

SWELLING OF COAL EXTRACTS

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INTRODUCTION

Coals are considered macromolecular solids. (1) Although they are not polymers in the sense that they possess a repeating unit, they do possess several fundamental properties typical of synthetic crosslinked polymers. (2) One of these properties is the ability of coals to swell in organic solvents without dissolving.

In recent years, there has been a rapid growth in the number of publications that deal with the solvent swelling of coal. Much of this effort has been directed toward the application of modern polymer and network theories to coal, with the purpose of better understanding their network structures. One of the most fundamental properties of a network structure is \bar{M}_c , the average molecular weight between crosslinks. Consequently, several research groups have attempted to estimate \bar{M}_c 's for coal from solvent swelling data and the Flory-Rehner equation. (3-8) The equation incorporates both the Flory-Huggins theory of polymer solutions and the Gaussian elastic network theory. An important parameter embodied in the Flory-Huggins theory is the interaction parameter, χ . χ is a thermodynamic parameter describing the energetics of the polymer-solvent interaction. A reliable evaluation of χ is essential to an estimation of \bar{M}_c for crosslinked networks using the Flory-Rehner equation. Very few reliable methods have been developed to evaluate χ for coal-solvent systems. It is the purpose of this research to develop a reliable method for its evaluation.

Approach. One of the most common techniques for determining χ parameters for polymer-solvent systems is the vapor sorption method. (9) In this approach, the uncrosslinked polymer is exposed to solvent vapor of known pressure, p . The polymer absorbs solvent until equilibrium is established. χ is related to p and v_2 , the volume fraction of polymer at equilibrium, by

$$\chi = \frac{\ln [(p/p_0)/(1-v_2)]}{v_2^2} - v_2 \quad 1)$$

Measurement of p as a function of v_2 can be used with Equation 1 to obtain values for χ over a wide range of concentrations.

It is important to recognize that Equation 1 applies to polymers that are not crosslinked. Most vapor sorption studies on coal have been conducted on the crosslinked, or insoluble portion of coals. Under this condition, simultaneous evaluation of χ and \bar{M}_c must be made. Two groups of researchers have adopted this approach. (7,8) We have adopted an alternative approach by conducting vapor sorption studies on the uncrosslinked portion of the coal. χ parameters can thus be directly calculated from the pressure-sorption data using Equation 1.

The uncrosslinked portion of the coal is obtained by Soxhlet-extraction of the coal with pyridine. Pyridine is a particularly good solvent for coals, and it is thought to remove a majority of the uncrosslinked molecules from the coal matrix. There is evidence that the pyridine-soluble portion is representative of the larger, crosslinked portion, although this aspect remains controversial.

EXPERIMENTAL

Sample Preparation. Dry Illinois No. 6 (Herrin seam, -60 mesh) was used in the sorption studies. Analysis Found: C, 74.37; H, 4.83; N, 1.76; S, 1.76; O (by difference), 8.74; Ash, 8.33 (duplicate). Approximately 10 g of the sample was exhaustively Soxhlet-extracted with pyridine. Extractability was 18.7% (wt.). The pyridine solution was then filtered through a 0.4 μ m filter. Most of the pyridine was removed by rotovaporization under reduced pressure at 70-80°C. Approximately 200 mL of a methanol/water (80/20 vol) mixture and 2 mL of conc. HCl were added to the flask and the mixture was stirred under nitrogen for two days. The solid extract was then filtered and dried under vacuum at 105°C for 24 hours. Analysis Found: C, 82.97; H, 5.87; N, 1.80 (duplicate).

O-Methylation Procedure. The extract was O-methylated according to a method described earlier by Liotta (10) using tetrabutylammonium hydroxide and methyl iodide.

Sorption Experiments. Sorption experiments were carried out using a Cahn 1000 recording balance, with an accuracy of ± 0.03 mg. The balance and its accessories are shown in Figure 1. The instrument is equipped with an MKS Baratron pressure transducer (0-100 torr, 0.15% accuracy) with a digital readout for pressure measurements.

Prior to conducting the sorption experiment, the coal extract (200 mg) was first placed in a Wig-L-Bug capsule and ground for 1 minute under nitrogen. This grinding effectively reduces the extract to a fine powder, which is then used for the sorption experiment. Approximately 50-70 mg of the extract was then placed on the sample pan and the hangdown tube was replaced. The sample was maintained at 30.00 ± 0.02 °C by means of a constant temperature bath which surrounded the hangdown tube.

