Coal Swelling in n-Amines and n-Alcohols

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Introduction. Recent studies of the solvent swelling of coals have yielded considerable insight into their macromolecular structure.(1-6) It is becoming increasingly evident that hydrogen bond crosslinks play a central role in the swelling behavior of many coals. Larsen and co-workers, for example, demonstrated that the degree of swelling of two bituminous coals in good nonpolar solvents increases in the order unextracted < pyridine-extracted < O-methylated and O-acetylated.(6) This order is attributed primarily to the progressive disruption of the hydrogen bond crosslinks in the coal. The unextracted coal contains many hydrogen bond crosslinks and since the nonpolar solvent cannot disrupt them, the swelling remains low. The pyridine-extraction serves to only partially disrupt the crosslinks. The crosslinks are absent in the chemically-modified coals, and these coals can expand to contain the solvent. Their ultimate dissolution is prevented by the presence of covalent crosslinks.

The swelling of coals in polar solvents has also been studied extensively.(1-5, 7,8) Polar solvents are capable of interacting specifically with polar functional groups in the coal. Amines are particularly effective, with the coal often doubling in volume upon exposure to solvent. Brenner, for example, exposed a thin section of Illinois No. 6 coal to vapors of n-propylamine.(1) The sample approximately doubled in size, and the process was found to be highly reversible. The coal was also found to be highly flexible in the swollen state. This flexibility is attributed primarily to the breaking of coal-coal hydrogen bonds (i.e. crosslinks) by the n-propylamine during the swelling process.

Brenner's results suggest that the n-propylamine is hydrogen bonding to specific sites within the Illinois No. 6 structure. If so, we thought the number of sites might be quantified by solvent swelling measurements. We extended the study to include other n-alkylamines to see if they might behave similarly to n-propylamine. The results on four different coals are presented and contrasted with those using n-alkylalcohols as swelling solvents.

Experimental.

Swelling Measurements. All solvents were purified according to standard methods.(9) The experimental technique has been previously described.(10) Briefly, about 100-200 mg of dry coal was placed in a 7 mm o.d. Pyrex tube sealed on one end. The coal was centrifuged at 1750 rpm for 5 minutes and the height of coal in the tube was measured as h_1. Excess solvent (3-4 mL) was added to the tube, which was sealed with a rubber stopper and immediately shaken. Periodically, the tube was shaken and centrifuged again for 5 minutes. The height of swollen coal was measured as h_2. The degree of swelling was calculated as Q, the swelling ratio.

$$Q = h_1/h_2 = \frac{\text{volume of swollen coal}}{\text{volume of unswollen coal}} \qquad 1)$$

The measurements were continued until no further change in Q occurred during a two week period. All swelling measurements were conducted at ambient temperature.

Coal Analyses. The four coals used in the study were dried under vacuum at 110°C for 24 hrs prior to swelling. Their elemental analyses on a dry, mineral-matter-free basis are presented in Table I.

TABLE I

Elemental Analyses of Coals (Wt %)

Coal	C	H	N	S_{org}	O[a]	Mineral Matter
Wyoming Rawhide	72.3	5.2	0.95	0.51	21.0	7.5
Texas lignite	70.6	5.5	1.3	1.2	21.4	8.3
Illinois No. 6	78.9	5.6	1.4	3.4	10.7	14.0
Bruceton	85.4	5.7	1.5	0.7	6.7	6.1

[a] by difference

Results.

Swelling in n-Alkylamines. A series of n-alkylamines were used as swelling solvents for the various coals. The swelling ratios are presented in Table II. Each value represents the average of 3 or 4 measurements and the reproducibility was on the order of ±3 percent. The pyridine-extracted (Soxhlet) Illinois No. 6 and Rawhide coals were also studied to determine what effect the extraction process might have on the equilibrium swelling ratios. The extractabilities were found to be 18.3 percent and 5.8 percent for the Illinois No. 6 and Rawhide coals, respectively.

