

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

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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, will 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 1) 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 regular and predictable physio-chemical properties similar to weak acid ion exchange resins (polyelectrolytes).

RESULTS AND DISCUSSION

Swelling values (Q in units of mL/g) were obtained by mixing dry, powdered coal(16) with an appropriate base solution in graduated centrifuge tubes and reading the volume of the solid after centrifugation. Before conducting an experiment, the

coal was exhaustively extracted 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_4NOH , 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 will depend not only on particle shape but also on particle size distribution(18). Figure 1 shows a plot of $-\ln[(Q_\infty - Q)/(Q_\infty - Q_0)]$ versus $t^{1/2}$ 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 base cation size(19). Swelling of the sample with tetra-methylammonium 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, ranging from 2.3 to 43 mL/g(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.

Figure 2 shows a plot of the extent of reaction, expressed as $(V_0 - V)/(V_0 - V_f) \times 100$ versus 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 previous 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*-Bu₄NOH/methanol solution neutralizes the coal about seven times slower during the first twenty minutes than either the 0.20 M *n*-Bu₄NOH/THF, H₂O (4:1) or the 0.25 M KOH/methanol solution. At constant ion size, the rate of neutralization is greater for *n*-Bu₄NOH in aqueous THF than 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*-Bu₄N⁺ ion. However, a solvent mixture (THF/H₂O) 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 (Equation 1) can be used to analyze the diffusion mechanism(22). We can write:

$$\begin{aligned} ((V_0 - V)/(V_0 - V_f)) &= kt^n \\ \ln((V_0 - V)/(V_0 - V_f)) &= \ln k + n(\ln t) \end{aligned} \quad 1)$$

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 $\ln[(V_0 - V)/(V_0 - V_f)]$ versus $\ln t$ gives a straight line with slope equal to n . Least squares treatment of the data for $0.2 \text{ M } n\text{-Bu}_4\text{NOH/THF}$, H_2O and $0.25 \text{ M KOH/methanol}$ 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 tetra-alkylammonium ions.

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 2). 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 tetra-methyl and tetra- n -hexyl ammonium ions, respectively. 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, tetra- n -propyl through tetra- n -octyl. In this series, the change in base capacity was small, however, over the range studied. A decrease in base capacity with increasing cation size is typical for cross-linked polyacids(23). In 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 macro-ion and lowered ionization constants. Titration studies of linear polyacrylic acids with quarternary ammonium bases have demonstrated that pK_a increases with cation size(24). Evidently, cross-linking limits the conformational mobility of the poly-anion, produces a higher density of charges in a given volume element, and again raises the potential of the macro-ion.

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_2O)(25). The latter explanation has been proposed based on evidence obtained from potentiometric titration(26).

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 $n\text{-Bu}_4\text{NOH}$ 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 $n\text{-Bu}_4\text{NOH/H}_2\text{O}$ mixtures where base capacity increased from 0.47 to 1.17 (mmol/g) upon the addition of $n\text{-Bu}_4\text{NBr}$ (four fold excess). A similar salt effect, although attenuated, was observed for $n\text{-Bu}_4\text{NOH/MeOH}$ solutions. Such salt effects are expected for polyelectrolytes and have been observed in many macromolecular systems (synthetic resins, pectic acid, etc.)(27-29).

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 versus 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^+ (30). The increased swelling at constant capacity may indicate that sodium is well solvated in the coal.

Table IV also gives final swelling values Q_∞ (mL/g) and base capacities (mmol/Lg) for 0.25 M potassium and tetra- n -butyl ammonium hydroxides as well as 0.125

M tetra-n-hexyl ammonium hydroxide in various solvents. For 0.25 M KOH, MeOH leads to a 67% increase in swelling over that observed for H₂O 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 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.

Examination of bulk swelling versus time curves for several concentrations of tetra-n-butylammonium hydroxide in methanol revealed an unusual effect. 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 six times greater than the rate observed for the 1.0 M solution. One possible explanation involves osmotic pressure effects(31). 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; although a cross over in swelling value is observed at long times which leads to a substantial increase for the solution of higher ionic strength.

In Figure 3, 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 versus 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 one hour 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(32-34) that influence local structure. Such hydrophobic interactions would not be expected from solvated potassium ions and should be minimized if the acidic sites were uniformly dispersed throughout the the cross-linked structure. Similar speculations have been made regarding the structure of globular proteins(35).

CONCLUSION

The physio-chemical behavior of bituminous coal with base and salt mixtures has been shown to be in accord with a simple polyelectrolyte model, derived from more regular 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 using a Soxhlet extraction apparatus. The coal was extracted with pyridine until the solution filtering through the extraction thimble was clear (~four days), then with distilled tetrahydrofuran (~one day). Drying of the sample was accomplished using a vacuum oven (1-5 torr.) at 105-110°C for a minimum of twenty-four hours. 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, Texas).

Swelling Measurements. In a typical swelling experiment, a 15 mL graduated screwtop centrifuge tube (Kimax Cat. No. 45166) was charged with 1.0 grams of dry, fractionated coal and 14 mL of the appropriate swelling solution(36). The tube was sealed immediately 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, ~2200 G's) for five minutes 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 five minutes. 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 measurements 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 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 two 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 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 grams of THF insoluble Illinois No. 6 coal. The solid coal was stirred and 55.0 mL of 0.26 M KOH (1 equivalent assuming 3.5 meq. 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 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 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 de-ionized, 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 twenty-four hours. 2. Base Capacity Measurements. Equilibrium base capacities were measured after two 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.