In a typical experiment, benzene vapor was admitted into the evacuated balance chamber by means of stopcock D. After achieving the desired pressure, stopcock D was closed. The maximum uncertainty in p/p₀ during the course of any one experiment was ± 0.008 units. Equilibrium was judged to be established when there was less than a 1 percent change in weight over a 12 hour period.

RESULTS

Characterization of the Pyridine-Extract. Pyridine is known to cling to coals. The extract was therefore stirred with a methanol/water/HCl mixture for two days as suggested by Buchanan. (11) Elemental analysis of the extract revealed 1.80% N. The original coal contained 1.92% N (daf) so it is apparent that the methanol/water/HCl treatment followed by drying successfully removed pyridine from the extract.

Synthesis and Characterization of O-Methylated Extract. The O-alkylation of coals has been discussed by Liotta *et al.* (10) Alkylation occurs when tetrabutylammonium hydroxide is used to promote the reaction of the alkyl iodide with the coal in tetrahydrofuran. The alkylation reaction occurs primarily on acidic oxygen functionalities such as phenolic hydroxyl and carboxylic acid groups, as shown below.



The hydrogen to carbon ratios of the extract and O-alkylated extract established that 4 hydroxyl groups per 100 carbon atoms were alkylated. FT-IR and ^{13}C NMR analysis confirmed that O-methylation had occurred.

Sorption Experiments. The extracts were exposed to benzene vapor at several relative vapor pressures (p/p_0). Two types of sorption experiments were conducted. Experiments in which the benzene vapor pressure is raised from zero to a higher value are termed integral sorptions. Sorption experiments starting with the extract and vapor in equilibrium at a finite, non-zero pressure, and proceeding to a higher pressure, are termed incremental sorptions.

Figures 2 and 3 show the sorption curves of mass uptake versus time for the extract and O-methylated extract. Three different experiments are shown in each figure; a single integral sorption and two subsequent incremental sorptions. Both extracts required 30 to 150 hours to reach equilibrium, depending on the particular experiment.

Sorption-Desorption Isotherms. Sorption-desorption isotherms for the extracts are presented in Figures 4 and 5, where the relative vapor pressure of benzene (p/p_0) is plotted against the cumulative equilibrium uptake of benzene. Both isotherms are characterized by strong hysteresis (non-reversible sorption behavior). For both extracts, a considerable amount of benzene cannot be desorbed under vacuum (~ 0.01 torr). However, the benzene could be completely removed from the O-methylated extract by heating to 105°C under vacuum. Thus benzene is not irreversibly bound to the O-methylated extract. Once the benzene was driven off, the sorption curve could be reproduced. We did not apply this procedure to the extract, but we expect it to behave similarly.

DISCUSSION

The sorption of benzene by the extract and the O-methylated extract is characterized by a rapid, initial uptake followed by a slow approach to equilibrium. Such sorption behavior is very similar to that of glassy polymers. Thus we have chosen to interpret the sorption curves shown in Figures 2 and 3 in terms of the Berens-Hopfenberg model developed for sorption of organic vapors into glassy polymers.⁽¹²⁾

The Berens-Hopfenberg Model. The Berens and Hopfenberg model considers the sorption process in glassy polymers as a linear superposition of independent contributions of a rapid Fickian diffusion into pre-existing holes or vacancies (adsorption) and a slower relaxation of the polymeric network (swelling). The total amount of sorption per unit weight of polymer may be expressed as

$$M_t = M_{t,F} + M_{t,R} \quad 2)$$

where $M_{t,F}$ and $M_{t,R}$ are the contributions of the Fickian and relaxation processes, respectively.

The relaxation or swelling process is assumed to be first order in the concentration difference which drives the relaxation and is expressed as

$$M_{t,R} = M_{\infty,R} [1 - \exp(-kt)] \quad 3)$$

where k is the relaxation rate constant and $M_{\infty,R}$ is the ultimate amount of sorption due to relaxation. The relaxation process is interpreted as a structural reordering

or swelling of the polymeric network. It is the swelling term which is of crucial importance to our study.

