Coal Swelling and Neutralization: Reactions within a Three-Dimensional Organic Matrix

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Reactions within three-dimensional organic matrices are often controlled by diffusion processes. Bituminous coal was treated with a series of tetra-*n*-alkylammonium hydroxides (R_4NOH, R = methyl, ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, and *n*-octyl) in CH_3OH and H_2O to study the transport of reagents into a heterogeneous, cross-linked, solid matrix, and bulk swelling Q (mL/g) and base uptake curves were measured. Half-times for neutralization in methanol range from 30 to 200 min for potassium and tetra-*n*-butylammonium hydroxides, respectively. Base capacity measurements showed a strong dependence on ion size, solvent, and electrolyte concentration. Comparison of neutralization and swelling reveal that during absorption of base, $(n\text{-}C_4H_9)_4N^+$ ions act as a wedge in the coal's structure and lead to a bulk swelling curve that is not linearly correlated with the extent of neutralization. This behavior was not observed with potassium hydroxide and suggests that polar regions exist in the coal wherein strong hydrophobic effects apparently dominate swelling of the matrix. In general, the physicochemical properties of coal are found to be qualitatively predictable and consistent with a polyelectrolyte model.

The physical transport of chemical reagents into cross-linked solids such as functionalized polymers, ion exchange resins, or coal is generally a slow process.[1-3] Unlike reactions in solution, where bulk mass transport is limiting only for very fast reactions such as proton transfer, the rates of reactions within organic networks are often limited by diffusion through the solvent-swollen solid. When coal contacts a base solution, the base diffuses into the solid, over the course of several hours, and reacts with the acidic sites that are present. As a result of this neutralization and the absorption of solvent, the coal physically swells to a greater volume. Under some conditions the volume increase can be on the order of 400%. The rate and extent of the swelling are highly dependent on the nature of the swelling solution. To study this diffusion process and learn more about the physical and chemical interactions of coal with solvents and reagents, we have examined and compared the rates and equilibria of coal swelling and neutralization as a function of base cation size, concentration, and solvent.

Coals are highly heterogeneous materials, with complicated three-dimensional structures[4-6] that contain entrained organic material known as bitumen.[7] The connectivity, conformation, and topology of actual coal macromolecules are unknown. Connectivity refers to the fundamental atomic connectivity and includes the identity and quantity of cross-links, the arrangement and type of fused-ring systems, and the average molecular weight between cross-links. Collectively, these features comprise what is called the primary structure. The conformation of coal is related to the noncovalent cross-links which, in part, maintain the general shape of the macrostructure. These cross-links include the inter- and intramolecular associations in the form of hydrogen bonds,[8-11] dipole-molecule interactions, and simple entanglements in the structure.

Typically, low rank coals (subbituminous and lignitic) are characterized by significant quantities of phenolic and carboxyl groups (~4–8 per 100 carbons).[11] The ionization of these groups, depending upon their proximity and the degree of cross-linking in the organic network, affect the overall acid–base equilibria as well as the degree of swelling of the material. The ion-exchange properties of such coals in aqueous media have recently been discussed.[12,13]

We have examined a bituminous coal (Illinois No. 6, Table I) which contains only five acidic centers per 100 carbon atoms. Most of these sites are represented by phenols.[11] Our work has focused primarily on development of swelling as a macroscopic observable that relates the known chemistry of well-characterized ion-exchange resins to the chemistry of coal. Swelling measurements in conjunction with swollen polymer theories have been used to provide information about the macromolecular structure of bituminous coals (e.g., number average molecular weight per cross-link).[4,14,15] In general, we have found that bituminous coal, although a complicated heterogeneous organic material, possesses orderly and predictable physicochemical properties similar to weak acid ion-exchange resins (polyelectrolytes). Furthermore, comparison of neutralization and swelling data has shown that large bulky cations such as the tetra-*n*-butylammonium ion act as a wedge in the coal's structure and lead to rapid swelling of the matrix which is not linearly correlated with the extent of neutralization. This behavior is not observed with potassium hydroxide.

Results and Discussion

Swelling values (Q in units of mL/g) were obtained by mixing dry, powdered coal[16] with an appropriate base so-

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(13) Bobman, M. H.; Golden, T. C.; Jenkins, R. G. *Solvent Extr. Ion Exch.* **1983**, *7*, 813.
(14) Sanada Y.; Honda, H. *Fuel* **1966**, *45*, 295.
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Table I. Typical Analysis for Raw, Perdeuteromethylated, and Solvent Extracted Illinois No. 6 Coal[a]

wt %	raw	PNE	PE	PNE-CD$_3$	TNE-CD$_3$	RAW-CD$_3$
C	68.4	64.9	77.8			
H	5.2	4.8	5.8			
D				2.4	1.7	1.8
N	1.3	1.2	1.4			
S$_{SO_4^{2-}}$	0.01	0.01				
S$_{pyr}$[b]	1.3	1.7				
S$_{org}$	3.1	3.6	3.2			
S$_{total}$	4.4	5.3	3.2			
ash	9.4	13.7				
O$_{NAA}$[c]	14.4	17.2				
MM[d]	11.2	16.3				
O$_{diff}$	10.8	9.2	11.8			
			Empirical Formula on C$_{100}$ Basis			
C	100.00	100.0	100.0	100.0	100.0	100.0
H	90.5	88.1	88.8	72.8	78.4	82.3
D[e]				22.0	15.3	15.5
N	1.6	1.6	1.5			
S	1.7	2.1	1.5			
O	11.8	10.6	11.4			
CD$_3$ groups[f]				7.9	5.4	5.4

