_s^{**}	$D, \text{ cm}^2/\text{sec}$	$K, 1/\text{sec}$
Initial		Final						
0	→	0.10	0.0304	0.019	0.0494	0.047	1.08×10^{-10}	0.471×10^{-5}
0	→	0.28	0.0488	0.0137	0.0625	0.059	3.12×10^{-10}	0.869×10^{-5}
0	→	0.50	0.0554	0.0381	0.0935	0.086	5.34×10^{-10}	1.225×10^{-5}
0	→	0.80	0.0897	0.0359	0.1256	0.112	8.09×10^{-10}	5.343×10^{-5}

* Fresh pyridine-extracted coal sample was used in each sorption.

** $\omega_s = M_{\infty} / (1 + M_{\infty})$.

Figure 25. Dependence of diffusivity on mass fraction for toluene--pyridined-extracted coal PSOC-375 at 110°C

Figure 26. Amount of solvent gain due to diffusion or relaxation as a function of solvent activity

the sorption data are substituted into equation (41c), the optimal values for the four parameters θ_1 , D , θ_2 and β in this equation are determined by a nonlinear regression analysis. After these four parameters are obtained, a theoretical sorption curve by this model can be established and is compared with the sorption data at these four solvent activities. As a result, this model fits the sorption data at these four solvent activities quite well. Figure 27 shows the comparison between the theoretical sorption curve and the sorption data at solvent activity 0.28. The comparisons at three other solvent activities are presented in Figures 47, 48 and 49 in Appendix A.

The optimal values for the four parameters in Long and Richman's model at these four solvent activities are summarized in Table 4. From Table 4 it is found that both the diffusion coefficient D and the relaxation parameter β increase with the increase of the weight fraction of toluene.

Although both models fit the sorption data quite well, it appears that the model of Long and Richman makes more physical sense. In Berens and Hopfenberg's model the amount of sorption is attributed to the Fickian diffusion and a relaxation process. A first order dependence on concentration is assumed for the rate of the relaxation. As discussed by Joshi and Astarita (24), Berens and Hopfenberg's model is only valid in a limiting case that the diffusion time is much less than the relaxation time. In contrast, Long and Richman's model provides a better interpretation of the kinetics of sorption in glassy polymers and can be applied to not only in a limiting case where the diffusion time is much less than the relaxation time, but also in a case where the diffusion time and the relaxation time

Figure 27. Comparison of Long and Richman's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity = 0.28

Table 4

Summarized Results of L6ng and Richman's Model at Four Solvent Activities and at 110°C

Activity [*]		θ_1 g/g	θ_2 g/g	θ g/g	ω_s^{**}	D, cm ² /sec	β , 1/sec
Initial	Final						
0	→ 0.10	0.0306	0.0188	0.0494	0.047	1.08×10^{-10}	0.473×10^{-5}
0	→ 0.28	0.0489	0.0138	0.0627	0.059	3.12×10^{-10}	0.873×10^{-5}
0	→ 0.50	0.0556	0.0379	0.0935	0.086	5.32×10^{-10}	1.223×10^{-5}
0	→ 0.80	0.0904	0.0353	0.1257	0.112	8.09×10^{-10}	5.259×10^{-5}

* Fresh pyridine-extracted coal sample was used in each sorption.

** $\omega_s = \theta_1 / (1 + \theta_1)$.

become comparable. According to the criteria set by Joshi and Astarita (24), Berens and Hopfenberg's model is not appropriate to interpret the integral sorption data for toluene because the diffusion time and the relaxation time are comparable.

The relaxation process is a very complex phenomenon and no mathematical model can be used to describe such a phenomenon completely. Although Long and Richman's model provides a greater physical significance, the relaxation process yet cannot be explained completely by this model because the relaxation does not only occur at the surface. Instead, the relaxation process occurs through the whole sample at different rates as discussed by Crank (8).

