SOLVENT SWELLING OF COAL 2. INVESTIGATION OF STERIC REQUIREMENTS

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INTRODUCTION

Some time ago it was established that, as a solid, microporous material, coal behaves as a molecular sieve (1), i.e. it discriminates among molecules diffusing into the pore system on the basis of size, shape, and functionality. It seems to us that the process by which solvent molecules penetrate the solid coal matrix should be similarly selective. The investigation of such phenomena is important, not only from the perspective of understanding the accessibility of chemical agents to sites within the coal matrix (2), but for the rational design of chemical conversion processes.

Recently, we developed a new method for accurately measuring both the dynamic and equilibrium solvent swelling behavior of coal (3). Here, we report the initial application of these techniques to the investigation of accessibility phenomena. From this study, which examines the steric interactions between solvent and coal, we expect to obtain a better understanding of the mechanism by which chemical agents penetrate the coal matrix.

EXPERIMENTAL

The swelling measurements were carried out as described in the previous paper (3); and the initial swelling rates were determined graphically. All coals used in these studies were from the Ames Laboratory Coal Library. Prior to use, the coals were ground, sized to 100 x 200 mesh, 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.

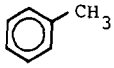
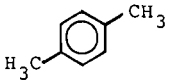
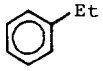
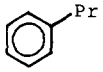
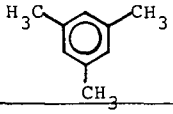
RESULTS AND DISCUSSION

Swelling of Illinois No. 6 Coal in Hydrocarbon Solvents

The swelling data obtained with hydrocarbon solvents are shown in Table I. There apparently is no simple relationship between the initial swelling rate, V_i, and the equilibrium swelling ratio, Q, for this series of solvents. Neither is there an obvious relationship between viscosity and swelling behavior. However, with the exception

*Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

Table I. Swelling Behavior of Illinois No. 6 Coal in Hydrocarbons[a]

Hydrocarbon	Q	V_{Ret}[b]	η_{20}
	1.04	1.00[c]	0.65
	1.06	0.40	0.59
	1.06	1.18	0.65
	--	4.00	0.69
	--	16.7	--
	--	30	--

a. 100-200 mesh, measured at 21.0°C
b. Rate Retardation Factor: V_i(benzene)/V_i(hydrocarbon)
c. $V_i = 2.73 \times 10^{-4}$ min.$^{-1}$

of toluene which initially swells about 2.5 times as fast as benzene, the sharp decrease in V_i from benzene to mesitylene suggests that there is a steric component to the rate constant for solvent penetration of the coal matrix.

Solvent Swelling Behavior of Illnois No. 6 Coal in Alcohols

The initial swelling rates (V_i) and equilibrium swelling ratios (Q) were measured for C_1 through C_4 alcohols, and the results are summarized in Table II. Except for methanol, Q-values for the unbranched primary alcohols were almost identical, while, with increasing chain length, a twelve-fold decrease in initial swelling rates was noted for this series. Although the latter behavior is consistent with that predicted on the basis of steric considerations, it is also consistent with the trend in solvent viscosities.

However, comparison of the initial swelling rates of n-propyl and isopropyl alcohol reveals a rate retardation factor (V_{Ret}) of 4 for the branched isomer despite almost identical viscosities. Similar behavior is exhibited by the butyl alcohol series: compared to n-butyl alcohol, the initial swelling rates of isobutyl and sec-butyl alcohol are retarded by factors of 9 and 40, respectively. These large effects cannot be rationalized on the basis of viscosities.