[a] PNE = pyridine nonextractable component, PE = pyridine extract, the TNE = THF nonextractable component. [b] Percent pyritic sulfur. [c] By neutron activation analysis. [d] MM = mineral matter calculated as 1.13 (ash) + 0.47 (pyritic S). [e] By combustion/mass spectral analysis. [f] Alkylation procedure taken from ref 9 and 11, CD$_3$ groups = $D/3 \times 1/(100 - D)$ where D = number of deuterium atoms per C$_{100}$.
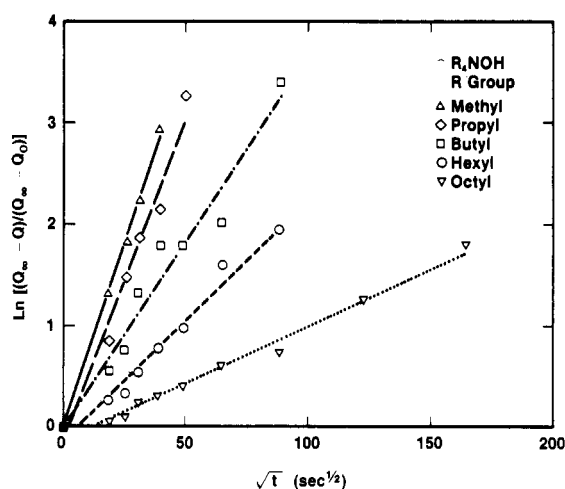

Figure 1. Normalized swelling values for pyridine extracted Illinois No. 6 coal as a function of $t^{1/2}$ ($s^{1/2}$) for a series of tetraalkylammonium hydroxides.

Figure 2. Coal swelling rate vs. cation radius (Å).
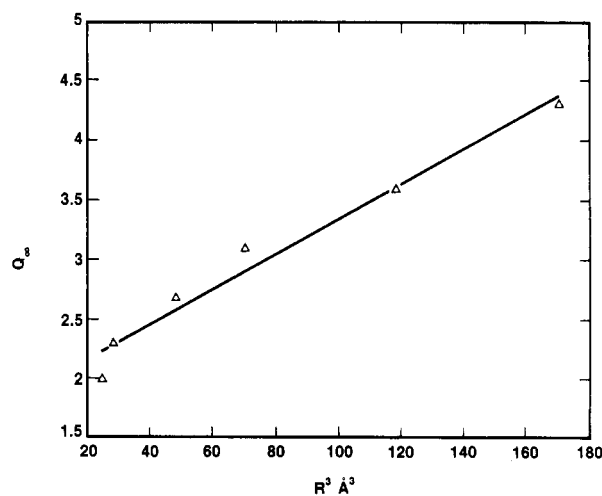
Figure 3. Final swelling values Q_∞ as a function of cation radius cubed, R^3 (Å^3).

lution in graduated centrifuge tubes and reading the volume of the solid after centrifugation. Before conducting an experiment, the coal was exhaustively extracted by using pyridine to remove occluded organic material (25–30%).[17] Pyridine is known to disrupt hydrogen bonds in the coal and to swell the organic matrix. When the pyridine nonextractable component (PNE) of Illinois No. 6 coal was treated with methanolic solutions of a series of tetra-n-alkylammonium hydroxides (R$_4$NOH, R = methyl, n-propyl, n-butyl, n-hexyl, and n-octyl), the neutralization and concomitant swelling were found to be strongly dependent on the size of the ammonium ions. To obtain a convenient and useful correlation of our data, we use an empirical rate derived by treating the swelling process as a "first-order" approach to equilibrium with a typical
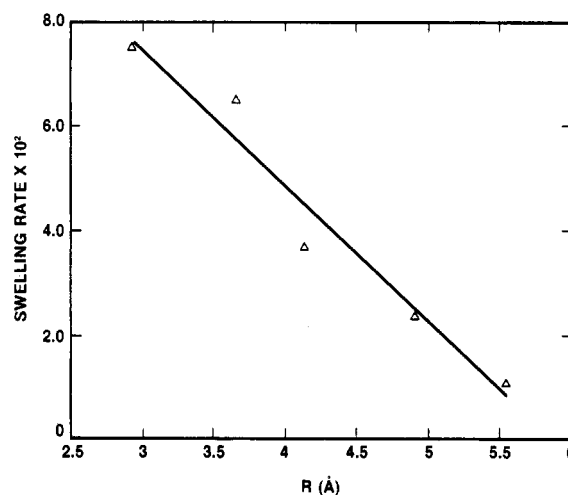
diffusion time dependence. The mass transport process is quite complex and the type of diffusion mechanism operating depends not only on particle shape but also on particle size distribution.[18] Figure 1 shows a plot of –ln

(16) Control experiments revealed that bulk swelling measurements were insensitive to shifts in particle size distribution produced by hand grinding and suggest that interparticle spacing is not a large component of the total swelling. A typical starting sample gave the following distribution: (ASTM mesh size, wt %) 20–40, 31; 40–60, 29; 60–80, 14; 80–100, 6; 100–200, 16; 200–325, 2; 325, 2.