Interpretation of Sorption Curves. The slow asymptotic approach to equilibrium exhibited by the extract and O-methylated extract, as shown in Figures 2 and 3, strongly suggest that this process might correspond to the first-order relaxation or swelling process described in the Berens-Hopfenberg model, and that the initial rapid uptake may correspond to hole filling and/or adsorption onto surfaces. To test whether this slow process follows first-order behavior, we have plotted the natural log of the difference between the equilibrium sorption value, M_{∞} , and the sorption value at any time, M_t , against time. The results are shown in Figures 6 and 7. Note that a substantial portion of each curve is linear or nearly linear at long times, indicating a first-order process. This is particularly evident for the incremental sorption where linearity is observed over a 50 to 60 hour period. At short times, the curves clearly deviate from linearity, suggesting that other processes are dominating.

We suggest that the rapid process corresponds to hole-filling and/or adsorption onto external surfaces, and that the slow process, which follows first-order behavior, corresponds to swelling of the coal extract. Extrapolation of the linear portion of the curves shown in Figures 6 and 7 to time zero should yield the total uptake of benzene attributed to swelling. The results of this analysis are summarized in Table I, where the total benzene uptake, M_{∞} , and the uptake attributed to the hole-filling/adsorption and the swelling processes, M_{ads} and M_{swell} , are shown.

If this interpretation of the sorption process is correct, it indicates that when the benzene pressure is raised from zero to an activity of 0.22, the dominant process is hole-filling and/or adsorption, with only a relatively minor contribution from actual swelling. However, in subsequent incremental sorptions, the swelling process is clearly dominant. These results are similar to those of Berens and Hopfenberg in their studies on glassy polyvinylchloride.(12) According to their interpretation, the polymer is initially penetrant-free in an integral sorption experiment, and the hole-filling process therefore dominates. Incremental sorptions, however, proceed with polymer in which most of the sorption holes are pre-saturated. The relative contribution of swelling is therefore larger in these experiments.

The data in Table I also indicate that the O-methylated extract swells roughly one and a half times the extract. These results are consistent with those of Larsen et al.(6), who observed that O-methylated coals swell substantially more than underivatized coals.

The swelling data in Table I can be used to calculate χ parameters for the extract and O-methylated extract using Equation (1). A knowledge of the densities of the extracts is required to convert the masses to volume fractions. We have assumed densities of 1.4 and 1.3 g/mL for the extract and O-methylated extract, respectively. These are the helium densities (dmf basis) for the Illinois No. 6 coal and its O-methylated derivative as determined by Liotta.(10) A density of 0.88 g/mL for benzene was used. Additivity of volumes was also assumed. The results of these calculations are shown in Table II.

The χ parameters are observed to be positive and independent of vapor pressure (or concentration). According to Flory-Huggins theory, polymer-solvent systems with χ parameters above 0.5 should show only limited solubility.(2) Thus the extracts

should not dissolve in liquid benzene but should show limited swelling. Liquid volumetric swelling measurements verify this expectation. The bulk of both extracts remain insoluble in liquid benzene, although some dissolution occurs. Moreover, both extracts exhibit limiting swelling, with the O-methylated extract swelling more than the extract, consistent with the gravimetric data presented in Table I. χ parameters were calculated from the volumetric data assuming a p/p_0 of 1.0, and are shown in Table II. The volumetric method yields χ parameters consistent with those calculated from the gravimetric data.

Finally, a calculation of the solubility parameter of the extracts can be made using the equation

$$\delta_e = \left(\frac{(\chi - 0.30)RT}{V} \right)^{1/2} + \delta_s \quad (4)$$

where δ_e and δ_s are the solubility parameters of the extract and solvent, respectively, and V is the molar volume of benzene (89 mL/mol). Using a δ_s of 9.2 Hildebrands for benzene and a χ of 1.5 for the extract, δ_e of 12.0 Hildebrands is calculated for the extract. The same calculation using a χ of 1.1 for the O-methylated extract yields a δ_e of 11.5 Hildebrands. Van Krevelen has estimated solubility parameters of coals using a group contribution method and has calculated values ranging from 10.6 to 15.2 Hildebrands.(13) Thus the solubility parameters calculated for the extracts fall within the accepted range of solubility parameters for coals.