2. The Results of Incremental Sorption

The technique of the incremental sorption was applied to the sorption of toluene in pyridine-extracted coal PSOC-375. This incremental sorption experiment included seven steps. Results of these seven steps are shown in Figure 28. During the first three steps, the value of the solvent activity was raised from 0 to 0.28, then to 0.55, and, finally, to 0.85. These three steps are labeled as 1, 2 and 3, respectively. Step 1 is actually an integral sorption and its result has been shown and discussed in the previous section. Sorption at state 2 is different from that at stage 1. There is no strong evidence to show that the solvent uptake is proportional to the square root of time at the early stage of sorption. The weight gain increases slowly with time with no sign to show that this sorption would reach equilibrium after 6 days exposure. Next, the value of the solvent activity was raised to 0.85. The result indicates that the sorption at stage 3 is

Figure 28. Incremental sorption data for toluene by pyridine-extracted coal at 110°C

similar to that at stage 2. Slow sorption was observed and no equilibrium was achieved.

After one week exposure at activity 0.85, the system was desorbed in a vacuum. The result of this desorption is shown by stage 4. The solvent uptake dropped very fast at the beginning of the desorption, then leveled out and reached a constant. Some solvent was trapped in the coal and did not come out after 2 days exposure to a vacuum at 110°C. The reason why some solvent was entrapped inside the coal is open to question. Probably the structure of the coal was changed due to the solvent sorption. A similar result has been obtained in the desorption of dimethylformamide (DMF) from poly-(ethylene terephthalate) (PET) (22). A small amount of DMF was entrapped in PET after desorption, because the solvent-induced crystal held some solvent inside. However, whether entrapment of the solvent in coal is due to the solvent-induced crystallization is very questionable. A further study is needed to better understand the phenomenon.

The coal sample was re-exposed to toluene vapor at activity 0.28 after the desorption. The result of this resorption is shown by stage 5. The solvent uptake reached an equilibrium in a very short period, compared to the sorption in stage 1. In addition, the value of this equilibrium was higher than the final equilibrium value in stage 1, although stage 1 and stage 5 were operated at the same activity 0.28.

Sorption at stage 5 was followed by two incremental sorptions. One was at activity 0.55, labeled as stage 6. The other was at activity 0.85, labeled as stage 7. Results of these two incremental sorptions indicate that higher solvent uptake was observed at the end of each stage, compared to that at the same solvent activity shown by stage 2 and 3, respectively.

Finally, a desorption was conducted at the end of stage 7. The result of this desorption is shown in Figure 29 and termed as stage 8. Similarly to stage 4, the solvent weight dropped very rapidly and reached a constant. However, more solvent was trapped at the end of stage 8 than stage 4.

If the weight of solvent held at the end of each stage is plotted against solvent activity, Figure 30 is obtained. This figure clearly indicates that hysteresis is prominent. The weight of solvent is not only a function of solvent activity, but also related to the past history, which influences the structure of coal.

Since the incremental sorption has been complicated by the hysteresis of the sorption, it becomes very difficult to investigate the dependence of diffusion coefficient on solvent concentration.

D. Sorption of Tetralin in Coal

The high temperature sorption balance I has been utilized to conduct experiments on the sorption of tetralin in coal at 110°C. The jacket-type sorption column provides a uniform temperature distribution. The temperature of the sorption column is regulated at $110^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$.

The sorption of tetralin in the untreated coal with particle size 0.0037 cm has been studied at 110°C and at activity 0.44. This sorption was followed by a desorption. The results of the sorption and the desorption are shown in Figure 31. The sorption in untreated coal is an endless process, and it is consistent with the suggestion that extraction by condensed penetrant is the major reason for the continuity in sorption. The result of the desorption indicates that a small amount of solvent comes out rapidly and then the rate of the desorption slows down.

