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Role of Solvation for Coal Swelling in Slurry

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The structure of coal is not a covalently cross-linked network, but rather, is represented by the physically associated model. Furthermore, the solvent swelling of coal is dependent on coal concentrations. The swelling kinetics of coal in slurry is, therefore, different from swelling kinetics during the sorption process of cross-linked macromolecules. By applying theoretical and experimental analyses, this paper explores the reevaluation of swelling kinetics of coal in *slurry*. Conventional analysis may lead to erroneous parameters when based solely on the premise of using the empirical equation derived from the sorption process. For this reason, normalized swelling curves of the first-order process, in addition to Fickian and Case II diffusion, were introduced to analyze swelling kinetics. Analysis consisted of tests under various conditions, where each swelling process adhered to the steps dictated by the first-order process. Interpretation of the results concludes that solvation of intra- and intermolecular complexes is the essential rate-determining step for coal swelling in slurry. This finding counters the concept that solvent diffusion in a coal network is considered the rate-determining step.

Introduction

Coal is mainly utilized through reactions in gas−solid or liquid−solid phases. For a liquid−solid mixture or a slurry system, swelling is a critical process to determine coal reactivity. Since the properties and reactions of material are a function of its structure, the swelling kinetics of coal must be evaluated on the basis of coal structure. Unfortunately, up to this point, coal swelling has been investigated on the basis of only a questionable structural model, the covalently cross-linked network, thus making the results on swelling kinetics unreliable.[1]

It has been recognized that intra- and intermolecular interactions, so-called noncovalent bonds, play an important role for coal structure.[2] Noncovalent bonds in coal may include ionic forces,[3] charge-transfer interactions,[4] and interactions due to π-electrons in polycyclic aromatics groups.[5,6] It is believed that coal molecules are associated by these noncovalent bonds and associated sites behave as if they are covalently cross-linked even in good solvents such as pyridine. Several lines of evidence to support the coal structure associated with these noncovalent bonds are now available. These include: (1) irreversibility of swelling,[7] (2) dependence of solvent swelling on coal concentration,[8] and (3) larger swelling of coal residue vis-à-vis coal extract.[9]

The dependence of solvent swelling on coal concentration was theoretically investigated on the basis of the associated structural model.[10] The investigation has confirmed that the structure of coal is represented by the associated model and not by the covalently cross-linked model. The following were suggested:

1. The average molar mass of insolubles is comparable to those of the high-molar-mass fractions of solubles.
2. The average molar mass of coal is estimated to be a few thousand, and decreases with an increase of the rank of coal.
3. Since the covalently cross-linked network model is questionable, the swelling kinetics of coal needs to be carefully reevaluated.

Coal swells in many organic solvents. The easiest method to measure its swelling ratios is to observe coal−liquid mixtures in a glass tube before and after swelling. Unlike a cross-linked macromolecular network, swelling ratios change depending on coal concentrations.[8] Coal swells more at low coal concentrations, meaning that noncovalent bonds are solvated at the lower concentrations. As such, noncovalent bonds behave as if they are covalently cross-linked, which is a typical behavior illustrated at high coal concentrations, but here, they are solvated at low coal concentrations. Solvation results in a change in an apparent cross-link density.

The dependence of solvent swelling on coal concentration is shown in eq 1:[8]

$$Q' = [Q']\left(\frac{C}{S}\right)^{-n} \tag{1}$$

where C/S is the coal/solvent mass ratio, $[Q']$ and n are constants, and Q' is defined in eq 2:

$$Q' = Q/\mathrm{BD} \tag{2}$$

where BD is the bulk density of powder samples, and Q is a volumetric swelling ratio. Since Q changes with

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the BD of coal powder samples, the value Q changes from sample to sample and from measurement to measurement. Specific swelling ratios calibrated with eq 2 must be used. The value of Q' corresponds to the swollen volume (mL) of a 1 g sample. $[Q']$ is defined as the intrinsic swelling ratio, which is independent of coal concentration (eq 3):

$$[Q'] = \lim_{\log(C/S) \to 0} Q' \qquad (3)$$

According to the theoretical investigation, the constant n is estimated to be between 0.14 and 0.25 when the interaction parameter of coal and a solvent is between 0.4 and 0.55.[10]