(17) Calculated for the organic component (dry, mineral matter free basis).
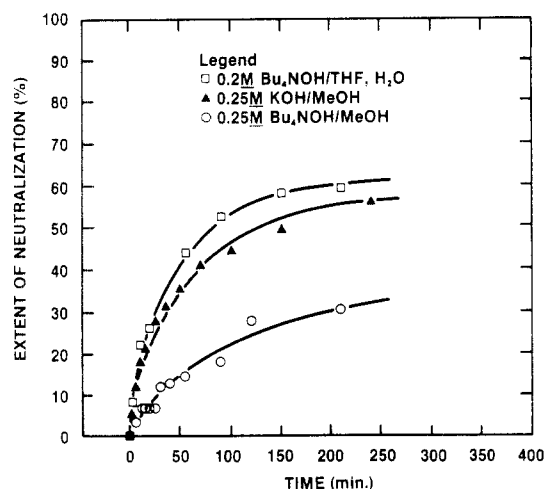
Figure 4. Normalized base uptake curves for the pyridine nonextractable component of Illinois No. 6 Coal. 100% = theoretical number of sites measured by alkylation.

Table II. Solvent-Swelling Values for the Pyridine Nonextractable Component of Illinois No. 6 Coal

solvent	Q (mL/g)
H$_2$O	1.8
MeOH	2.3
THF	3.6
THF/H$_2$O (3:1 by volume)	4.0
pyridine	4.5

$[(Q_\infty - Q)/(Q_\infty - Q_0)]$ vs. $t^{1/2}$ where Q_0 is the initial swelling value and Q_∞ is the final value after equilibration. The slopes of these lines give a measure of the swelling rate, which was found to decrease with increasing cation size (Figure 2).[19] Swelling of the sample with tetramethylammonium hydroxide was ~3.5 times faster than with the corresponding n-octyl-substituted cation, a surprisingly large difference.

Examination of the final equilibrium swelling values Q_∞ for the series showed a uniform increase with the nonsolvated volume of the tetra-n-alkylammonium ions (Figure 3).[20] This is analogous to the bulk volume increases observed for ion-exchange resins in aqueous solution as a function of hydrated ion volume.[21] The increase in volume of the coal upon contact with base is many orders of magnitude greater than the volume increase calculated for the absorbed quaternary ammonium ions. Evidently, large voids are created within the coals structure (assuming a constant interparticle void volume) during the neutralization.

Figure 4 shows a plot of the extent of reaction, expressed as $[(V_0 - V)/(V_0 - V_f) \times 100]$ vs. time (min), for several base solutions studied with the PNE component of Illinois No. 6 coal. The value V is the volume of standard acid used to titrate an aliquot removed from the reaction mixture. The value V_0 was determined by titration of the starting base solution and the value V_f is the calculated volume for neutralization of the total number of acidic sites (phenols and carboxylic acids) in the coal based on pre-

(18) Brenner, D.; Hagan, P. S. "Diffusive Uptake of Fluids by Coal Particles", "Abstracts of Papers", Symposium on "Physical Methods for Fossil Fuels Characterization", 189th National Meeting of the American Chemical Society, Miami, FL, April 1985; American Chemical Society: Washington, DC.
(19) The rate data is plotted vs. the radius of the cations for illustrative purposes and does not provide mechanistic detail concerning the diffusion process. Similar plots using R^2 and R$^{1/2}$ give an equally good straight line and indicate that the range of ion sizes examined may be insufficient to differentiate the nature of the functional dependence.
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Table III. Least-Squares Treatment (eq 1) of Neutralization Data for the Tetrahydrofuran Nonextractable Component of Illinois No. 6 Coal

base	concn, M	solvent	n	k	r^2
n-Bu$_4$NOH	0.20	THF/H$_2$O	0.43	1.9	0.97
KOH	0.25	MeOH	0.46	2.1	0.99

Table IV. Base Capacities and Equilibrium Swell Values as of Function of Cation Size for the Tetrahydrofuran Nonextractable Component of Illinois No. 6 Coal

cation	radius[a] Å	base capacity, mmol/g		$Q_\infty - Q_0$ (mL/g)	
		H$_2$O	MeOH	H$_2$O	MeOH
Na$^+$	0.95	−1.92		2.2	
K$^+$	1.33	1.40	1.89	0.4	1.5
Me$_4$N$^+$	2.91	1.45		0.6	
Et$_4$N$^+$	3.04	1.42	1.72	0.6	1.7
n-Pr$_4$N$^+$	3.64	0.70	1.60	0.4	1.9
n-Bu$_4$N$^+$	4.13	0.47	1.49	0.2	2.5
n-Hex$_4$N$^+$	4.91	0.41	1.51	0.3	3.2
n-Oct$_4$N$^+$	5.54	−1.51		3.1	

[a] Obtained from ref 20 and 23.