Figure 29. Data for the second desorption of toluene-pyridine extracted coal system

Figure 30. Hysteresis of toluene in pyridine-extracted coal PSOC-375

Figure 31. The sorption of tetralin in untreated coal and the desorption of tetralin from untreated coal

For comparison of the sorption in untreated coal with the sorption in pyridine-extracted coal, sorption of tetralin in pyridine-extracted coal was studied at the same operating conditions as the untreated coal. The result of this sorption is shown in Figure 32. A fast solvent uptake due to adsorption was observed at the beginning of the exposure to tetralin. A slow sorption process attributed to molecular diffusion in the coal matrix followed. A linear relationship between the solvent uptake and the square root of time was obtained. Then the sorption curve levels off and reaches an equilibrium. This result is consistent with the sorption model for pyridine-extracted coal proposed in the theory.

The conventional Fickian model and the model by Berens and Hopfenberg have been employed to interpret the sorption of tetralin by pyridine-extracted coal. Since the sorption of tetralin in pyridine-extracted coal shows a small degree of relaxation, conventional Fickian diffusion is adequate to interpret the sorption data. Figure 33 shows the comparison between Fickian diffusion and the sorption data. The amount of solvent uptake due to adsorption is not included in this figure. The curve in Figure 33 represents the Fickian sorption with a constant diffusivity $1.341 \times 10^{-11} \text{ cm}^2/\text{sec}$. The comparison indicates that although few sorption data points are below the sorption curve, Fickian diffusion is in good agreement with sorption data at the beginning and at the end of the sorption.

Two incremental sorption experiments were conducted after the integral sorption at activity 0.44. When the sorption at activity 0.44 reached an equilibrium, the vapor inlet valve between the boiler and the sorption chamber was closed. The boiler was regulated at a higher temperature to achieve a solvent activity higher than 0.44. Then the

Figure 32. Sorption of tetralin in pyridine-extracted coal PSOC-375

Figure 33. The sorption of tetralin in pyridine-extracted coal

vapor inlet valve was reopened and an incremental sorption was studied. The integral sorption is labeled as stage 1 and the two incremental sorptions, one at activity 0.64 and the other at activity 0.85, are labeled as stage 2 and stage 3, respectively. Stage 1 represents the integral sorption mentioned above and the curve represents Fickian sorption. As the activity was raised from 0.44 to 0.64, solvent uptake increased slowly. Similar behavior was observed when solvent activity was increased from 0.64 to 0.85. A desorption was conducted at the end of the sorption at activity 0.85. The result of this desorption is labeled as stage 4 in Figure 34.

An integral sorption of tetralin in pyridine-extracted coal PSOC-375 was also conducted. The result is shown in Figure 35. The sorption result at activity 0.3 is similar to that at activity 0.44. Therefore, the Fickian diffusion model is employed to interpret the sorption data at activity 0.3. The line in Figure 35 represents the Fickian diffusion with the constant diffusion coefficient $1.2425 \times 10^{-11} \text{ cm}^2/\text{sec}$.

Results of the sorption at activity 0.3 are compared with those at activity 0.44. The comparison is summarized in Table 5. This comparison indicates that the dependence of the diffusion coefficient on concentration is very weak.

The hysteresis of sorption of tetralin in pyridine-extracted coal has been tested by the sorption and the resorption at solvent activity 0.3. First, the sample was exposed to tetralin at activity 0.3. After the solvent uptake approached an equilibrium state, desorption was performed. As the desorption curve leveled off, the coal sample was re-exposed to tetralin vapor at activity 0.3 until an equilibrium state was achieved. Finally, the system was desorbed until the solvent uptake leveled off.

Figure 34. Incremental sorption for tetralin-pyridine extracted coal system

Figure 35. Comparison of conventional diffusion model with sorption data for tetralin in pyridine-extracted coal PSOC-375 at 110°C and activity 0.3 .

