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THERMODYNAMICS AND SURFACE STRUCTURE OF COALS

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Thermodynamics and Surface Structure of Argonne Coals

SCOPE AND OBJECTIVES OF WORK

Scope. An understanding of the surface structure and chemistry of coals is necessary for a true understanding and optimization of coal cleaning and other surface interactions. In all chemical reactions of solid coal, the reagent first encounters the coal surface. The extent of surface which is available to a molecule and the interactions which occur during the molecule/surface encounter are critical parameters to understanding the chemistry of the interaction of coals with various solvents. The present studies have been undertaken with the objective of understanding these complex interactions.

Objectives. The present work involves investigations of the surface structure and thermodynamics of coals and treated coals in order to develop a detailed understanding of the coal surface and its transformations and interactions as a result of various chemical treatments. To this end we are using several types of experimental probes:

- 1.) NMR relaxation agents are deposited on coals and the resulting spectra provide information about the structure and chemistry of the atoms at the coal surface.
- 2.) ^{129}Xe NMR is being used as a probe of pore distributions and surface polarity of coals.
- 3.) Classical calorimetric studies and inverse gas chromatography are being used to determine the strengths of interaction between

various probe molecules and coals.

Surface Characterization of Coals

Objectives. We have reported the determination of the average micropore diameter of an Argonne Illinois No. 6 coal (77% C, daf) and a standard 15 Å diameter Sphero carb sample by ^{129}Xe NMR spectroscopy¹. We have successfully applied this technique to determine the average micropore diameter of the full series of Argonne coals. We have recently developed a computer program (Appendix A) which correlates the ^{129}Xe NMR spectrum of coals directly to the micropore size distribution of each Argonne coal. The micropore size distribution of Argonne: Pocahontas No. 3 (91.8% C, dmmf); Pittsburgh No. 8 (85.0% C, dmmf); and Blind Canyon (81.3% C, dmmf) coals, determined by ^{129}Xe NMR spectroscopy are shown in Figures 2, 4, and 6, respectively.

Background. The NMR chemical shift of ^{129}Xe is a useful probe of micropore (<20 Å diameter) size and surface characteristics.²⁻⁶ This application was developed principally by Fraissard and co-workers to determine pore size distributions and the degree of crystallinity in zeolites.^{2,6} The observed ^{129}Xe NMR chemical shift can be attributed to 4 factors: 1) the number of Xe-Xe collisions; 2) the electric field established by neighboring ions in the solid sample, found to be negligible for monovalent cations in zeolites; 3) the number of Xe-wall collisions; and 4) the nature of the interaction of Xe with the pore wall.³⁻⁵ The chemical shift due to Xe-wall collisions can be determined by

extrapolation of ^{129}Xe NMR resonances to zero Xe pressure. The ^{129}Xe NMR chemical shift due to Xe-wall collisions is directly related to the mean free path of the Xe atom in the pore. From the diameter of the Xe atom (4.4 Å) and its mean free path in the pore, the dimensions of the pore can be calculated if the pore shape is assumed.^{2,6}

Demarquay and Fraissard have developed a semi-empirical relationship between the ^{129}Xe NMR chemical shift at zero Xe concentration and the mean free path of the Xe atom adsorbed in some model zeolites.^{2,6} The diameter of a spherical pore applying this relationship is:

$$D_s = 2i + D_{\text{Xe}} \quad (1)$$

where D_s is the diameter of the spherical pore, i is the mean free path of the Xe atom in the pore, and D_{Xe} is the diameter of a Xe atom (4.4 Å).

Experimental. As previously reported, the Argonne coal samples were transferred to the NMR sample tubes in a $\text{N}_{2(g)}$ filled glovebox. Argonne: Pocahontas No. 3 (91.8% C, dmmf), Pittsburgh No. 8 (85.0% C, dmmf), and Blind Canyon (81.3% C, dmmf) coal samples were desorbed overnight at 10^{-6} torr on a Micromeritics Digisorb 2500 stainless steel vacuum rig equipped with a diffusion pump and a Datametrix differential capacitance-type pressure sensor to measure Xe gas pressures. Air Products Co. 99.995% pure

Xe gas was used in all experiments. The ^{129}Xe spectra were obtained on a Bruker AM 500 MHz spectrometer operating at 138.3 MHz.

The ^{129}Xe -coal spectra were transferred from the NMR Aspect 3000 computer to an IBM compatible computer via a KERMIT⁷ software communications package. The ^{129}Xe NMR spectra of each Argonne coal was converted from a quadrature hexadecimal file to an integer file using a BASIC program developed by O. Yamada and P. Wernett at Lehigh University (Appendix A). NMR integer files were converted to a micropore size distribution using STATGRAPHICS⁸ statistical graphics computer program.