Table II. Swelling Behavior of Illinois No. 6 Coal in Alcohols[a]

Alcohol	Q	V_{Ret}[b]	η_{20}
MeOH	1.23	1.00[c]	0.60
EtOH	1.34	1.92	1.2
n-PrOH	1.36	3.96	2.3
i-PrOH	--	14.18	2.3
n-BuOH	1.34	12.17	2.9
i-BuOH	--	103.4	4.2
s-BuOH	--	499.0	3.9

a. 100-200 mesh, measured at 20.0°C
b. Rate Retardation Factor: V_i(methanol)/V_i(alcohol)
c. $V_i = 3.18 \times 10^{-2}$ min.$^{-1}$

Solvent Swelling Behavior of Illinois No. 6 Coal in Amines

The swelling behavior of Illinois No. 6 Coal in various aliphatic amines was also examined. Once again, we can ascertain no significant differences among the Q-values for the entire series of amines. On the other hand, initial swelling rates for this series vary over a range of 10^6 and provide an unambiguous basis for establishing the importance of steric requirements. In fact, the evidence is so compelling that the results are simply reported, with minimum discussion, in Tables III-VI.

Table III. Swelling Behavior in Primary Amines.[a] Effect of Chain Length.

Structure	Q	V_{Ret}[b]
$CH_3CH_2CH_2NH_2$	2.45	1.00[c]
$CH_3(CH_2)_2CH_2NH_2$	2.64	2.05
$CH_3(CH_2)_4CH_2NH_2$	2.19	9.31

a. Illinois No. 6 Coal (100 x 200 mesh), measured at 21.0°C
b. Rate Retardation Factor: V_i(n-Propylamine)/V_i(amine)
c. $V_i = 5.86 \times 10^{-1}$ min.$^{-1}$

Table IV. Swelling Behavior in Primary Butyl Amines.[a] Effect of Chain Branching

Structure	Q	V_{Ret}[b]
$CH_3(CH_2)_2CH_2NH_2$	2.64	1.00
$(CH_3)_2CHCH_2NH_2$	2.46	4.38
$(CH_3)_3CNH_2$	1.95	732

a. Illinois No. 6 Coal (100 x 200 mesh), measured at 21.0°C
b. Rate Retardation Factor: V_i(n-Butylamine)/V_i(amine)

Table V. Swelling Behavior in $C_6H_{13}N$ Amines.[a] Comparison of Primary, Secondary and Tertiary Isomers

Structure	Q	V_{Ret}[b]
$CH_3(CH_2)_4CH_2NH_2$	2.19	1.00
$(CH_3CH_2CH_2)_2NH$	2.05	15.4
$(CH_3CH_2)_3N$	--	1.5×10^5

a. Illinois No. 6 Coal (100 x 200 mesh), measured at 21.0°C
b. Rate Retardation Factor: V_i(n-Hexylamine)/V_i(amine)

Table VI. Swelling Behavior in Secondary $C_6H_{13}N$ Amines.[a] Effect of Chain Branching.

Structure	Q	V_{Ret}[b]
$(CH_3CH_2CH_2)_2NH$	2.05	1.00
$\left[(CH_3)_2CH\right]_2NH$	--	1830

a. Illinois No. 6 Coal (100 x 200 mesh), measured at 21.0°C
b. Rate Retardation Factor: V_i(Di-n-Propylamine)/V_i(amine)

The nature and divergency of these comparisons leave little doubt that steric factors play an important role in coal accessibility phenomena and can provide answers to a number of troublesome questions. For example, the lack of coal solubility in solvents such as triethyl amine and hexamethyl phosphoramide (HMPA), which (because of their "solubility parameters") should be good solvents (4), is clearly consistent with steric inhibition of coal matrix penetration by these hindered solvents.

Effect of Coal Rank on Solvent Swelling Behavior

In a final series of experiments, the rank dependent solvent swelling behavior of coals in three isomers of primary butyl amine was investigated. While we found small differences in the equilibrium swelling ratios for various coal/amine systems, we can detect no systematic relationship between rank and Q-values; and we have focused our attention on initial swelling rates. In order to correlate this data, we have defined two swelling parameters,

$$\Theta_s = V_n/V_s \qquad \text{and} \qquad \Theta_t = V_n/V_t$$

where Θ_s and Θ_t represent the steric sensitivity of coal toward secondary and tertiary branching in the butylamine isomers, and V_n, V_s, and V_t are the initial swelling rates of coal in n-butylamine, sec-butylamine, and t-butylamine, respectively. These rate parameters, analogous equilibrium parameters, and carbon contents of the coals used in these studies are presented in Table VII.