CONCLUSIONS

The sorption of benzene by an extract and O-methylated extract of an Illinois No. 6 coal is characterized by an initial, rapid uptake of solvent vapor, followed by a slow asymptotic approach to equilibrium. The slow process appears to follow first-order behavior. We have suggested that this slow, first-order process corresponds to the swelling of the extract. There are several lines of indirect evidence to suggest that this interpretation is correct.

- (1) The results show that the O-methylated extract swells more than the underivatized extract, consistent with other swelling studies.
- (2) The χ parameters calculated for the benzene-extract systems are consistent with the fact that the bulk of these extracts remain insoluble in liquid benzene. The extracts, however, exhibit limited swelling. The χ parameters calculated from the volumetric data are consistent with those derived from the gravimetric data.
- (3) The solubility parameters of the extracts calculated from the χ parameters fall within the accepted range of solubility parameters for coals.

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TABLE I

Benzene Sorption Data for Extract and O-Methylated
Extract of Illinois No. 6 Coal at 30°C

Pressure Interval <u>p/p₀</u>	Extract (mg/g)			O-Methylated (mg/g)		
	<u>M_a</u>	<u>M_{ads}</u>	<u>M_{swell}</u>	<u>M_a</u>	<u>M_{ads}</u>	<u>M_{swell}</u>
0 - 0.22	76	64	12	78	56	22
0.22-0.44	38	17	21	32	7	25
0.44-0.66	<u>34</u>	<u>12</u>	<u>22</u>	<u>50^a</u>	<u>6</u>	<u>44</u>
Total:	148	93	55	160	69	91

^a p/p₀ = 0.44 - 0.67

TABLE II

Volume Fractions of Solvent and χ Parameters
for the Extract and O-Methylated Extract of
Illinois No. 6 Coal and Benzene

p/p_0	Extract		O-Methylated	
	v_1	χ	v_1	χ
0.22	0.019	1.5	0.031	1.1
0.44	0.050	1.4	0.065	1.1
0.66	0.080	1.4	0.12	1.1 ^a
1.0 ^b	0.12	1.6	0.25	1.1

^a $p/p_0 = 0.67$

^b v_1 determined from direct volumetric swelling
method using liquid benzene.

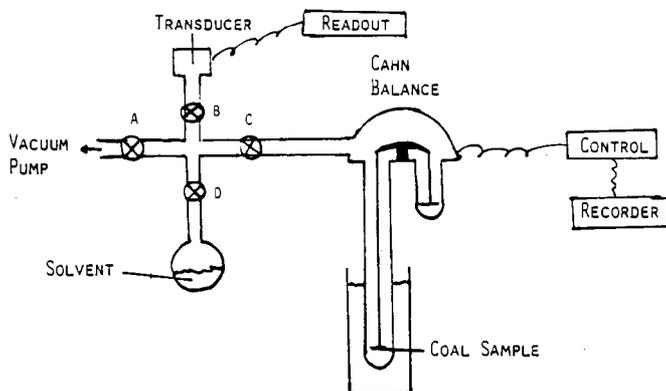


Figure 1. Sorption Apparatus

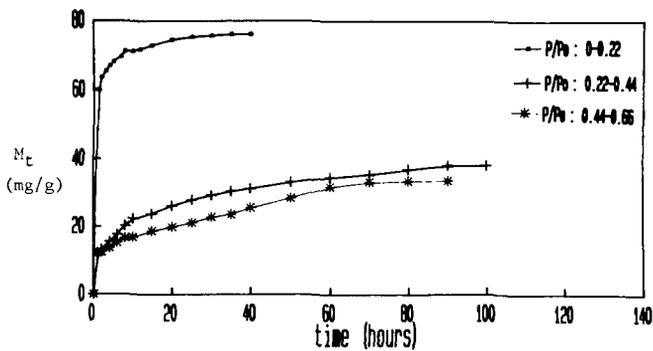


Figure 2. Sorption of Benzene by the Pyridine-Extract of Illinois No. 6 Coal at 30°C.