Results. The ^{129}Xe NMR spectra as a function of decreasing Xe(g) pressure is shown in Figure 1 for Argonne Pocahontas No. 3 coal. The peak furthest upfield is due to free Xe(g) and is assigned a chemical shift value of 0 ppm. The downfield resonance, corresponding to Xe in the Pocahontas coal shows a ^{129}Xe NMR chemical shift dependence on Xe(g) pressure. This is what is expected of Xe in a pore. The width of the ^{129}Xe NMR resonance in the coal is assumed to be due to a distribution of micropore sizes. The ^{129}Xe NMR resonance due to Xe in the Pocahontas coal at the highest Xe gas pressure was extrapolated to 0 Xe(g) concentration using the STATGRAPHICS computer program. The NMR chemical shift was converted to the coal micropore size distribution applying the method developed by Demarquay and Fraissard, assuming spherically shaped micropores for the

Pocahontas No. 3 coal. A spherical micropore model for all the coals was assumed based on SANS⁹ and spin probe EPR¹⁰ experimental evidence on coal pore shapes. Figure 2 shows the micropore size distribution of the Argonne Pocahontas No. 3 coal by this NMR method using the STATGRAPHICS statistical software package.

The ¹²⁹Xe NMR spectra in decreasing Xe(g) concentration are presented in Figures 3 and 5 for the Argonne Pittsburgh No. 8 and Blind Canyon coals, respectively. The micropore size distribution for the Pittsburgh No. 8 and Blind Canyon coals (Figures 4 and 6, respectively) were determined by applying the same NMR data analysis that was performed on the Pocahontas coal.

Inverse Gas Chromatography Studies

Background

We are using the technique of Inverse Gas Chromatography (IGC) to determine thermodynamic parameters for representative adsorbate molecules on Argonne coals with the objective of understanding the underlying chemistry of coal swelling and cleaning. Calorimetry may be used to obtain thermodynamic data, but in this case, a bulk, average effect is measured and the underlying distribution of adsorption energies cannot be ascertained. In contrast, IGC can be used to measure thermodynamic parameters at very low and at varying adsorbate concentrations, so that heats of adsorption can be determined as a function of surface coverage, and the heterogeneity of the surface adsorption energetics may be assessed.

IGC has been used to characterize physisorption on oxides,

carbons, and polymers^{11,12}. The technique is able to discriminate between polar and dispersion type interactions and thermodynamic parameters such as heats of adsorption, surface free energies, and adsorption isotherms may be obtained for particular adsorbate/substrate pairs. The technique has the potential to monitor structural transitions as a function of temperature, as has been shown for polymer¹³. Such transitions are indicated by changes in the slopes of plots of the log of the retention time (V_R) vs. $1/T$, where T is the column temperature.

In the linear region of the adsorption isotherm, an IGC probe molecule/substrate interaction is analogous to a solute/solvent interaction which can be described by Henry's law¹⁴:

$$x = kp \quad (1)$$

where p is the solute partial pressure, k is the Henry's law constant, and x is the solute mole fraction. In the corresponding region of the adsorption isotherm, the adsorbate uptake is independent of adsorbate concentration. The interaction is characteristic of a single type of adsorption site and therefore thermodynamic parameters may be determined directly from k , which in IGC is the partition coefficient of the adsorbate between the solid and gaseous phases, determined from the measured retention time. For example, in the Henry's law region, the adsorption enthalpy is given by:

$$H_{ads} = RT^2 d \ln k / dT \quad (2)$$

where R is the gas constant and T is the temperature. A plot of $\ln k$ vs. $1/T$ has a slope proportional to H_{ads} . In the

non-linear region of the isotherm, the retention time in IGC varies with adsorbate concentration. In this case we must speak of a differential heat of adsorption,

$$H_{\text{diff}} = (dQ/dN)_T \quad (3)$$

In IGC, H_{diff} is obtained as a function of adsorbate concentration.

The objective of the present work is to use IGC to obtain thermodynamic data describing the interactions of various probe molecules with Argonne coal surfaces. Previously, IGC has been used by Roy and Guha to obtain elution profiles, plate heights, and permeabilities of various probes on coals and on carbonized coals¹⁵⁻¹⁹. For lignites, anthracites, and bituminous coals which had not been subjected to any prior treatments, these workers observed sharp and symmetric IGC peaks¹⁷⁻¹⁹. However, conditioning of the coals at ~175 °C produced asymmetric, concentration-dependent elution profiles. These data indicate that the nonconditioned coals of Roy and Guha were completely oxidized so that they were not representative of virgin coal surfaces. The authors attributed asymmetric elution peaks for the conditioned coals to adsorption heterogeneity and/or slow mass transport in coal micropores. Both of these effects, nonlinearity of the adsorption isotherm and slow diffusion, are known to produce peak asymmetry, thus complicating the extraction of thermodynamic parameters from the data¹⁴. Winans et al. used IGC to study the retention time of methane on oxidized and unoxidized Argonne coals heated to various temperatures from about 100 to 400