Table 5

Summarized Results for the Sorption of Tetralin in Pyridine-
Extracted Coal PSOC-375 at Two Solvent Activities
and at 110°C

Activity*		M_{∞} , g/g	ω_s	D , cm ² /sec
Initial	Final			
0	→ 0.30	0.0394	0.038	1.243×10^{-11}
0	→ 0.44	0.0550	0.052	1.341×10^{-11}

* Fresh pyridine-extracted coal sample was used in each sorption.

Results of this test are shown in Figure 36. The line in the first sorption represents the Fickian diffusion model with a constant diffusion coefficient $1.243 \times 10^{-11} \text{ cm}^2/\text{sec}$. Lines in the other three regions are the best curve fittings for the data points.

To better explain the hysteresis, the plot of solvent uptake vs. solvent activity is drawn and shown in Figure 37. This plot clearly indicates that solvent uptake is not only a function of solvent activity but also the past history which influences the structure of the coal.

Hysteresis effects were also found by other investigators (27,40). For example, King et al. (27) found hysteresis effects in the sorption of water vapor in a coal of 82% carbon. Similar hysteresis effects were observed by Nelson (40) in the sorption of tetralin and benzene in coal PSOC-246.

E. The Summary of Sorption Results for These Three Solvent-Coal Systems

The sorption of benzene and tetralin in untreated coal PSOC-375 indicates that the sorption of solvent in untreated coal is a complex coupling of adsorption, capillary condensation, molecular diffusion and extraction, and no equilibrium has been obtained.

Results of sorption of solvents including benzene, toluene and tetralin in pyridine-extracted coal PSOC-375 indicate the following common features.

1. A fast solvent uptake due to adsorption is followed by a slow sorption process.
2. This slow sorption is attributed to solvent diffusion into the coal matrix. A linear relationship between solvent uptake and the square root of time at the early stage of this sorption

Figure 36. Hysteresis of tetralin in pyridine-extracted coal PSOC-375

Figure 37. Hysteresis of tetralin in pyridine-extracted coal PSOC-375 at 110°C

process is obtained. This linear behavior exhibits the characteristic of Fickian diffusion.

3. A relaxation effect is prominent for the sorption of toluene in pyridine-extracted coal, but is not apparent for tetralin or benzene.
4. Desorption does not obey Fickian diffusion with a constant diffusion coefficient determined from sorption data, and some solvent is trapped inside the coal.
5. The amount of solvent entrapment is not equal to the solvent uptake due to adsorption or relaxation.
6. Resorption is a faster process than the first sorption.

Hysteresis effects are prominent for the sorption of toluene and tetralin in pyridine-extracted coal. Results indicate that the solvent uptake is not only a function of solvent activity but is also dependent upon the past history which influences the structure of the coal.

F. The Determination of Coal Structure from the Solvent Swelling

Thermodynamic data for the integral sorption of toluene in pyridine-extracted coal PSOC-375 at four different solvent activities are employed to test the Flory model which was developed for the sorption of solvents in crosslinked polymers. Data in terms of solvent activity a_1 vs. volume fraction of solvent ϕ_1 are listed in Table 6.

After the substitution of thermodynamic data into Flory model, the optimal values for the two parameters χ and M_c are determined by a nonlinear regression analysis. The value of χ is equal to -4.86 and the value of M_c is equal to 20.1. As these two parameters are substituted into equation (10), a relationship between solvent activity and volume

Table 6
Thermodynamic Data of Sorption of Toluene
in Pyridine-Extracted Coal
PSOC-375 at 110°C

a_1	ϕ_1
0.10	0.0757
0.278	0.0964
0.50	0.1365
0.80	0.1732

fraction of solvent is established and is shown by the curve in Figure 38.

Although the Flory model is in good agreement with thermodynamic data as shown in Figure 38, the values for χ and M_c are not appropriate. A value of -4.86 for χ is out of the range of any data which have been reported for polymer-solvents interactions. The low value of M_c would indicate that the crosslinks in coal are impossibly close together.