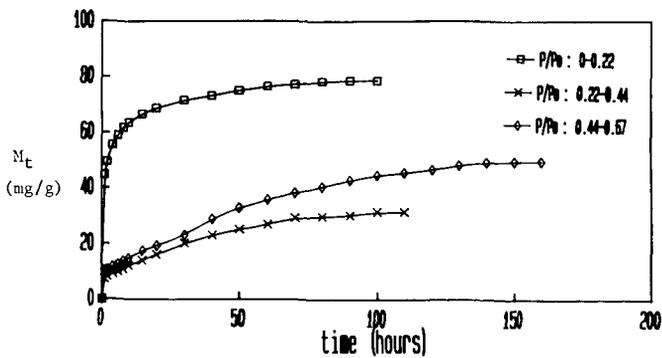


Figure 3. Sorption of Benzene by the O-methylated Extract of Illinois No. 6 Coal at 30°C.

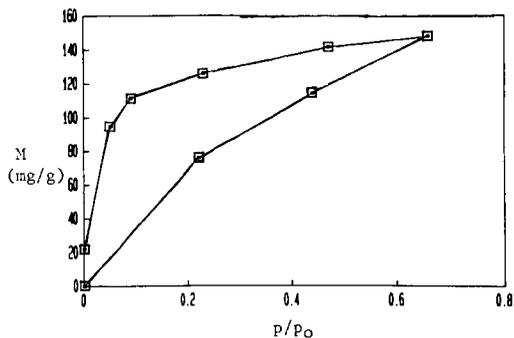


Figure 4. Sorption-desorption Isotherm for the Extract of Illinois No. 6 Coal and Benzene at 30°C.

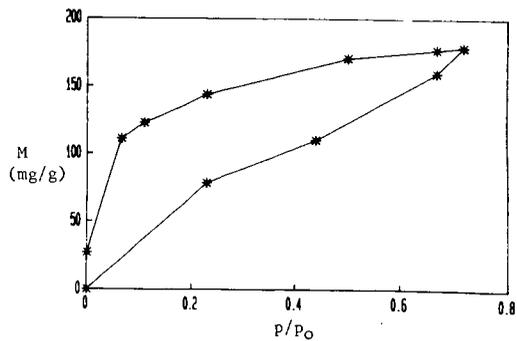


Figure 5. Sorption-desorption Isotherm for the O-methylated Extract of Illinois No. 6 Coal and Benzene at 30°C.

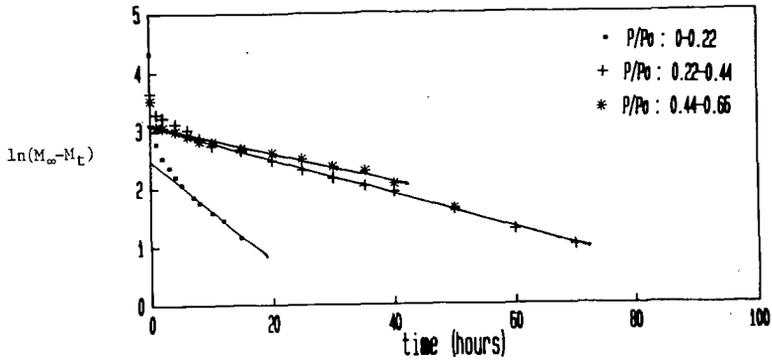


Figure 6. Plot of $\ln(M_\infty - M_t)$ versus Time for Extract-Benzene System.

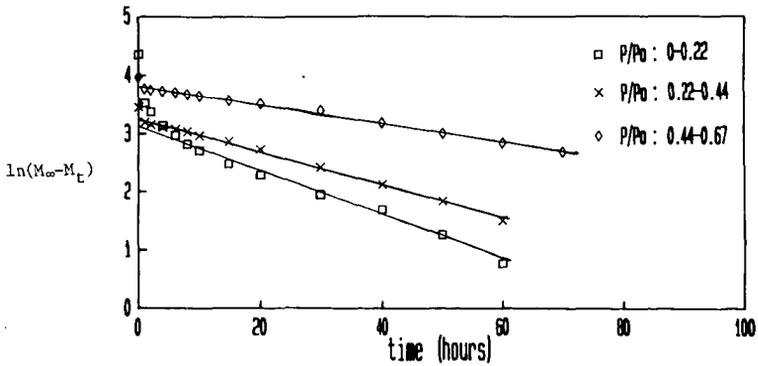


Figure 7. Plot of $\ln(M_\infty - M_t)$ versus Time for O-methylated Extract-Benzene System.