The calculated amounts (mmoles) of solvent absorbed per g of dmmf coal are also presented in Table II. The values were calculated according to the equation

$$\frac{\text{mmoles absorbed}}{\text{g of dmmf coal}} = \frac{(Q - 1)}{\rho \ V} \times 1000 \qquad 2)$$

where Q is the swelling ratio, V is the molar volume of the solvent at 25°C, and ρ is the density of the coal. A value of 1.3 g/mL was assumed for the density of all coals. This calculation assumes additivity of volumes between coal and solvent. This assumption was not tested.

TABLE II

Swelling Data of n-Alkylamines and Four Coals

	Bruceton		Illinois No. 6			
	Unextracted		Unextracted		Extracted	
Solvent	Q	mmoles abs / g dmmf coal	Q	mmoles abs / g dmmf coal	Q	mmoles abs / g dmmf coal
n-propylamine	1.80	7.5	2.04	9.7	2.21	11.3
n-butylamine	2.09	8.5	2.23	9.6	2.25	9.8
n-hexylamine	2.32	7.7	2.72	10.0	2.62	9.4
n-octylamine	2.61	7.5	2.94	9.0	2.79	8.3
Average:		7.8		9.6		9.7

	Big Brown		Rawhide			
	Unextracted		Unextracted		Extracted	
Solvent	Q	mmoles abs / g dmmf coal	Q	mmoles abs / g dmmf coal	Q	mmoles abs / g dmmf coal
n-propylamine	2.64	15.3	2.30	12.2	2.22	11.4
n-butylamine	2.94	15.1	2.44	11.2	2.34	10.4
n-hexylamine	3.27[a]	13.2[b]	3.03	11.8	2.74	10.1
n-octylamine	3.14[a]	10.0[b]	3.14[a]	10.0[b]	3.08[a]	9.7[b]
Average:		15.2		11.2		10.6

[a] Not at equilibrium after 1200 hrs.

[b] Excluded from average because swelling had not reached equilibrium.

Swelling in n-Alkyl Alcohols. A series of n-alkyl alcohols were used to swell the Bruceton and Big Brown coals so that the results could be compared with those using the n-alkylamines as swelling solvents. The swelling ratios and the amounts absorbed by the coals are presented in Table III.

TABLE III

Swelling Data for n-Alkyl Alcohols and Two Coals

	Bruceton Unextracted		Big Brown Unextracted	
Solvent	Q	mmoles abs / g dmmf coal	Q	mmoles abs / g dmmf coal
methanol	1.18	3.4	1.67	12.7
n-propanol	1.20	2.6	1.69	9.0
n-butanol	1.21	2.2	1.66	6.8
n-hexanol	1.20	1.2	1.33	2.0
n-octanol	1.22	1.1	1.30	1.5

Discussion.

Swelling in n-Alkylamines. The degree of swelling of each coal is observed to increase linearly with increasing size of the amine. This result is shown in Figure 1, where Q is plotted against the molar volume of the solvent. Bruceton coal swells the least in each solvent, whereas Big Brown lignite swells the most. (Note that some Q values were omitted from Figure 1 since they were not equilibrium values).

As shown in Table II, each coal absorbs nearly a constant amount of each amine. This result suggest that the amines are binding to specific sites within the coal, and that each amine, regardless of its size, has equal accesibility to the binding sites. The degree of swelling increases with increasing chain length of the amine because the coal network must expand more to accommodate the larger alkyl groups.

The amines are probably interacting through hydrogen bonding with oxygen functionalities in the coals, since oxygen is the most abundant heteroatom in the coals and the amines are known to be strong hydrogen bonding solvents. If this is true, then the amounts of amine absorbed by the coals should roughly correlate with the oxygen contents of the coals. This general trend is observed, with the amounts of amine absorbed by the coal increasing in the order Bruceton $<$ Illinois No. 6 $<$ Rawhide $<$ Big Brown lignite. The amines are probably hydrogen bonding to phenolic hydroxyl groups in the coal. However, the amounts absorbed by the coals exceed the number of phenolic hydroxyl groups known to be present in the coals. For example, Illinois No. 6 and Rawhide coals are reported to contain approximately 3 and 5 mmoles hydroxyl groups per g of dmmf coal.(11,12) These amounts are much less than the amounts of amine absorbed by the coals (see Table II). Apparently, the amines are interacting with other sites in the coals as well. These sites may include ether and carboxylic functional groups, which are known to be present in coals.