A vapor sorption method has often been used to evaluate the swelling kinetics of cross-linked macromolecules.[11] The most important factor during swelling is solvent diffusion into the network of macromolecules. The Fickian law is applicable for the diffusion of solvent into the network, but complex diffusion, which is deviated from the Fickian process, is often observed due to the segmental motions (relaxation) of the network. This same method was also applied to the investigation of the swelling kinetics of coal,[1,12] whereby its kinetics was interpreted by diffusion and coal segmental relaxation. Alternatively, a piston type of apparatus has been utilized.[13−15] Care should be exercised to differentiate phases between coal and solvents. These systems are not slurry phases, and coal and gas or liquid are isolated at the early stage of sorption or swelling. It is characterized by a sharp front separating the swollen and unswollen regions of the coal for the sorption and the piston types of apparatus methods, and by solvents being distinctly separate glassy and rubbery coal molecules. On the other hand, coal in a slurry system may be approximately regarded as a rubber state when good solvents are used. Furthermore, association of swollen coal equilibrates between associated complexes and solvated components. The degree of coal association is dependent on coal concentrations, which affects changes in apparent cross-linking density as discussed above. Such analysis leads to the definitive conclusion that in the swelling kinetics of coal, there is no correlation between sorption and slurry systems.

Experimental procedures and theoretical analyses used for covalently cross-linked macromolecules cannot be applied to evaluate the swelling kinetics of coal in slurry. However, the same analysis used for cross-linked macromolecules has been applied for analyzing the swelling kinetics of coal in slurry. In this paper, the swelling kinetics of coal in *slurry* has been reevaluated by theoretical and experimental analyses.

Experimental Section

For this experiment, American Chemical Society reagents and HPLC-grade solvents were used without further purification. Wyodak subbituminous (DECS-8), Illinois No. 6 (DECS-2), and Blind Canyon (DECS-16) high-volatile bituminous coals were obtained from the Pennsylvania State University Coal Bank. Their analyses are listed in Table 1. The coal (5 g) was extracted under a nitrogen atmosphere with 200 mL of pyridine for 3 days in a Soxhlet apparatus. The residue (PI) was Soxhlet-rinsed with methanol for 24 h. The PI was dried in a vacuum oven at 95 °C overnight.

Table 1. Elemental Analyses of Coals Used (wt%)

				element (daf)				
symbol	sample	H_2O	ash	C	H	N	S	O (diff.)
DECS-2	Illinois No. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4	9.8
DECS-8	Wyodak (subb)	28.4	9.9	74.4	5.2	1.0	0.9	18.5
DECS-16	Blind Canyon (hvb)	5.2	13.2	81.0	5.9	1.5	0.6	11.0

The experimental procedure of coal swelling is based upon the earlier reported method.[3,7−9] Measurements were made using a disposable Wintrobe Tube (Fisher Scientific) of 3 mm inner diameter and 115 mm length graduated in 1 mm divisions. After placing three weighed coal samples into separate tubes, these tubes were centrifuged for 5 min (at 3600 rev $\min^{-1}$ in a 30 cm diameter horizontal rotor). The bulk density (BD) of coal was determined by the average centrifuged height and its mass. A specific swelling ratio Q' defined in eq 2 is used in this paper. Solvent volume was measured and added to each weighed sample and the contents were vigorously stirred with a thin rod. Experiments were generally conducted using the coal/solvent ratio of 4.4 ± 0.2 (wt/wt %). Separate samples were employed for determining the extent of swelling as a function of time.

