

## SOLVENT SWELLING OF COAL 1. DEVELOPMENT OF AN IMPROVED METHOD FOR MEASURING SWELLING PHENOMENA

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### INTRODUCTION

Although the polymeric nature of coal was established over a quarter of a century ago (1), many phenomena which derive from its cross-linked, macromolecular structure are still not well understood. This includes one of the most important aspects of coal chemistry, the accessibility of solvents and/or chemical reagents to sites buried within the solid coal matrix (2). Thus, the rate and extent of chemical conversion and/or solubilization of these interior sites are governed by penetration of the macromolecular structure by an appropriate chemical agent. Generally, penetration of cross-linked, macromolecular solids by organic chemicals has been investigated using swelling techniques.

The swelling induced by contacting coal with organic solvents has been investigated intensively in recent years; and several convenient methods using both liquids and saturated vapors have been developed for measuring coal swelling properties (3). The liquid phase swelling behavior is particularly interesting because it is a reasonable measure of a solvent's ability to penetrate the coal matrix. Previously, investigators of this phenomenon have utilized some variation of the test tube technique developed by Dryden (4). In this method, the initial height of a dry coal bed,  $h_i$  is compared to the final swollen height,  $h_f$ , after equilibration with solvent. These values are used to compute the equilibrium swelling ratio,  $Q = h_f/h_i$ , for each solvent.

However, the accuracy of this method is not satisfactory, particularly at lower ( $Q < 1.3$ ) and higher ( $Q > 3.0$ ) swelling ratios; and it is also quite difficult to investigate dynamic swelling behavior. Moreover, the  $Q$ -value reflects not only interactions between solvent and coal, but is also grossly affected by complicated elastic restoring forces in the coal network due to covalent bond cross-linking, hydrogen bonding, or  $\pi-\pi$  interactions between condensed aromatics. On the other hand, initial swelling rates may isolate interactions between solvent and coal by minimizing the involvement of such complicated restoring forces.

On the basis of these considerations, we have developed a new method for the dynamic measurement of liquid phase solvent swelling phenomena which is 100 times more accurate than conventional methods. We have used this technique to determine  $Q$ -values and initial swelling rates for Illinois No. 6 Coal with a variety of solvents. Here we present our initial experimental results and compare these findings with those obtained using conventional methods.

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## EXPERIMENTAL

### Materials

Illinois No. 6 Coal from the Ames Laboratory Coal Library was used in these studies. This coal has the following ultimate analysis (dmmf basis): 78.82% C; 5.50% H; 1.59% N; 2.29% S<sub>org</sub>; and 10.05% ash. Prior to use, this coal was ground, sized, and dried at 110°C overnight under vacuum. Except for commercial "Gold Label Grade" reagents (Aldrich Co.) which were used without further purification, solvents were distilled by ordinary procedures before use.

### Apparatus

As shown in Figure 1, this apparatus is similar in principle to an osmotic pressure measurement device, except that coal and solvent are separated by 10  $\mu$  stainless steel filter. In each experiment, the movement of the piston as a function of time was recorded; and the initial swelling rate ( $V_i$ ) was determined graphically as shown in Figure 1. The Q-value was calculated by dividing the final volume,  $S_0 + \Delta S$ , by the initial volume,  $S_0$ .

### General Procedure

In a typical experiment, 500 mg. of Illinois No. 6 Coal was placed in the cylinder bottom and covered by the piston. The pressure on the piston was adjusted to 5.0 g/cm<sup>2</sup> and was maintained at this level throughout the experiment. After positioning the piston, the entire system was evacuated to 0.20 - 0.15 mm Hg for 10 minutes. The valve of the solvent container was then opened allowing the solvent to contact the coal; and the movement of the piston was recorded as a function of time.

## RESULTS AND DISCUSSION

### Comparison of New Method and Conventional Method

Conventional swelling measurements were carried out using a 10 mm x 75 mm test tube, 2.0 g of Illinois No. 6 Coal, and 8.0 ml. of THF. The height of coal bed was read at five minute intervals after shaking the mixture vigorously each time. As shown in Figure 2, there is an interesting contrast in swelling behavior as measured by the two methods. In the case of the conventional method, the rate is retarded in the early stages of swelling, possibly because many pores are filled with air and the solvent cannot achieve intimate contact with the coal surface during this initial stage.

For the more interactive solvents, a higher Q-value was observed using the new method. This is probably because, in contrast to the conventional method, there is no mechanical agitation of the coal bed; and the integrity of the coal bed is thus maintained throughout the swelling measurement. In support of this hypothesis, the new apparatus was found to be quite sensitive to mechanical shock which usually resulted in an instant drop in the reading.