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FOOTNOTES AND REFERENCES

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TABLE I
Typical Analysis for Raw, Perdeuteromethylated,
and Solvent Extracted Illinois No. 6 Coal

WT %	RAW	PNE	PE	PNE-CD ₃	TNE-CD ₃	RAW-CD ₃
C	68.4	64.9	77.8	65.5	66.9	69.5
H	5.2	4.8	5.8	4.0	4.4	4.8
D	-	-	-	2.4	1.7	1.8
N	1.3	1.2	1.4	-	-	-
S(SO ₄) ⁼	0.01	0.01	-	-	-	-
S(pyr) ^a	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) ^b	14.4	17.2	-	-	-	-
MM ^c	11.2	16.3	-	-	-	-
O(diff)	10.8	9.1	11.8	-	-	-

Empirical Formula on C₁₀₀ Basis

C	100.0	100.0	100.0	100.0	100.0	100.0
H	91.8	89.1	89.2	73.0	79.6	82.2
D ^d	-	-	-	22.1	15.3	15.4
N	1.6	1.6	1.5	-	-	-
S	1.7	2.1	1.5	-	-	-
O	11.8	10.5	11.4	-	-	-
CD ₃ Groups ^e	-	-	-	7.4	5.1	5.1

a PNE = pyridine nonextractable component, PE = pyridine extract, and TNE = THF nonextractable component

b % pyritic sulfur

c MM = mineral matter calculated as 1.13 (ash) + 0.47 (pyritic S)

d by combustion/mass spectral analysis

e alkylation procedure taken from References 9 and 11

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

<u>Solvent</u>	<u>Q(mL/g)</u>
H ₂ O	1.8
MeOH	2.3
THF	3.6
THF/H ₂ O (3:1 by volume)	4.0
Pyridine	4.5

TABLE III
Least Squares Treatment (Eq. 1) of Neutralization Data for the
Tetrahydrofuran Nonextractable Component of Illinois No. 6 Coal

<u>Base</u>	<u>Concentration (M)</u>	<u>Solvent</u>	<u>n</u>	<u>k</u>	<u>r²</u>
<u>n</u> -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 Swelling Values Q as a function of Solvent,
Salt Concentration, and Base for the TNE Nonextractable Component
of Illinois No. 6 Coal.

<u>Base</u> (0.25 M)	<u>Solvent</u>	<u>Salt</u> (1.0 M)	<u>Q(mL/g)</u>	<u>Base Capacity</u> (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
<u>n</u> -Bu ₄ NOH	H ₂ O	-	2.0	0.47
<u>n</u> -Bu ₄ NOH	H ₂ O	<u>n</u> -Bu ₄ NBr	3.5	1.17
<u>n</u> -Bu ₄ NOH	MeOH	-	4.8	1.49
<u>n</u> -Bu ₄ NOH	MeOH	<u>n</u> -Bu ₄ NBr	5.4	1.83
<u>n</u> -Bu ₄ NOH	THF/H ₂ O(3:1) ^a	-	7.0	>1.65 ^b
<u>n</u> -Hex ₄ NOH ^c	H ₂ O	-	2.1	0.41
<u>n</u> -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

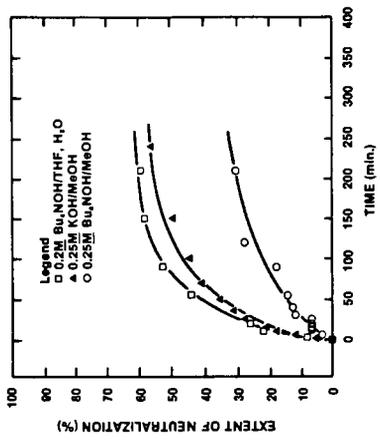


FIGURE 2

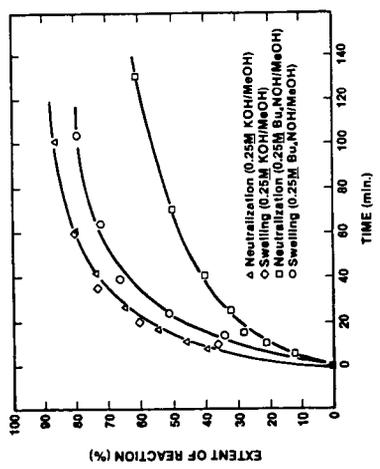


FIGURE 3

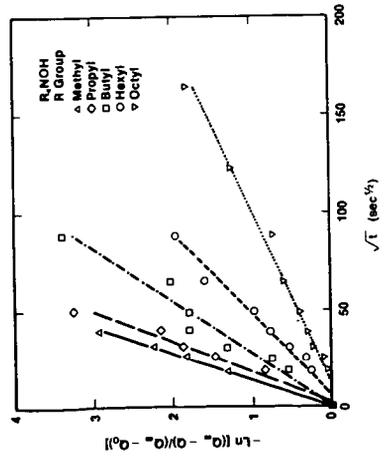


FIGURE 1