Table VII. The Effect of Coal Rank on Steric Sensitivity.

Coal[a,b]	C(%, dmmf)[c]	θ_s	$\theta_t \times 10^3$	Q_n/Q_s[d]
A	72.2	18.8	--	1.136
B	72.2	17.3	60.8	1.120
C	74.8	10.3	0.83	1.078
D	80.4	4.5	0.62	1.073
E	82.4	10.89	4.7	1.083
F	84.9	19.16	--	1.040

a. 100-200 mesh, measured at 21.0°C
b. A: Hanna No. 80; B: Dietz No. 1 & 2; C: Adaville No. 11; D: Illinois No. 6; E: West Kentucky No. 9; F: Pittsburgh No. 8
c. mm = 1.08 Ash + 0.55 S
d. Q_n: Q-value in n-butylamine; Q_s: Q-value in sec-butylamine

We have plotted θ_s versus carbon content for the six coals used in this investigation. There appears to be some relaxation of steric requirements around 80% carbon content. While it is too early to speculate about the underlying basis for this behavior, we believe that it is related to the balance between covalent and non-covalent (hydrogen bonded) crosslinking (4). Investigation of these phenomena will be the target of future efforts.

ACKNOWLEDGEMENTS

We wish to thank Professors R. S. Hansen and D. K. Finnemore for their useful discussion and encouragement. We are grateful for support from The State of Iowa, and from the U. S. Department of Energy through the Ames Laboratory under Contract No. W-7405-ENG-82. The opinions, findings, and conclusion expressed herein are those of the authors, and do not necessarily reflect the views of DOE or the State of Iowa.

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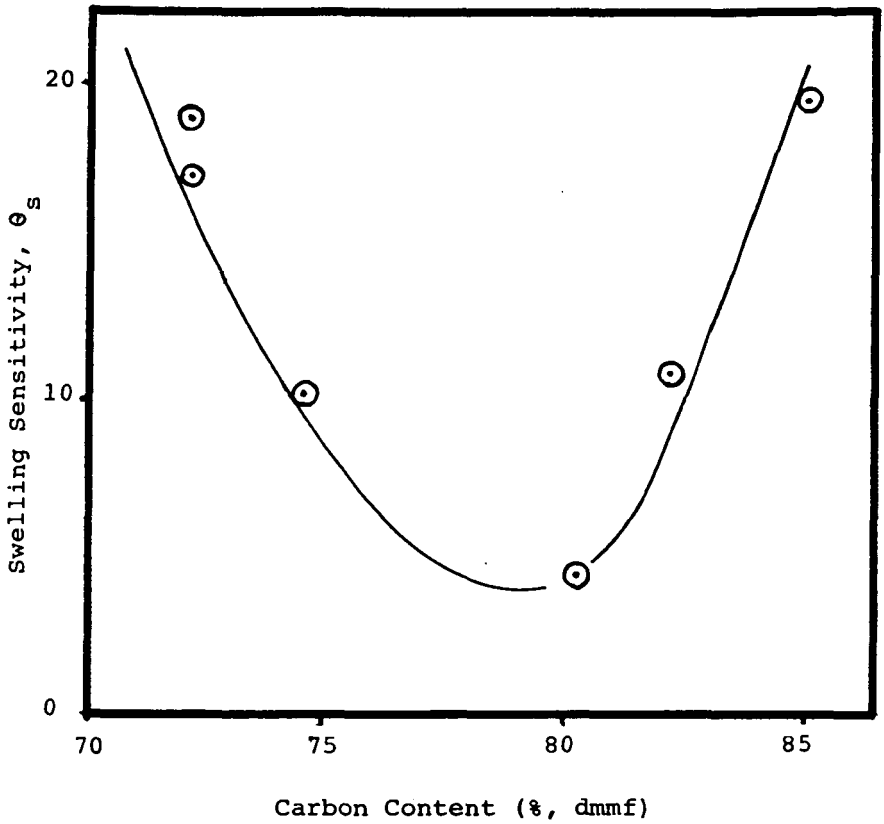

Figure 1. Dependence of Swelling Sensitivity on Coal Rank.