°C²⁰⁻²³. In plots of $\ln V_R$ vs. $1/T$ these workers found increasing retention times with heat treatment temperature of the coals and a transition region at about 350°C corresponding to greatly increased retention times. It is not clear whether or not corrections were made for the effects of carrier gas flow rate on retention times, nor if the effects of mass transport and isotherm nonlinearity were considered. No thermodynamic data were presented. Preliminary data of Larsen et al. for adsorption enthalpies of various probes on Bruceton coal determined by IGC indicate rough trends²⁴. In that work, some interesting effects were observed. For example, a surface saturation effect was seen for pyridine.

The present work involves determination of thermodynamic parameters for various adsorbates on well-characterized, virgin Argonne coal. The concentration dependence of the adsorbate/coal interaction as well as the effects of diffusion of the probe in the coal will be assessed.

Experimental

The experiments are being performed using a Hewlett-Packard 5890 gas chromatograph with a TCD detector. In order to correct for the velocity profile along the column, the pressure drop across the column is measured using an open ended manometer. Helium carrier gas flow rate is maintained constant by a Tylan flow controller at the column inlet, and column temperature is maintained constant to within $\pm 0.3^\circ\text{C}$, measurable to 0.1°C . Argonne coal sieved to obtain the -35 to -70 mesh fraction is

packed into 1/8 inch O.D. ss tubing. The column is conditioned by outgassing in dry He overnight at 115 °C.

Experiments involve injections of the probe with a Hamilton microliter syringe. Initial experiments are being performed at sample concentrations in the Henry's law or zero coverage regime, so that peak broadening and asymmetry due to nonlinear effects are minimized, and so that possible diffusion effects can be observed⁴. Retention times and peak variances will be extrapolated to zero flow rate in order to correct for effects caused by noninstantaneous equilibrium. While thermodynamic parameters can be determined from retention times, diffusion constants can be determined from peak variances. Various models have been proposed using different treatments of the continuity equation for the distribution of sample between mobile and stationary phase²⁵⁻²⁷. We plan to use these different data reduction schemes in order to model the diffusion and thermodynamic effects for various probes on coals.

Determination of the Surface Structure of Coals By the Deposition of NMR Relaxation Agents

Present Work:

Our work this quarter has been directed at looking at the effect of depositing copper(II) ions on the surface of coal. We have also been examining the effect of another relaxation agent on our model system.

Background:

The use of NMR as a surface technique has never been applied to coals to the best of our knowledge. Solid state NMR has been applied extensively to coal and related systems. It is a powerful technique because line positions and intensities are indicative of geometry, bonding hybridization and population of distinct functionalities as well as local environment effects. The NMR spectrum can be influenced by many factors including dipolar through-space coupling between an unpaired electron spin and the spin of the carbon atom. The unpaired electron can act as a relaxation sink, significantly shortening the spin-lattice relaxation time (T_1) of the coupled carbon-13 atom. This shortening of the T_1 can theoretically broaden the signal to the point where it disappears. The effective range of interaction is proportional to the inverse sixth power of the separation of two spins (r^{-6})²⁸. This is a relatively short distance on the order of one nanometer. Assuming that the paramagnetic centers are deposited on the surface of our sample, this would indicate that this is indeed capable of being a surface technique.

We are depositing NMR relaxation and shift reagents on the surface of coals. The dipolar coupling of the unpaired electron spin of the relaxation agent and the carbon atom should significantly shorten the carbon T_1 , which may broaden it away. We propose to take the NMR spectrum of a coal before and after deposition and subtract the spectra. The difference spectra will represent the functionalities within one nanometer of the surface and should represent the surface composition of the coal.

In order to see the effect of paramagnetics on coal, we deposited a large excess of copper(II) chloride on a sample of Beulah Zap lignite²⁹. We chose Buelah Zap lignite primarily because it is low rank and it has a high concentration of oxygen functional groups. We expect the oxygen and carboxylate groups to bind the copper(II). We also made a sample with a known quantity of copper(II) to determine T_1 times. We found that the sample with the vast excess of copper(II) had a significantly reduced carbonyl peak. See Figure 1. We also compared the relaxation times of an sodium treated sample with the copper(II) treated sample. The sample with the known quantity of copper(II) showed shorter T_1 relaxation times than did the sodium treated sample. See Table 1. We also started using a new relaxation agent. We deposited 30% (charge equivalence basis) dysprosium nitrate on our model compound, an aryl sulfonate silica gel. (Charge equivalence means that we determine the number of dysprosiums with a +3 charge needed to balance the sulfonates with a charge of -1. For complete coverage we would need one dysprosium for every three sulfonates. A 30% coverage means we calculate the amount of dysprosium needed for complete coverage and then apply 30% of that to the gel.) We chose dysprosium because it appears that dysprosium may be a better relaxation agent than copper(II). When compared to the other lanthanides, dysprosium exhibits the largest downfield shifting behavior³⁰. We chose a downfield shifting lanthide so that when applied to coal the carbonyl peak if shifted would not shift into the highly congested aromatic region.