### Sensitivity of New Method

In a 500 mg. experiment, our new apparatus can detect a volume change of  $10^{-4}$  ml, that is the Q-value can be determined to  $\pm 0.0001$ . However, for practical reasons, we prefer to report the data to  $\pm 0.01$  Q-value units. Typical Q-values measured by this method are included in Table I along with data obtained by conventional measurements.

Table I. Comparison of Methods for Measuring Q-values<sup>a</sup>

SOLVENT	Benzene	Toluene	p-Xylene	Methanol	THF	$0.5N^b$ $Bu_4NOH$
$Q_N^c$	1.04	1.06	1.06	1.24	2.20	4.15
$Q_C^d$	~1.3	~1.3	~1.3	1.4	1.8	--

- Illinois No.6 Coal measured at 21.0°C
- Solution in pyridine/methanol (1:1 vol.)
- Present method
- Conventional method

Our new method exhibits some obvious advantages, both at lower and higher swelling conditions, which will allow us to examine subtle differences in swelling behavior. An interesting contrast in the two methods is found in the relative Q-values for methanol and hydrocarbons. The reason for the difference is not clear at the present time, but may involve non-swelling volume increase processes like particle-particle repulsions. In the new method such forces are apparently overcome by the pressure of the piston. At the other extreme,  $Q = 4.15$  for the tetrabutyl ammonium hydroxide solution is the highest swelling ratio which we have ever measured for Illinois No. 6 Coal.

### Determination of Initial Swelling Rate

In order to evaluate the capability of this method for investigating kinetic phenomena, several experiments were conducted. The effect of particle size on coal swelling rates was first examined. As expected, swelling rates are very sensitive to particle size. As shown in Figure 3, 200 x 400 mesh Illinois No. 6 Coal swells in THF at approximately 10 times the rate of 25 x 60 mesh coal. The temperature dependence of the THF-coal interaction in the range of 20 to 40°C was also examined. Interestingly, the Q-value was not affected by temperature, while the initial swelling rate increased by 15% for each 10°C increase (see Figure 4).

Although the actual penetration of the solvent and/or chemical reagent will not always be reflected by the Q-value or initial swelling rate, we believe that they provide a quite useful basis for designing chemical conversions or extractions of coal. One such basis for evaluating solvents is presented in Table II. Here, the swelling rates of common solvents; including some hydrogen donor solvents, are compared using a new parameter,  $\tau_{10}$ , which is defined as the time which would be necessary to swell the initial volume by 10%. This value is calculated on the basis of the initial swelling rate.

Table II. Comparison of Swelling Rates Using  $\tau_{10}$ <sup>a</sup>

Solvent	$\tau_{10}$	Solvent	$\tau_{10}$
n-Propylamine	10 sec.	Benzene	1.7 hrs.
Pyridine	48 sec.	Quinoline	5.0 hrs.
DMSO <sup>b</sup>	1.8 min.	Indoline	16.6 hrs.
THF <sup>c</sup>	1.6 min.	THQ <sup>d</sup>	2.0 mos.
Acetone	2.7 min.	Tetralin	>1.0 year
Methanol	3.1 min.		
Dichloromethane	4.7 min.		

a. Illinois No.6 Coal, 60 x 100 mesh, measured at 21°C.

b. Dimethylsulfoxide

c. Tetrahydrofuran

d. 1,2,3,4-Tetrahydroquinoline

Relation Between Initial Swelling Rate ( $V_i$ ) and Q-Value

Prior to undertaking these experiments, we expected a direct relationship between Q-values and  $V_i$ 's because we understood that both are a measure of the relative affinity of solvent for coal. The results obtained are presented in Table III.

Table III. Comparison of Q-Value and  $V_i$ <sup>a</sup>

SOLVENT	Q-Value	$V_i \times 10^2$
Methanol	1.24	3.2
CH <sub>2</sub> Cl <sub>2</sub>	1.23	2.1
Acetone	1.50	3.7
THF	2.20	6.2
Quinoline	2.35	0.03
n-Propylamine	2.45	58.6
NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	2.60	46.4
DMSO	2.80	4.8
Pyridine	2.90	12.5

a. Illinois No.6 Coal, 60 x 100 mesh, measured at 21°C.

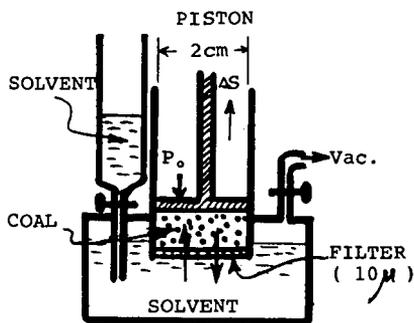
We are puzzled by the lack of correlation between  $V_i$  and Q-value. However, two possible explanations come to mind. Initial swelling rates could be more sensitive than Q-values to solvent viscosities and steric requirements. A more detailed study of these factors, especially steric requirements for solvent swelling of coal, will be presented in the next paper.