vious alkylation experiments[9] using isotopically labeled methyl iodide. The data are, therefore, scaled so that 100% represents the total number of acidic hydrogens per gram of coal. By examining the initial slopes, it can be seen that the 0.25 M n-Bu$_4$NOH/methanol solution neutralizes the coal about 7 times slower during the first 20 min than either the 0.20 M n-Bu$_4$NOH/THF, H$_2$O (4:1), or the 0.25 M KOH/methanol solution. At constant ion size, the rate of neutralization is greater for n-Bu$_4$NOH in aqueous THF than that in methanol and is apparently related to the solvent-swelling potential. When the coal was placed in methanol, a swelling value Q (mL/g) of 2.3 was obtained while aqueous THF led to value of 4.0, a 74% increase in volume (typical swelling values for several solvents are given in Table II). The rate of neutralization was consistent with the previous findings that the size of quaternary ammonium ions was inversely related to the rate of their diffusion into coal as measured by swelling studies. We would expect that potassium ions should, because of their small size, diffuse into the coal at a faster rate than the n-Bu$_4$N$^+$ ion. However, a solvent mixture (THF/H$_2$O) that swells the organic matrix to a greater extent increases the diffusion rate of the tetra-n-butylammonium ions into the coal to a point where the order is reversed.

An empirical relationship (eq 1) can be used to analyze the diffusion mechanism.[22] We can write

$$[(V_0 - V)/(V_0 - V_f)] = kt^n$$

$$\ln [(V_0 - V)/(V_0 - V_f)] = \ln k + n(\ln t) \qquad (1)$$

The quantities, V, V_0, and V_f are the same as described above. The value k is a constant and n is an unknown exponent that defines the diffusion process ($n = 0.5$ for Fickian diffusion). A plot of $\ln [(V_0 - V)/(V_0 - V_f)]$ vs. $\ln t$ gives a straight line with slope equal to n. Least-squares treatment of the data for 0.2 M n-Bu$_4$NOH/THF, H$_2$O, and 0.25 M KOH/methanol gave the results shown in Table III. The exponents 0.43 and 0.46 indicate that a diffusion-limited mechanism is operating, the detailed nature of which will depend upon particle size distribution.[18] Base uptake rates were not measured for the other tetralkylammonium ions.

(22) Peppas, N. A.; Lucht, L. M.; Hill-Livense, M. E.; Hooker, D. R. "Macromolecular Structural Changes in Bituminous Coals during Extraction and Solubilization", 1983, Department of Energy, Pittsburgh Energy Technology Center, Contract No. DE-FG22-80PC3022.
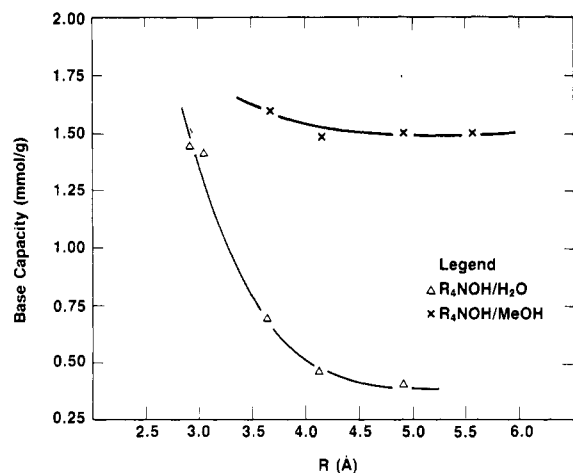
Figure 5. Base capacity vs. cation radius, R (Å).

Table V.[a] Base Capacities (mequiv) of Divinylbenzene (DVB) Cross-Linked Methacrylic Acid Resins as a Function of Ion Size and Nominal DVB Content

wt % DVB	calcd	Li^{+}	K^{+}	Me$_4$N[+]	Et$_4$N[+]
0.25	11.5	10.17	10.01	9.95	9.78
0.5	11.5		10.70		10.02
1	11.3	11.00	10.70	10.52	10.11
2	11.1	10.70	10.73	10.12	9.38
5	10.3		9.76		7.90
9	9.1		8.63	7.35	6.24
16	7.2	6.66	6.60	5.25	4.20
24	4.7	3.28	3.22	2.69	2.08

[a] Taken from ref 24; values represent milliequivalents absorbed at base concentrations of 0.03–0.06 M.

The extent of neutralization at equilibrium falls below the theoretical neutralization point in all cases and is strongly dependent on cation size and solvent (Figure 4). Table IV gives base capacities as a function of ion size for the tetrahydrofuran nonextractable component (TNE) of Illinois No. 6 coal along with the corresponding changes in volume. For each capacity measurement, a sample of coal was placed in a centrifuge tube and mixed with a solution of the appropriate hydroxide. The tubes were capped, sealed with tape, and shaken for 13 days. At that time the samples were centrifuged to facilitate separation of the suspended solid from the liquid phase. A known-volume aliquot was then removed from the supernatant and titrated along with the starting base solution with a standardized acid solution. The difference in these titration volumes and the mass of starting coal gave the tabulated base capacities (mmol/g). The ionic radii for the alkali-metal ions, K^+ and Na^+, are the accepted Pauling values (hydration volumes are not included),[23] and the radii for the quaternary ammonium ions represent the Stokes radii calculated from single-ion conductances.[20] The swelling values are the final equilibrium measurements corresponding to the same sample from which the base capacity was measured.