Experimental:

The coal used is Beulah Zap lignite of the Argonne Premium Coal Sample Program²⁹. All NMR spectra were obtained using a General Electric GN-300 NMR spectrometer operating at 75.4 MHz for ^{13}C and utilizing a Doty 5mm or 7mm probe. The samples were examined under Magic Angle Sample Spinning (MASS) conditions³¹. The model compound used was an aryl sulfonate ion exchange resin produced by J.T. Baker, Inc.

The Beulah Zap was treated by mixing with a sodium bicarbonate buffer for one week. It was then dialyzed for 24 hours in deionized water three times. The sample was split one half was mixed with a copper (II) chloride solution for one week. The other half, our control, was kept in water for one week. The solvent was evaporated from both samples which were then dried in a 110°C oven under vacuum. All manipulations of coal samples were done in a nitrogen environment to minimize oxidation.

The silica gel was prepared by titrating a known quantity of aqueous dysprosium nitrate solution into a slurry of the gel with gentle stirring. The solvent was then evaporated and the samples dried under vacuum at 50°C.

NMR spin-lattice relaxation (T_1) studies were then conducted in order to compare treated and untreated samples T_1 times.

Discussion:

The spin-lattice relaxation time (T_1) studies employed cross-polarization conditions. Cross polarization is a technique commonly employed in solid state NMR involving the transfer of

magnetization from the protons to the carbons³¹. Cross polarization is used to improve carbon sensitivity. The technique has been described in an earlier Quarterly Report DE-AC22-89PC89757-4. The pulse sequences employed for the relaxation studies referred to in our laboratory as T1CP1H (proton T₁) and T1NOE (carbon-13 T₁) have also been described in Quarterly Report DE-AC22-89PC89757-4³².

Figure 1 contains both copper(II) and sodium (untreated) Buelah Zap spectra. The copper(II) treated spectrum was treated with a vast excess of copper, approximately a 5:1 copper : coal ratio by mass. The carbonyl peak at approximately 190 ppm is significantly reduced in the copper(II) treated spectrum. Please note the line on Figure 7. This indicates that with sufficient relaxation agent the signals can be broadened away.

Our next copper(II) sample was a 50X excess based on a charge equivalence basis assuming that there are three carboxylate groups per 100 carbon atoms in Buelah Zap. This is approximately a 1:3 copper: coal ratio by mass. We ran T₁ experiments on these samples. There was no obvious difference observed between the copper(II) and sodium treated spectra, but we did see a drop in T₁ times for the copper treated sample. Table 1 lists the relaxation times. We observe different relaxation times for the aliphatic and aromatic protons. Different proton T₁ values within a sample are not commonly observed for most solid samples. Due to spin diffusion among the protons, most chemical systems have a uniform proton T₁. This difference seems to indicate that we have at least two separate domains of protons in our coal sample. Differences in

aliphatic and aromatic proton T_1 values have been observed by other groups³³. The T_1 values decreased with the addition of copper(II) and the greater the amount of copper the more significant the effect on the spectrum. This behavior is similar to what was observed with our model compound³².

We then applied 30% (charge equivalence) dysprosium nitrate to our aryl sulfonate resin. We chose 30% as a starting place because that was where we saw a significant drop with our copper samples. We did not observe a signal. We attempted both cross-polarization³² and single pulse, Bloch decay experiments³³. Spectra with both copper and dysprosium can be observed Figure 8. This indicates that dysprosium is indeed a more efficient relaxation agent than copper. A 30% dysprosium sample completely broadened away the signal, while a greater than 90% copper(II) sample still had signal³². These percentages are based on charge equivalence. (Since copper has a +2 charge, we balance the charges of 2 sulfonates with every one copper(II) ion. A greater than 90% coverage means that we determined the amount of copper for complete coverage and applied it to the resin.)

Future Work:

Next quarter, we plan to do relaxation studies on a series of samples in which we will vary the amount of dysprosium on a carboxylic acid silica gel resin. A sample spectrum of this resin can be observed in Figure 9. We plan to switch to the carboxylic acid resin because it will more closely resemble the functional groups we expect to find in coal and because it is a simpler NMR

spectrum. We also plan to apply dysprosium to a Buelah Zap sample. We hope that we can selectively broaden away the surface functionalities of the Buelah Zap and leave the bulk signal.

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