Results and Discussion

Theory of Coal Swelling. A sorption process in glassy polymers was considered as the linear superposition of phenomenologically independent contributions from Fickian diffusion and polymeric relaxation (eq 4).[11] If the relaxation process is assumed to be the first order in the concentration difference which drives the relaxation,[11] then the overall swelling process is expressed by eq 5 for *sphere* particles.

$$\frac{M_t}{M_e} = f_F\left(\frac{m_t}{m_e}\right)_F + f_R\left(\frac{m_t}{m_e}\right)_R \qquad (4)$$

$$= f_F\left\{1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2 k_F t)\right\} + \sum_{i=1}^{\infty} f_{Rt}\{1 - \exp(-k_{Rt}\, t)\} \qquad (5)$$

where

$$k_F = 4\pi^2 \frac{D}{d^2} \qquad (6)$$

and M_t is the mass uptake at time t, M_e is the equilibrium mass uptake, f_F and f_R are fractions of each contribution from Fickian diffusion and relaxation, m_t and m_e are the mass uptake at time t and equilibrium time for each contribution, D is the diffusion coefficient, d is the particle diameter, and k_{Ri} is a constant.

In the limiting case of diffusion referred to as Case II, the mass uptake is expressed for *sphere* particles by eq 7:

$$\frac{M_t}{M_e} = 1 - \left(1 - \frac{k_0}{C_0 a}t\right)^3 \qquad (7)$$

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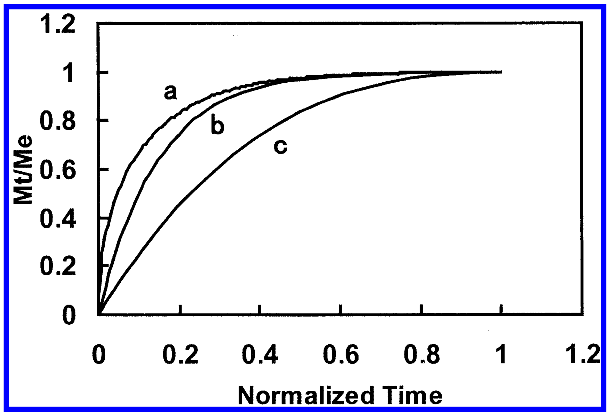

Figure 1. Normalized calculated curves of the mass uptake for sphere particles during swelling for (a) Fickian, (b) the first-order, and (c) Case II processes with normalized time scale.

where k_0 is the relaxation constant and C_0 is the equilibrium solvent concentration.[16] Other mathematical models for different geometric samples were presented by Ritger and Peppas.[17]

If the structure of coal is represented by the physically associated model, then the interaction of coal with solvents during swelling in slurry would be controlled by the solvation of noncovalent bonds. In this process, the dependence of time on swelling ratios is expressed by the following first-order equation:[3]

$$Q - Q_0 = (Q_e - Q_0)\{1 - \exp(-k_1 t)\} \tag{8}$$

where Q, Q_0, and Q_e are swelling ratios at time t, initial time, and equilibrium time, respectively, and k_1 is a constant. Equation 8 is essentially the same as the case of $f_{Ri} = 1.0$ in eq 5. High-volatile bituminous coal promptly swells in slurry with a good solvent of pyridine, and analysis of swelling kinetics is difficult using the volumetric method[9] whereas the coal slowly swells in poor solvents. Low rank coal, particularly a dried sample, also swells slowly. These swellings followed the first-order process shown in eq 8.[3] It was interpreted that associative equilibria caused by the ionic forces are the rate-determining step for the volumetric swelling of lower rank coal.

Figure 1 shows normalized curves calculated from eqs 5, 7, and 8 for Fickian, Case II, and the first-order processes. Fickian diffusion corresponds to $f_F = 1.0$ in eq 5. Normalized values shown in Figure 1 are not affected by swelling constants and equilibrium swelling ratios.