Examination of the quarternary ammonium ion data in water as a function of ion radius shows a profound decrease in capacity as ion size increases. The capacity drops from 1.45 to 0.41 mmol/g for tetramethyl- and tetra-n-hexyl-ammonium ions, respectively. The bottom curve in Figure 5 shows a plot of these data. The base capacity levels off as the size of the cation increases, apparently to some constant value independent of chain length. A similar leveling effect is seen in methanol for the ammonium ions,

Table VI. Base Capacities and Swelling Values Q as a Function of Solvent, Salt Concentration, and Base for the TNE Nonextractable Component of Illinois No. 6 Coal

base (0.25 M)	solvent	salt (1.0 M)	Q mL/g	base capacity mmol/g
KOH	H$_2$O		2.2	1.40
KOH	H$_2$O	KCl	2.4	1.90
KOH	MeOH		3.8	1.89
n-Bu$_4$NOH	H$_2$O		2.0	0.47
n-Bu$_4$NOH	H$_2$O	n-Bu$_4$NBr	3.5	1.17
n-Bu$_4$NOH	MeOH		4.8	1.49
n-Bu$_4$NOH	MeOH	n-Bu$_4$NBr	5.4	1.83
n-Bu$_4$NOH	THF/H$_2$O (3:1)[a]		7.0	>1.65[b]
n-Hex$_4$NOH[c]	H$_2$O		2.1	0.41
n-Hex$_4$NOH[c]	THF/H$_2$O (3:1)[a]		5.8	>1.17[b]

[a] By volume. [b] Corrected for partial dissolution of the sample. [c] 0.125 M.

tetra-n-propyl through tetra-n-octyl (Table IV). In this series, the change in base capacity is small over the range studied (see top curve on Figure 5). A decrease in base capacity with increasing cation size is typical for cross-linked polyacids.[24] Table V (data taken from ref 24) shows base capacities for polymethacrylic acid cross-linked with varying amounts of divinylbenzene (DVB) as a function of ion size. At all cross-link densities examined, base uptake at equilibrium also decreases with increasing base cation size. With nominally high levels of cross-linking (16 wt % DVB), a very pronounced shift in the extent of neutralization is observed, the tetraethylammonium ion gives an uptake value which is only 58% of the calculated total base capacity. For polyelectrolytes, these trends are explained by increased chain (polyanion) potentials. As ion size increases, average charge separation distance will also increase leading to destabilization of the macroion and lowered ionization constants. Titration studies of linear polyacrylic acids with quarternary ammonium bases have demonstrated that pK_a increases with cation size.[25] Evidently, cross-linking limits the conformational mobility of the polyanion, produces a higher density of charges in a given volume element, and again raises the potential of the macroion.

The leveling effect (Figure 5) observed in both solvents might be explained by anion penetration inside the external radii of the cations. Association parameters in methyl ethyl ketone calculated from conductometric studies and the Fuoss–Onsager equations reached nearly constant values as the quaternary ammonium ion size increased.[20] This suggested that the anion had penetrated sufficiently far into the cations structure so that additional methylene groups no longer had any effect on the association parameter. Hence, the ion–ion separation would reach a constant value for the larger tetra-n-alkyl-ammonium ions.

In coal, two explanations are possible for incomplete neutralization: (1) polyelectrolyte charging effects as discussed for cross-linked resins inhibit dissociation within the organic matrix or (2) specific structural features such as in a o-phthalic acid or catechol lead to a substantial decrease in the dissociation constant for a second deprotonation (o-phthalic acid; $k_1/k_2 = 3.3 \times 10^4$ at 25 °C in H$_2$O).[26] The latter explanation has been proposed on the basis of evidence obtained from potentiometric titration.[27]

(23) Cotton, E. A.; Wilkinson, G. "Advanced Inorganic Chemistry", Wiley: New York, 1980, p 52.

(24) Gregor, H. P.; Hamilton, M. J.; Becher, J.; Berstein, F. *J. Phys. Chem.* **1955**, *59*, 874.

(25) Gregor, H. P.; Luttinger, L. B.; Loebl, E. M. *J. Am. Chem. Soc.* **1954**, *76*, 5879.

(26) Weast, R. C.; Astle, M. J. "CRC Handbook of Chemistry and Physics"; CRC Press, Inc., Boca Raton, FL, p 171.

Although useful information about the proximity of acidic centers and the average dielectric of coal might be available by an analysis of electrostatic charging models of other macromolecular structures, the heterogeniety of the coal complicates the comparison. As more data are available, reasonable structural models may be proposed to quantitatively account for the observed base capacities.

Also consistent with a polyelectrolyte model for bituminous coal is the observation that the addition of electrolytes, potassium chloride and tetra-n-butylammonium bromide, to KOH and n-Bu$_4$NOH solutions, respectively, increases both the swelling volume and base uptake during neutralization. Table VI gives the equilibrium swelling values and base capacities for Illinois No. 6 (TNE) coal treated with 0.25 M base solutions in methanol and water. Base capacity for an aqueous KOH/KCl mixture increased 36% over a corresponding base solution containing no salt. This effect was greatly augmented for n-Bu$_4$NOH/H$_2$O mixtures where base capacity increased from 0.47 to 1.17 (mmol/g) upon the addition of n-Bu$_4$NBr (fourfold excess). A similar salt effect, although attenuated, was observed for n-Bu$_4$NOH/MeOH solutions. Such salt effects are expected for polyelectrolytes and have been observed in many macromolecular systems (synthetic resins, pectic acid, etc.).[28-30]

The final swelling values in H$_2$O corresponding to the samples described above (Table IV) were positively correlated with base uptake. An increase in base uptake was matched by a slight increase in swelling. This change is small and may be derived from a superposition of two opposite effects. The greater the number of neutralized sites in the coal (increased by decreasing cation size) and the greater the size of the incorporated cation, the greater the bulk swelling will be. For the MeOH base solutions, tetra-n-propyl through tetra-n-octyl, where base capacity is nearly constant, the predicted general increase in bulk swelling is observed.