The value of M_c obtained in this study is compared with the values of M_c reported by other investigators. It is found that the value of M_c in this study is in good agreement with the values of M_c which ranges from 2.5 to 14 determined from mechanical measurements on the elasticity of coal (31). However, there is a large discrepancy in M_c between this study and the studies by Sanada and Honda (47), and Kirov et al. (28). The values of M_c studied by them range from 49.5 to 1840, as recalculated by Larsen and Kovac (31).

The thermodynamic data listed in Table 6 have been employed to test the molecular structure models proposed by Lucht and Peppas (34,53) and Larsen and Kovac (29,31). The three characteristic parameters, N , M_c and χ , for each model are summarized in Table 7. The comparison between their models and thermodynamic data are presented in Figures 39 and 40.

The value of M_c from Lucht and Peppas model in this study is 31.2 which is far below the value of M_c reported by Lucht and Peppas (34,35). However, there is one major problem in the work of Lucht and Peppas. The determination of the value for χ in their study seems not valid. Their values for χ were obtained from the results by Kirov et al. (28), who employed the Flory-Rehner equation, which was derived from the Gaussian model to determine the interaction parameter χ . However, Lucht

Figure 38. Comparison of Flory's model with thermodynamic data for toluene sorption in pyridine-extracted PSOC-375 coal, 110°C

Table 7
The Comparison of Different Molecular Models
for Coal

Model	N	χ	M_c
Flory	--	-4.86	20.1
Lucht and Peppas	9.24	-5.15	31.2
Kovac	20.67	-7.70	31.1

Figure 39. Comparison of Lucht and Peppas model with thermodynamic data for toluene sorption in pyridine-extracted coal PSOC-375 at 110°C.

Figure 40. Comparison of Kovac model with thermodynamic data for toluene sorption in pyridine-extracted coal PSOC-375 at 110°C

and Peppas were strongly convinced that the Gaussian model is not appropriate for coal structure. Obviously, it is a contradiction in their approach. Further, the solvent uptake used to determine the value for χ by Kirov et al. (28) was not corrected for solvent in pores, an effect considered important by Nelson (40). As a result, the value for χ determined by Kirov et al. (28) is very questionable.

The figures obtained from these three models, as shown in Table 7, are not reasonable. The failure of these three models may be attributed to two reasons. First of all, the Flory model is not applicable to the uptake of toluene at 110°C by a coal, presumably because this is a glassy rather than a rubbery system. With other solvents (e.g., pyridine) and other conditions, the theory may apply. Second, it is certain that these three models are quite inadequate for describing the solvent swelling in coal. A new model is needed in the future to elucidate the structure of the coal.

VI. CONCLUSIONS

The following conclusions are drawn from this research:

1. The sorption of solvent vapor such as benzene and tetralin into untreated coal PSOC-375 at temperatures of 175°C and 110°C, respectively, indicates that a fast solvent gain due to the adsorption and capillary condensation is followed by a slow process. This slow process is attributed to two simultaneous mechanisms: (a) the solvent vapor diffuses into the coal matrix; (b) soluble material in untreated coal is extracted out by the condensed penetrant to form a solution. Dissolution of coal lowers the chemical potential of the solvent. Therefore, more solvent is driven into this solution and no equilibrium will be reached in untreated coal-solvent system. As a result, the diffusion of solvent vapor into the coal matrix is coupled with adsorption and extraction, and it cannot be separated from these coupled processes. In addition, data for untreated coal show that the sorption process does not reach an equilibrium state even after several weeks of exposure. This is consistent with the proposed mechanisms. Hence, it is not possible to determine the diffusion coefficient for a solvent in untreated coal.

2. No correlation has been found between the solubility parameter of the solvent and the solvent uptake in untreated coal (PSOC-375) at 25°C after several weeks of exposure. However, it was found that the parameter donor number (DN) minus acceptor number (AN) can be used to interpret the solvent solubility in untreated coal. A solvent with a negative value of DN minus AN shows low solvent uptake. In contrast, the higher the positive number of DN minus AN, the more the solvent is

dissolved. Similar results have been found by Marzec et al. in coal extraction. It appears that the solvent uptake in untreated coal may be dominated by an extraction process.