The following empirical eq 9 was derived from sorption experiments and has been used to analyze the swelling kinetics of coal even in slurry without justification:[18-20]

$$Q - Q_0 = (Q_e - Q_0)k_2 t^{n_2} \tag{9}$$

where k_2 and n_2 are constants. The constant n_2 is 0.5 for Fickian diffusion, 0.5 to 1 for non-Fickian diffusion, and 1 for the Case II diffusion in which relaxation of coal molecules changes diffusion kinetics. Equation 9 is transformed to eq 10:

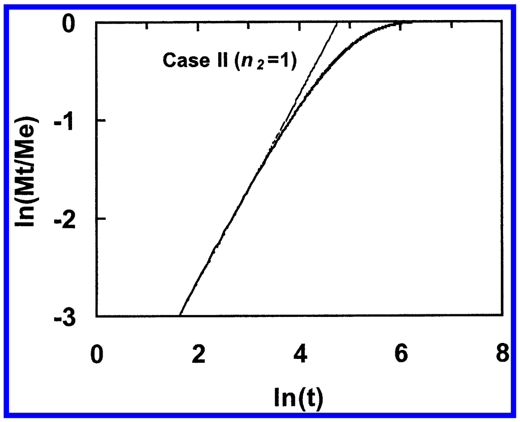

Figure 2. The logarithm of the mass uptake versus the logarithm of time for the first-order process, eq 8. The linear line shows the case of $n_2 = 1$ in eq 10 for comparison.

$$\ln\frac{M_t}{M_e} = \ln k_2 + n_2 \ln t \tag{10}$$

Empirical eq 10 was simply used to analyze the early stage of volumetric swelling.[18-20] In these works, a diffusion process including a non-Fickian transport was assumed to be the rate-determining step. It should be noted that eq 10 only fits with observed values at the early stage of swelling,[18-20] while observed swelling agreed with values calculated with eq 8 for an entire range of swelling.[3]

In the case of $k_1 t \ll 1$, eq 8 can be approximated as follows:

$$\ln\frac{M_t}{M_e} = \ln(1 - e^{-k_1 t}) \tag{11}$$

$$\cong \ln\left\{k_1 t - \frac{1}{2!}(k_1 t)^2 + \frac{1}{3!}(k_1 t)^3 - ...\right\} \tag{12}$$

$$\cong \ln k_1 + \ln t \tag{13}$$

Therefore, the logarithm of M_t/M_e is also linear against the logarithm of time for the first-order process. Figure 2 shows eqs 10 ($n_2 = 1$), 11, and 13. When $n_2 = 1$ in eq 10, eqs 10 and 13 are linear and have the same slope. Accordingly, it is difficult to differentiate between diffusion and the first-order processes even if ln M_t/M_e vs ln t shows a linear relationship. A slope determined from the early stage of swelling may change depending on a selected region as shown in Figure 2. If swelling is fast, the slope of an observed linear range may be smaller, because a linear range at the early stage cannot be observed. It should be remembered that errors stemming from centrifugation time are significant. For example, $Q_0 = 1$ is not observed, although Q_0 is ideally "1". In general, a centrifugation is made for 5−10 min. Figure 3A shows observed results reported by Otake and Suuberg.[18] A solid line presents values calculated by eq 8. Figure 3B shows observed and calculated values with the logarithm scale. It is seen that swelling kinetics in slurry follows the first-order process. It is also noticed that the linear range is relatively narrow since the time unit is minute, not hour. The paper analyzed a linear