Although a detailed kinetic study was not undertaken, approximate times to equilibrium swelling were measured for some coals and solvents. Equilibrium times varied dramatically, depending upon both coal and solvent. These results are presented in Table IV for three coals and n-butyl- and n-octylamine. The coals reached equilibrium much faster in n-butylamine than in n-octylamine. The bulky octyl group apparently prevents rapid diffusion of the amine into the coal network. The equilibrium times in n-octylamine increase in the order Illinois No. 6 $<$ Rawhide $<$ Big Brown. The n-octylamine-Big Brown system was still not at equilibrium after 1200 hrs, demonstrating that coal swelling can be an extraordinarily slow process.

TABLE IV

Approximate Swelling Times for
n-Butylamine and n-Octylamine and Three Coals

Solvent	Illinois No. 6	Rawhide	Big Brown
n-butylamine	1 hr	1 hr	5 hrs
n-octylamine	5 hrs	170 hrs	1200 hrs[a]

[a] Not at equilibrium after 1200 hrs.

Finally, pyridine-extracted Illinois No. 6 and Rawhide coals were also studied to determine what effect the extraction process has on the equilibrium swelling ratios. The results in Table II reveal that the extracted coals swell to nearly the same degree as the unextracted coals, with nearly the same average amounts of amine being absorbed. The results suggest that the amines are interacting with the unextracted and extracted coals in a similar fashion, and that the binding sites within the coals are equally accessible to the amines.

Swelling in n-Alkyl Alcohols. Bruceton coal and Big Brown lignite were swollen in a series of n-alkyl alcohols in order determine if they behaved similarly to the amines. As shown in Figure 1, the swelling ratios remain constant at about 1.2 for the Bruceton coal, regardless of the size of the alcohol. For Big Brown lignite, three of the smaller alcohols give swelling ratios of 1.65. The swelling drops off for n-hexyl alcohol and n-octyl alcohol, suggesting that these swelling ratios are not yet at equilibrium. As with the amines, the alcohols swell the lignite more than the Bruceton coal.

The amounts of alcohol absorbed are seen to decrease with increasing size of the alcohol as shown in Table III. Thus the alcohols do not have equal accessibility into coal network, in contrast to the amines. These results are consistant with calorimetry studies of Wightman and Widyani, who measured the heats of immersion of a Pocahontas No. 3 coal in series of n-alkyl alcohols.(13) They observed the heats of immersion to decrease with increasing size of the alcohol, and concluded that the smaller alcohols were able to penetrate the coal structure more easily than the larger alcohols.

The different behaviors of the amines and the alcohols toward the coals must be related to the strengths of the coal-solvent interactions. The amines interact much more strongly with the coals than the alcohols because the degree of swelling is much greater in the amines. The amines can be expected to disrupt coal-coal hydrogen bond crosslinks and, by doing so, the coal will be much more flexible. The coal is then able to expand to contain even the large n-octylamine. The alcohols apparently lack this ability to disrupt the hydrogen bond crosslinks since the amounts absorbed by the coals decrease with increasing size of the alcohol instead of remaining constant.

Conclusion. The swelling of four different coals in series of n-alkylamines and n-alkyl alcohols were measured. For the amines, the amounts absorbed by the coals remains constant among the series, suggesting that the amines are binding to specific sites within the coal network. Thus, the principal driving force for the swelling process is enthalpic in nature for these solvents. The alcohols behave quite differently toward the coals, with the amounts absorbed by the coal decreasing with increasing size of the alcohol. This difference in behavior is attributed primarily to the inablity of the alcohol to disrupt the hydrogen bond crosslinks of the coal network.