Comparison of measurements for the alkali-metal, Na$^+$ and K$^+$, hydroxides to the quaternary ammonium ions is complicated by differences in solvation. The ammonium ions are not strongly solvated, while Na$^+$ and K$^+$ possess a substantial solvation sphere. The extent to which they might be desolvated in the associated form or in the coal is unknown. It is interesting to note that, although the measured base capacities for Na$^+$ and K$^+$ are 1.92 and 1.89 (mmol/g), respectively, and essentially the same, a significant increase in bulk swelling is observed for Na$^+$ (4.5 vs. 3.8 mL/g). This is consistent with a greater solvated volume for Na$^+$ than K$^+$ ions. The solvation number for Na$^+$ in methanol is known to be greater than that for K$^+$.[31] The increased swelling at constant capacity may indicate that sodium is well solvated in the coal.

Table VI also gives final swelling values Q_∞ (mL/g) and base capacities (mmol/g) for 0.25 M potassium and tetra-n-butylammonium hydroxides as well as 0.125 M tetra-n-hexylammonium hydroxide in various solvents. For 0.25 M KOH, MeOH leads to a 67% increase in swelling over that observed for H$_2$O and the base capacity increases by 35%. This general trend, where better coal swelling solvents lead to increased swelling and base uptake capacity, persists for the three bases examined. Presumably, a physical increase in the spacing of ionized groups via stretching of the cross-linked coal matrix (this could be
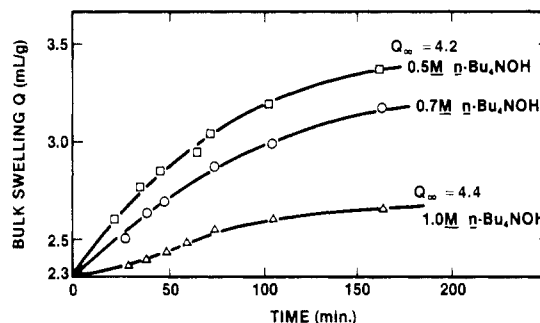

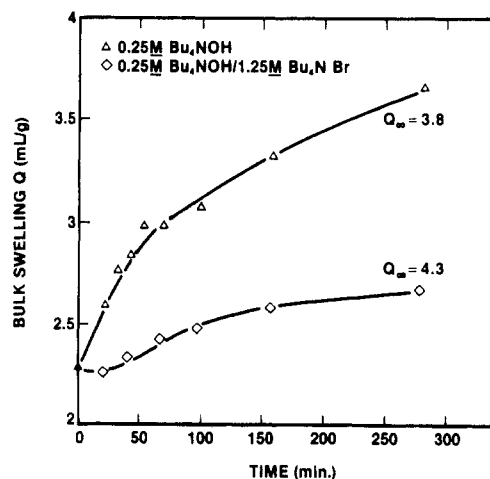**Figure 6.** Dependence of bulk swelling Q on base concentration.

Figure 7. Effect of added electrolyte on swelling.

a conformational change in the macromolecular structure) allows a greater base uptake. It must be noted, however, that changes in the dielectric of the medium with different solvents may act to stabilize the polyanion directly rather than via solvent–coal swelling.

Figure 6 shows a plot of the bulk swelling vs. time for several concentrations of tetra-n-butylammonium hydroxide in methanol. Although the equilibrium swelling values increased with base concentration, an inverse dependence was observed with respect to initial swelling rate (estimated from the initial slopes). The swelling rate for the 0.25 M solution is about 6 times greater than the rate observed for the 1.0 M solution. From an intuitive standpoint, this inverse relationship is unusual. If we consider the maximum rate increase for a second-order process, assuming very fast mass transport and a one-to-one correlation between swelling and neutralization during short reaction times, a swelling rate increase would necessarily be expected for higher concentrations. One possible explanation involves osmotic pressure effects.[32] Since the absorption of ions into the organic matrix is slow compared to the rate of solvent uptake, the swollen coal particles apparently behave as if enclosed in a semipermeable membrane. Solutions of high ionic strength "deswell" the coal or limit the amount of solvent that can be absorbed into the cross-linked matrix. Similar deswelling has been observed for weak acid ion-exchange resins.[24] A dramatically decreased rate of swelling is also observed when excess electrolyte is added to a 0.25 M solution of tetra-n-butylammonium hydroxide (Figure 7); although a crossover in swelling value is observed at long times which leads to a substantial increase for the solution of higher ionic strength. The unusual shape of the 1.0 M

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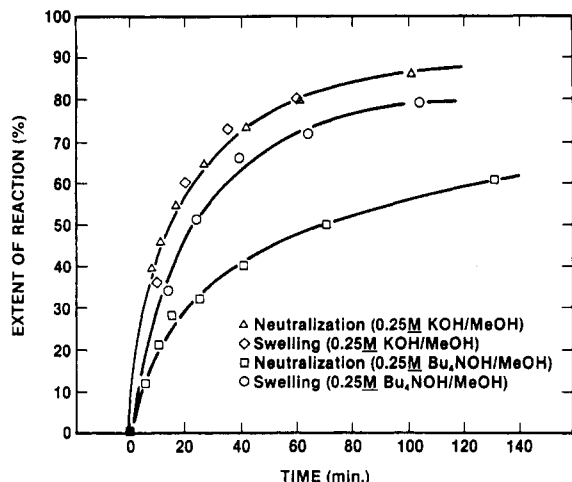(32) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; pp 100–104, 389.