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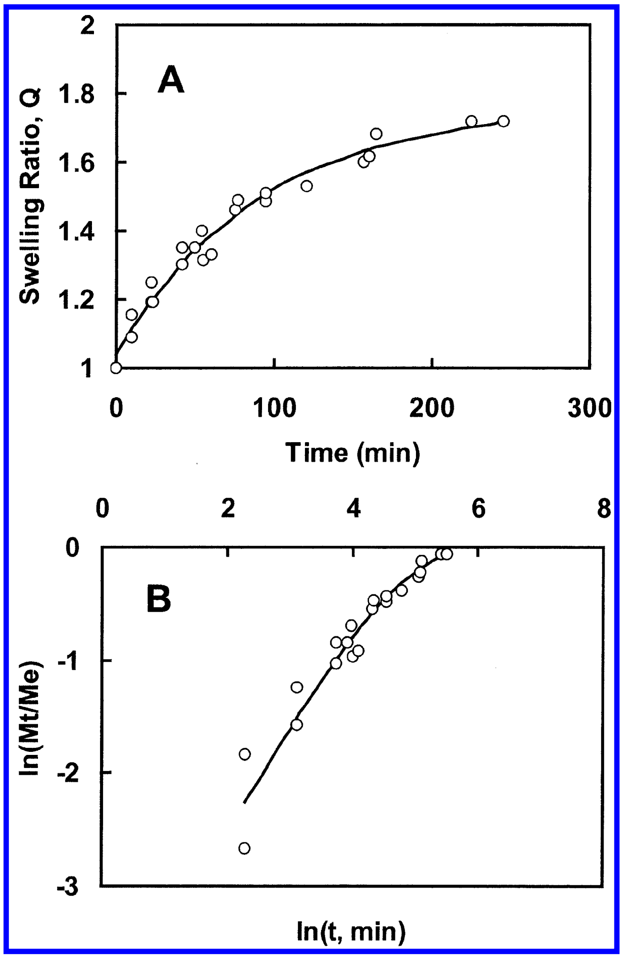

Figure 3. (A) Swelling ratios of Beulah lignite in pyridine reported by Otake and Suuberg.[18] The solid line shows calculated values with eq 8. (B) Comparison of observed values and calculated results with eq 11 shown with the logarithm scale for the above results (Figure 3A).

potion of observed values, and reported a slope of 0.67−0.69 instead of one. Actual Initial Q_0 values, a centrifugation time, and a calibration of bulk density must be considered to analyze swelling kinetics of coal in slurry.[21−23]

Swelling Kinetics and Coal Concentrations. In this paper, to further investigate the determining step of coal swelling in slurry, the swelling kinetics of the dried Blind Canyon high-volatile bituminous coal (DECS-16) was evaluated in *N*-methyl-2-pyrolidinone (NMP) at different coal concentrations (at 25 °C). These results are shown in Figure 4A with values calculated with the following eqs 14−16:

$$Q' = 1.42 \times (1 - e^{-0.263t}) + 1.40 \quad \text{(coal/solvent = 4.4 w/w\%)} \quad (14)$$

$$Q' = 1.26 \times (1 - e^{-0.357t}) + 1.32 \quad \text{(coal/solvent = 7.1 w/w\%)} \quad (15)$$

$$Q' = 0.87 \times (1 - e^{-0.351t}) + 1.35 \quad \text{(coal/solvent = 11 w/w\%)} \quad (16)$$