3. Equilibrium has been achieved as pyridine-extracted coal is exposed to solvents including benzene, toluene and tetralin which have a less extraction ability than pyridine. It appears that the extraction process has been eliminated as pyridine-extracted coal is brought in contact with these solvents. As a result, the sorption of these solvents in pyridine-extracted coal only involves adsorption, capillary condensation and the diffusion into the coal matrix. Furthermore, the adsorption and capillary condensation are fast processes compared with the diffusion into coal matrix. Hence, the diffusion process can be distinguished from these two fast processes, and it becomes possible to determine the diffusion coefficient for the solvent in pyridine-extracted coal.

4. No single parameter including the parameter DN minus AN , the composite solubility parameter and the hydrogen-bonding parameter can be employed to interpret the solvent uptake in pyridine-extracted coal well.

5. The sorption of benzene, toluene and tetralin into pyridine-extracted coal PSOC-3/5 at temperatures up to 175°C and at various solvent activities follows similar course. After fast solvent gain due to adsorption and capillary condensation, a slow sorption process is observed. This slow process results from diffusion of solvent into the coal matrix coupled with a relaxation process in which the structure of the coal is changing. A linear relationship between solvent gain and $\sqrt{t}$ is obtained at the early stage of this slow process. This behavior

may be classified as a feature of Fickian diffusion, but sorption does not approach the equilibrium state observed in a typical Fickian sorption process. Instead, sorption persists at a very slow rate for long periods of time. This very slow increase in sorption may be attributed to a relaxation process in which the structure of the coal is changing so that more solvent can be sorbed. Similar behavior is commonly observed for vapor sorption into glassy polymers.

6. Two mathematical models, one by Berens and Hopfenberg and the other by Long and Richman, which were derived to describe sorption in glassy polymers, have been employed to interpret the sorption behavior in pyridine-extracted coal. Both models fit sorption data quite well. However, Long and Richman's model gives a better physical significance.

7. Both the diffusion coefficient and the relaxation parameter of toluene in pyridine-extracted coal at temperature 110°C are weak functions of concentration.

8. Results of the desorption of solvent from the coal indicate that some solvent is trapped inside the coal and does not come out after a long exposure to vacuum. This solvent trapping may result from a structural change associated with the sorption swelling process.

9. Consecutive sorption and desorption experiments indicate that the amount of sorbed solvent in the coal is not a unique function of solvent activity but depends upon the past history, which influences the coal structure. Hysteresis effects are prominent in sorption behavior.

10. The remaining nonextractable part of the coal after pyridine extraction is conceived as a three-dimensional crosslinked polymer. To determine the structure of this polymer, thermodynamic data at different solvent activities are employed to obtain the interaction parameter χ

for the coal-solvent system, and the molecular weight between crosslinks M_c by use of the Flory model. The Flory model fits the thermodynamic data quite well, but the physical significance of these two parameters, χ and M_c , are questionable. The value of χ -4.86 is out of the range of any data which have been reported. The small value of M_c 20.1 indicates that the crosslinks in coal are impossibly close together. The figures are so improbable that one must conclude that Flory model does not apply to this system, most probably because the coal-solvent system is still in a glassy state.

11. It should be noted that the value of M_c determined from this study does not agree with M_c values reported in the literature which are based upon sorption data at activity 1.0 and at room temperature. The values of the interaction parameter, χ , in the literature were obtained from other measurements such as by assuming that the extract and the residue have a basic similarity.

12. The modified Gaussian models devised by Kovac and by Lucht and Peppas have been tested by use of the same thermodynamic data that have been employed to test the Flory model. In these modified models, there are three parameters: the interaction parameter χ , the number of repeating units in each chain, N , and the molecular weight between crosslinks M_c . These three parameters can be determined unambiguously from the thermodynamic data available from this study without making assumptions about the values of χ and N . Although these two models fit the sorption data quite well, the values of the parameters including χ and M_c are not reasonable.