Figure 8. Comparison of neutralization and swelling for potassium and tetra-*n*-butylammonium hydroxides.

curve (Figure 6) and the lower curve (Figure 7) may be the result of a phase transition in the matrix, analogous to that previously suggested for coal (glassy to rubbery state),[33] as more solvent and base is imbibed.

In Figure 8, a comparison between swelling and neutralization of the TNE component of Illinois No. 6 coal is presented. The figure shows a plot of reaction extent vs. time for neutralization and swelling with 0.25 M potassium and tetra-*n*-butylammonium hydroxides in methanol. It is important to note that, although the extent of swelling for tetra-*n*-butylammonium hydroxide in methanol appears less than, or equal to, the swelling observed in KOH/methanol solution, these curves have been normalized to their own final states. At equal concentrations, the tetra-*n*-butylammonium hydroxide solution swells coal to a much greater extent (4.8 mL/g) than potassium hydroxide (3.9 mL/g). This is a greater than 20% increase in the bulk swelling, even though fewer sites have been reacted. With potassium hydroxide, the degree of swelling of the matrix is directly correlated with neutralization. An incremental increase in base uptake leads to a corresponding increase in the expansion of the organic matrix. This is not the case, however, for tetra-*n*-butylammonium hydroxide. At a given time the extent of swelling is greater than the extent of neutralization. Within 1 h rapid swelling of the coal occurs (70% of Q_∞ while only half of the accessible acidic sites are neutralized). The large quaternary ammonium ions apparently act as a wedge in the organic structure and must lead to conformational changes in the matrix that do not occur with the smaller potassium ion. If hydrophilic regions exist in the coal, which contain clusters of the hydrogen bonded, acidic groups, the highly aliphatic character of the tetra-*n*-butylammonium ions may lead to strong hydrophobic interactions[34-36] that influence local structure. The gain in free energy for transfer of a methylene CH_2 group from an aqueous to a nonpolar medium is estimated to be ~1 kcal/mol.[37] Such hydrophobic interactions would not be expected from solvated potassium ions and should be minimized if the acidic sites were uniformly dispersed throughout the cross-linked structure. Similar speculations

have been made regarding the structure of globular proteins.[38]

Conclusion

The physicochemical behavior of bituminous coal with base and salt mixtures has been shown to be in accord with a simple polyelectrolyte model, derived from more homogeneous polymeric materials (functionalized, cross-linked resins). Bulk swelling measurements in conjunction with chemical probes have provided useful information about neutralization rates and equilibria. The understanding of these properties for heterogeneous, organic solids such as coal is needed for the controlled processing of fossil fuels and more generally for the control of reaction chemistry within solvent-swollen, three-dimensional organic matrices.

Experimental Section

Materials. The pyridine and tetrahydrofuran nonextractable component of Illinois No. 6 coal, a high-volatile C, bituminous rank coal, was used in the studies described. Solvent fractionated coal was prepared by using a Soxhlet extraction apparatus. The coal was extracted with pyridine until the solution filtering through the extraction thimble was clear (~4 days), and then with distilled tetrahydrofuran (~1 day). Drying of the sample was accomplished using a vacuum oven (1–5 torr) at 105–110 °C for a minimum of 24 h. In some cases the coal was pre-dried in a fritted funnel to remove most of the organic solvent under a stream of nitrogen before the final drying step. All solvents used were reagent grade and were not further purified before use unless otherwise specified. Tetra-*n*-butylammonium bromide (99%) was obtained from Aldrich Chemical Company and the tetra-*n*-alkylammonium hydroxides were obtained from Southwestern Analytical Chemical, Inc. (Austin, TX).

Swelling Measurements. In a typical swelling experiment, a 15-mL graduated screwtop centrifuge tube (Kimax Cat. No. 45166) was charged with 1.0 g of dry, fractionated coal and 14 mL of the appropriate swelling solution.[39] The tube was sealed immediately by using a Teflon-lined cap, taped to prevent solvent loss due to evaporation, and shaken at room temperature (24 °C) at a rate of about 170 cycles per minute using an Ederbach Corporation sample shaker (Model No. 6000) equipped with a utility carrier tray (Model No. 5865). When shaking was begun, the time was noted; this was taken as t_0 for kinetic runs. During the experiment, tubes were removed from the shaker periodically, the time was recorded, and the samples were centrifuged at 2800 rpm (25 cm rotor, ~2200g) for 5 min using a Sorvall Instruments RC-3B refrigerated centrifuge at 24 °C. The tubes were removed, briefly shaken to dislodge any solid material adhering to the upper portions of the tube, and spun down again at 2800 rpm for another 5 min. The samples were removed from the centrifuge, and the volume of solid was measured by visual inspection of the calibrated tubes. In some samples, darkening of the liquid layer and uneven settling of the coal during centrifugation led to small uncertainties in volume readings. Using repeat measurements, maximal errors were estimated to be ±0.1 mL. When the volume measurments were completed, the tubes were shaken vigorously by hand to break up the solid plug of coal produced by centrifugation and placed back into the shaker to resume the kinetic run. Swelling volumes were recorded by using the method described above until they were constant at long reaction times.