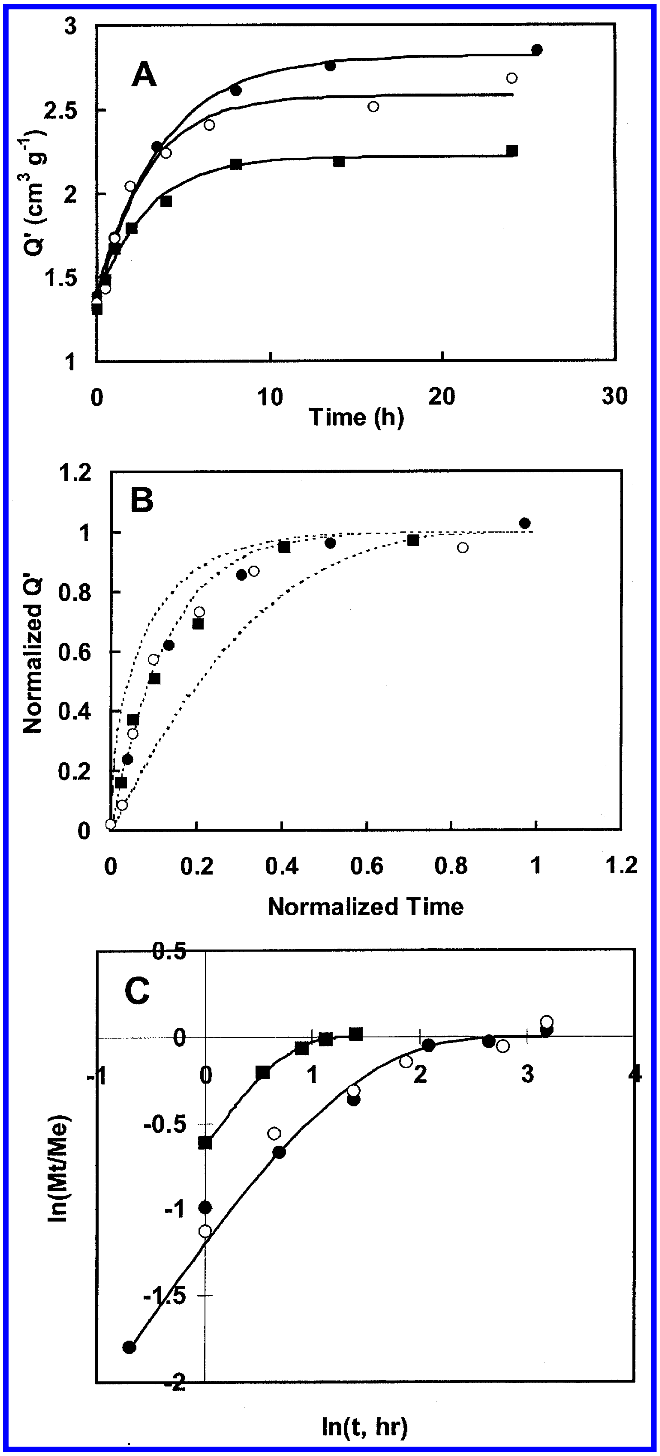

Figure 4. (A) Specific swelling ratios (Q') of dried DECS-16 coal in *N*-methyl-2-pyrolidinone at 25 °C, concentration of coal/solvent = 4.4 w/w% (●), coal/solvent = 7.1 w/w% (○), and coal/solvent = 11 w/w% (■). (B) Normalized specific swelling ratios (Q') of the above results (Figure 4A). See Figure 1 for dotted lines. (C) Specific swelling ratios of the above results (Figure 4A) with the logarithm scale (see eq 11).

Swelling kinetics follows the first-order process, and the ultimate swelling ratios are smaller at high coal concentrations.

Figure 4B shows these results with the normalized scale. For comparison, these results are also shown with logarithm scales in Figure 4C. In Figure 4C, it is observed that a slope of the early stage is linear as analyzed in eq 13. It is not concluded whether swelling kinetics is a diffusion or the first-order process by evaluation of only a linear portion of results.

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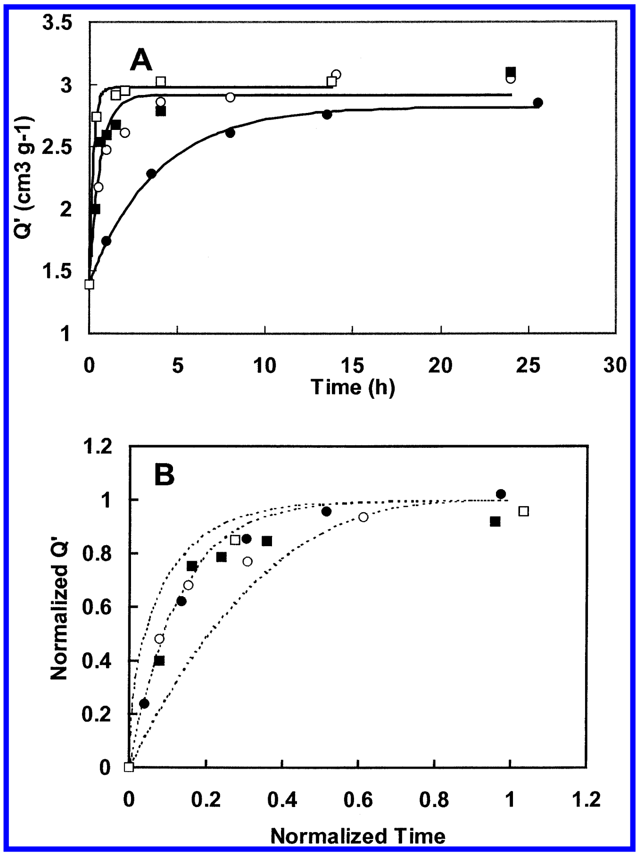