ACKNOWLEDGEMENTS

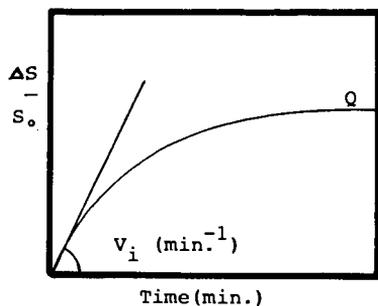
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$P_0$ : Initial Pressure  
 $\Delta S$ : Increased Volume



$S_0$ : Initial volume of coal  
 $V_i$ : Initial swelling rate

Figure 1. Method for Measuring Liquid Phase Solvent Swelling of Coal.

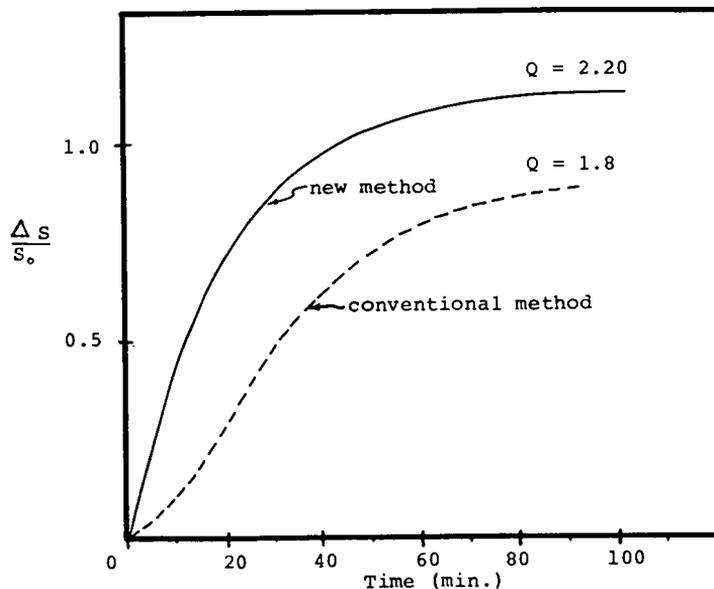


Figure 2. Comparison of THF Swelling Patterns for Illinois No. 6 Coal at 21.0°C.

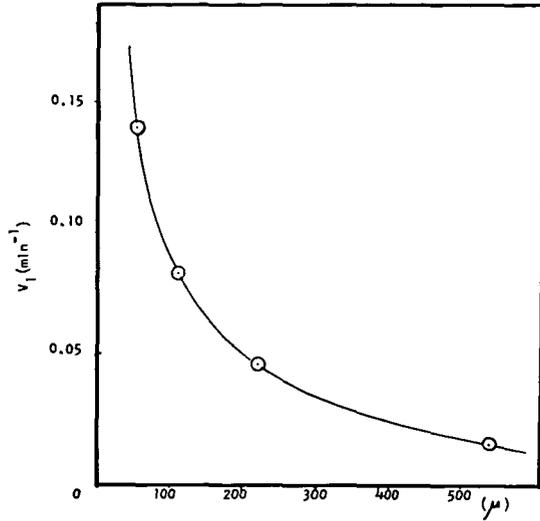


Figure 3. Effect of Particle Size on Initial THF Swelling Rate of Illinois No. 6 Coal (21.0°C).

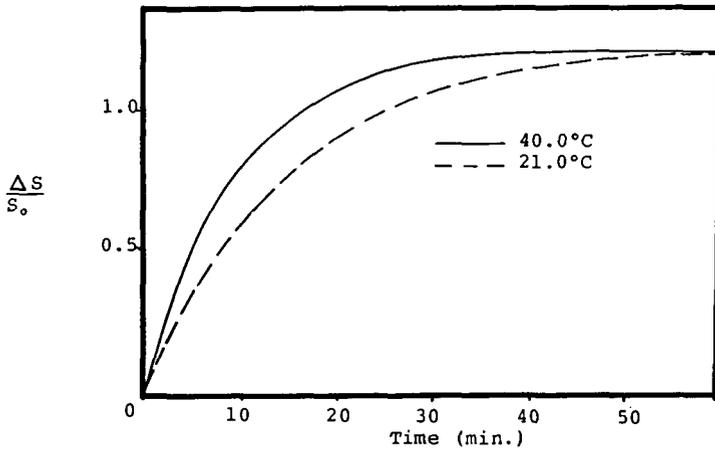


Figure 4. Temperature Effect on THF Swelling Behavior of 60 x 100 mesh Illinois No. 6 Coal