Equilibrium swelling values were obtained in a similar fashion after a total shaking time of 2 weeks. To eliminate errors in swelling measurements due to differences in particle size from one experiment to the next, all samples compared were obtained from the same batch of well-mixed coal.

Neutralization Rate and Base Capacity Measurements. A typical neutralization study was carried out in the manner described below for THF fractionated coal. All experiments were

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conducted at ambient temperature (24 °C).

1. Neutralization of the THF Nonextractable Component of Illinois No. 6 Coal. A 100-mL single-necked, round-bottomed flask was equipped with a magnetic stirring bar and charged with 4.00 g of THF-insoluble Illinois No. 6 coal. The solid coal was stirred and 55.0 mL of 0.26 M KOH (1 equiv assuming 3.5 mequiv of acidic hydrogens per gram of coal) in methanol was added in one portion rapidly. When addition of the base solution was completed, a timer was started and the kinetics run begun. During the course of the neutralization, the solution was maintained under a positive pressure of nitrogen. Periodically, the slurry was sampled by using a large bore calibrated glass tube and a Glasfirn "Pi-Pump" pipetting aid. A 2-mL aliquot was removed. Control experiments showed that the slurry was well agitated and that equal portions of coal and solution were removed regardless of the sampling depth of the pipette. The removed aliquot was filtered by using a sintered glass, medium frit filtration funnel. The coal was washed with 2 mL of methanol and the filtrate was diluted with 20 mL of deionized, degassed water. The aqueous methanol solution was then titrated with 0.020 M HCl to a pH of 7.0. Blank titrations, without coal, were done to determine the initial base concentration. Final base concentrations in the reaction mixture were determined after 24 h.

2. Base Capacity Measurements. Equilibrium base capacities were measured after 2 weeks by titration of a known volume aliquot removed from the supernatant of the centrifuged swelling samples. The titration was conducted at room temperature with standard acid solution (0.020 M HCl) using a Beckman Potentiograph (E 536) and a Metrohm (655) Dosimat.

Conjugate Addition of Acylate–Nickel Complexes to Quinone Monoketals: Formal Synthesis of the Naphthoquinone Antibiotics Nanaomycin A and Deoxyfrenolicin

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A direct approach to the synthesis of isochromanone antibiotics such as nanaomycin A (**2**) and deoxyfrenolicin (**3**) is the conjugate addition of a carbonyl anion equivalent to the appropriate naphthoquinone monoketal followed by trapping with an allylic halide. This provides a naphthoquinone nucleus with two side chains which are appropriate for the palladium-promoted heterocyclization developed earlier to complete the fused pyrano ring system. As previously observed in related systems, conjugate addition of carbonyl anion equivalents to benzoquinone and naphthoquinone monoketals leads to reductive cleavage as a major pathway, especially with the benzoquinone monoketals. The most general solution to the problem is the Corey–Hegedus procedure for preparation and reaction of acylate–nickel complexes. In the first tests with quinone monoketals, efficient conjugate addition is observed with naphthoquinone monoketals, and the intermediate enolate anions can be trapped with high efficiency by using allyl iodide. Manipulation of the quinone and acyl functionality allows the formation of the α-(hydroxyalkyl)naphthoquinone system, and the palladium(II)-catalyzed ring closure gives the desired isochromanone ring system. Use of the acyl–nickel complex from methyllithium and nickel carbonyl provides nanaomycin A (**2**), while the combination of *n*-propyllithium and nickel carbonyl leads to deoxyfrenolicin (**3**) by the same route.

Introduction

There is a set of natural products that have as common structural features a pyran ring with an alkyl substituent at C-2 and an acetic acid unit at C-6, usually trans, and fused to a naphthoquinone unit at C-3/C-4, as represented by structure **1**. Examples are nanaomycin A (**2**)[3] and

Scheme I
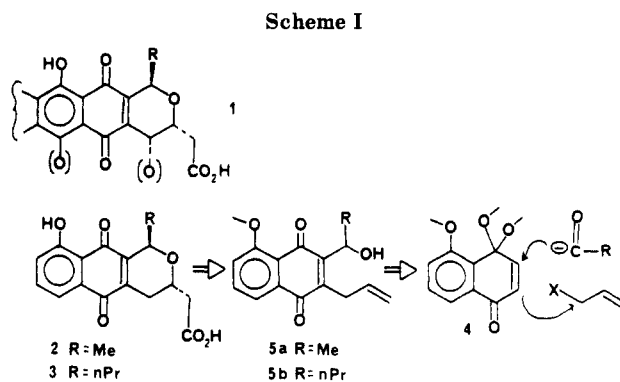
deoxyfrenolicin (**3**),[3,4] and more complex members exist. We have been interested in this set of compounds as a testing ground for synthesis methodology, and earlier papers give a more complete introduction.[5]

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