Figure 5. (A) Specific swelling ratios (Q') of dried DECS-16 coal in *N*-methyl-2-pyrolidinone at 25 °C (●), 40 °C (○), 50 °C (■), and 75 °C (□). (B) Normalized specific swelling ratios (Q') for the above results (Figure 5A). See Figure 1 for dotted lines.

Equilibrium swelling ratios vary with coal concentrations.[2,7−9] Swelling kinetics also changes with coal concentrations and follows the first-order process. These results demonstrate that coal swelling in slurry is controlled by the solvation of noncovalent bonds, and are not rationalized by a diffusion process. The degree of solvation is determined by equilibrium between associated complexes and solvated components.

Swelling Kinetics and Temperatures. Next, the swelling kinetics of the DECS-16 coal was evaluated in NMP at temperatures ranging from 25 to 75 °C (coal/solvent = 4.4 w/w%). Figure 5A shows these results compared to calculated values. Calculated values are as follows:

$$Q' = 1.42 \times (1 - e^{-0.263t}) + 1.40 \quad (25\ °\mathrm{C}) \tag{17}$$

$$Q' = 1.52 \times (1 - e^{-1.04t}) + 1.44 \quad (40\ °\mathrm{C}) \tag{18}$$

$$Q' = 1.52 \times (1 - e^{-1.65t}) + 1.40 \quad (50\ °\mathrm{C}) \tag{19}$$

$$Q' = 1.59 \times (1 - e^{-4.75t}) + 1.39 \quad (75\ °\mathrm{C}) \tag{20}$$

The calculated values closely agree with observed values at these temperatures. Figure 5B shows these results with the normalized scale. Results obtained again suggest that the swelling of this high-volatile bituminous coal is controlled by the solvation of noncovalent bonds.

Swelling rate constants significantly changed, but equilibrium specific swelling ratios did not change considerably ($Q_e' = 2.82-2.98$) at temperatures 25−75 °C. While swelling rate constants did not show significant change, equilibrium-specific swelling ratios changed drastically ($Q_e' = 2.22-2.82$) depending on coal concentration as shown in Figures 4 and 5. These results cannot be explicitly explained by a diffusion mechanism, but contribute to a reasonable interpretation that can be made regarding the solvation mechanism on the basis of the associated structural model: The degree of association of coal is not affected by changing temperatures ranging from 25 to 75 °C, but swelling rate constants become larger by overcoming the activation energy of swelling to some extent. While the degree of association changes depending on coal concentrations, the swelling constants maintain the same form at constant temperatures.