The swelling ratios of the coals in other larger n-alkylamines can be predicted from the results presented in Figure 1. For example, Big Brown lignite and Bruceton coal are predicted to have Q values of 7.8 and 3.5, respectively, in octadecylamine. However, the swelling process will probably be extraordinarily slow in this solvent, possibly requiring several months or years to reach equilibrium at room temperature.

The covalently crosslinked nature of the coal may also place a limitation on how much it will swell in larger n-alkylamines. For example, the lignite must expand to nearly 8 times its original volume in order to accommodate the predicted amount of octadecylamine. The existence of covalent crosslinks may prevent this degree of expansion. The swelling ratio may, in fact, level off at some critical amine size. Several factors will probably play a role in determining this critical size, including the strength of the coal-solvent interaction, the population of the oxygen functionalities in the coal, the covalent crosslink density of the coal, and the flexibility of the macromolecular chains.

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References

(1) D. Brenner, Fuel 1984, 63, 1325.
(2) D. Brenner, Fuel 1985, 64, 167.
(3) N. A. Peppas, L. M. Lucht, M. E. Hill-Lievense, and D. T. Hooker, "Macromolecular Changes in Bituminous Coal During Extraction and Solubilization," Final Technical Report, Contract No. DE-F22-80PC30222, PETC, Department of Energy, 1983.
(4) H. P. Hombach, Fuel 1980, 59, 465.
(5) J. R. Nelson, O. P. Mahajan, and P. L. Walker, Jr., Fuel 1980, 59, 831.
(6) T. K. Green, J. W. Larsen, and I. C. Chiri, Proc. Int. Conf. Coal Sci. 1983, 277.
(7) N. Y. Kirov, J. M. O'Shea, and C. D. Sergeant, Fuel 1967, 43, 615.
(8) Y. Sanada and H. Honda, Fuel 1967, 46, 451.
(9) D. D. Perrin, W. L. F. Armarego, and P. R. Perrin, "Purification of Laboratory Chemicals," 2nd Ed., Pergamon Press, 1980.
(10) T. K. Green, J. Kovac, J. W. Larsen, Fuel 1985, 63, 935.
(11) R. Liotta, K. Rose, and E. Hippo, J. Org. Chem. 1981, 46, 277.
(12) R. Liotta, G. Brons, J. Am. Chem. Soc., 1981, 103, 1735.
(13) E. Widyani and J. P. Wightman, Coll. Surf. 1982, 4, 209.

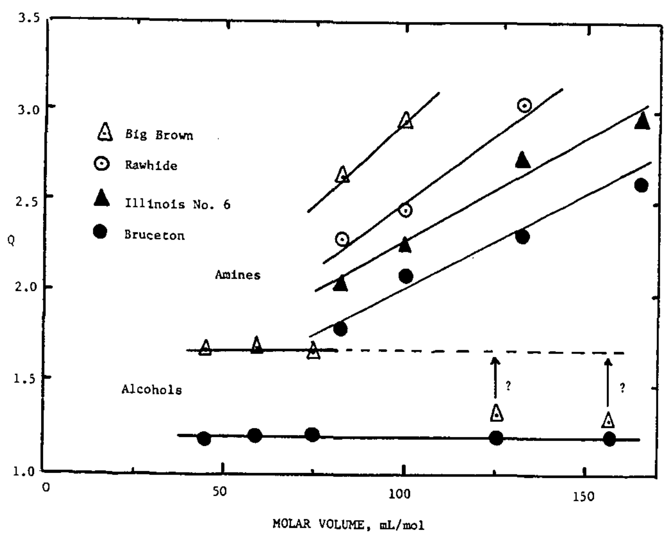

FIGURE 1. Plot of Swelling Ratios against Molar Volume of Solvent for a Series of n-Alcohols and n-Amines and Several Coals.