Some important inferences can be drawn from the results and conclusions presented in this thesis. In the past, the uptake of gases and

vapors by coals has been discussed in terms of diffusion into a system of pores, conceived of as having more or less rigid and permanent walls. It now appears that condensation in pores accounts for a relatively small fraction of the uptake of vapor by a coal at 110°C, and that the greater part dissolves in the solid matrix, occupying incidental imperfections of molecular packing which are not necessarily permanent. Thus, it is reasonable to say that converting the uptake of vapor by coal into surface area and pore volume is meaningless unless vapor does not dissolve in the coal matrix, or the uptake of vapor due to adsorption and condensation in the pores is distinguishable from the uptake of vapor in the coal matrix.

It is probable that the relaxation of the macromolecular structure to release stresses set up by solvent sorption traps much of the vapor and prevents its release when the sample is exposed to a vacuum; this behavior is not consistent with a pore model.

The original motive in undertaking this study was to attempt to solve what appeared to be a problem in the understanding of coal liquefaction. As noted in the introduction, the process of liquefaction is commonly thought to start with thermal dissociation reactions, generating free radicals which are then "capped off" by hydrogen from the donor solvent. This implies that solvent molecules are readily available inside coal particles at the locus of any free radical generation. Is it reasonable to postulate this ready availability? If diffusion through the coal matrix is required, then the postulate did not seem reasonable, because the diffusion was likely to be too slow. Was another mechanism possible?

It has been found here that direct dissolution of hydrocarbon vapors in the coal matrix is the predominant mode of uptake at somewhat elevated temperatures, and substantial uptake of toluene vapor has occurred within 24 hours at 110°C. If the same uptake fraction occurs at 400°C, it might take about 1/300th the time if the activation energy for diffusion is 10 kcal/mole. However, a coal particle may break up into many small pieces and becomes fluid at 400°C. These changes might cause two opposite effects on diffusion. On the one hand, diffusion is enhanced because the diffusion length is reduced by the breaking of the coal particle. On the other hand, diffusion decreases because pores are sealed after coal particles become fluid.

VII. . RECOMMENDATIONS

Some recommendations for future work are as follows:

1. Diffusivity data at various temperatures are needed to predict the diffusion coefficient at higher temperature.
2. The hysteresis effects in equilibrium sorption should be further investigated to find out the reason for them.
3. Sorption of solvent in coal should be investigated by NMR to better understand the sorption mechanism.
4. A new model for the solvent swelling in coal should be developed to elucidate the network structure in coal.
5. To study the transport and relaxation characteristics with respect to coal types, coals of different rank should be employed.
6. The effect of particle size on the mass transport should be investigated.
7. In order to test molecular models for coal, a good solvent such as pyridine should be used as the swelling agent to guarantee that the solvent-coal system is in the rubbery state.

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APPENDIX

Sorption of Toluene Into Pyridine-Extracted Coal at 110°C

Figure 41. Sorption of toluene into pyridine-extracted coal PSOC-375 at 110°C and solvent activity 0.1

Figure 42. Sorption of toluene into pyridine-extracted coal PSOC-375 at 110°C and solvent activity 0.5

Figure 43. Sorption of toluene into pyridine-extracted coal PSOC-375 at 110°C and solvent activity 0.8

Figure 44. Comparison of Berens and Hopfenberg's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.1

Figure 45. Comparison of Berens and Hopfenberg's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.5

Figure 46. Comparison of Berens and Hopfenberg's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.8

Figure 47. Comparison of Long and Richman's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.1

Figure 48. Comparison of Long and Richman's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.5

Figure 49. Comparison of Long and Richman's model with experimental sorption data for toluene-pyridine extracted coal system at 110°C and solvent activity 0.8