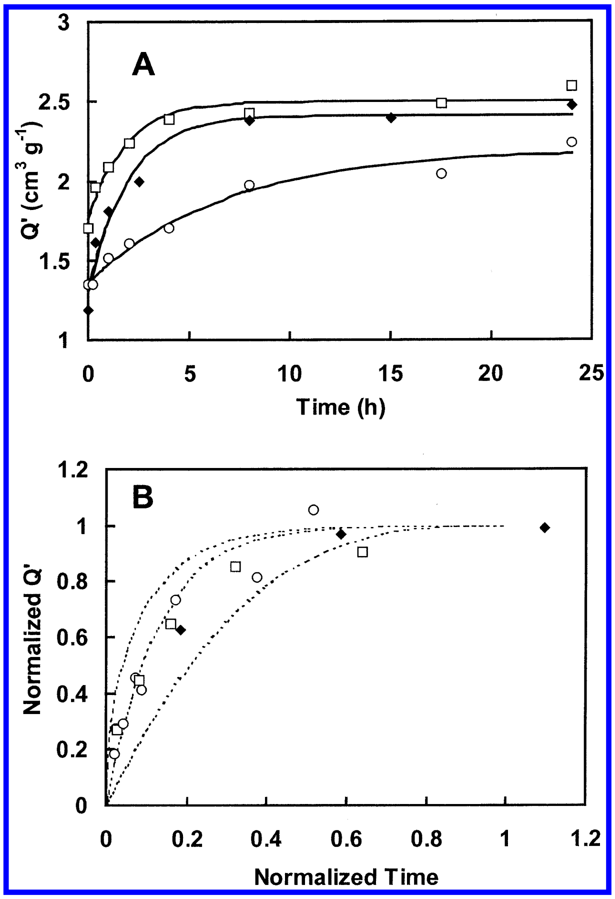

Figure 6. (A) Specific swelling ratios (Q') of PI from DECS-8 coal in pyridine (□), *sec*-butylamine (◆), and 4-methylpyridine (○) versus time. (B) Normalized specific swelling ratios (Q') of the above results (Figure 6A). See Figure 1 for dotted lines.

Swelling Kinetics and Solvents. In this section, additional solvents are evaluated using subbituminous Wyodak (DECS-8) coal. The swelling kinetics of PI from this coal was investigated in (±)-*sec*-butylamine, pyridine, and 4-methylpyridine. Figure 6A shows specific swelling ratios versus time using these solvents and the first-order curves calculated from equations shown below:

$$Q' = 1.11 \times (1 - e^{-0.505t}) + 1.31 \quad (sec\text{-butylamine}) \tag{21}$$

$$Q' = 0.74 \times (1 - e^{-0.552t}) + 1.76 \quad (\text{pyridine}) \tag{22}$$

$$Q' = 0.84 \times (1 - e^{-0.148t}) + 1.36 \quad (\text{4-methylpyridine}) \tag{23}$$

Table 2. Dependence of Physical Conditions on Coal Swelling

condition	swelling rate	
solvent dependence	slow in poor solvents	fast in good solvents
rank dependence in pyridine	slow for lower ranks of coal	fast for higher ranks of coal
moisture effect for lower ranks of coal	slow for dried coals	fast for raw coals
acid washing effect for lower ranks of coal	slow for raw coals	fast for washed coals

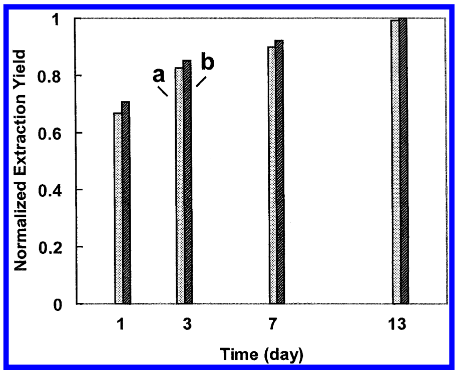

Figure 7. Toluene extraction yields versus time for DECS-2 pyridine extract (a) and dried DECS-2 coal (b).

Normalized observed and calculated values are shown in Figure 6B.

Although initial and equilibrium swelling values and swelling constants are different for these solvents, normalized observed values follow the same first-order process. This is particularly notable for pyridine and 4-methylpyridine. These results confirm that the swelling kinetics of this subbituminous coal is also controlled by the first-order process or solvation of noncovalent bonds rather than diffusion of solvent into a coal network.

Comparison between Swelling and Extraction Kinetics. The above results showed that coal swelling in slurry is primarily controlled by the solvation of noncovalent bonds. Since the Soxhlet extraction of coal is carried out in slurry, a supplemental experiment using Soxhlet extraction was conducted to confirm the proposed solvation mechanism. According to a diffusion mechanism, Soxhlet extracts and coal follow different extraction kinetics, because extracts are solubles, and solvents can easily accessible to molecules during extraction, while coal contains insolubles, and extraction may be controlled by diffusion of solvents into a coal network. Conversely, the solvation mechanism predicts that both extracts and coal may follow the same extraction kinetics. To confirm this, toluene extractability for Illinois No. 6 high-volatile bituminous (DECS-2) coal and its pyridine extract (PS) were evaluated.

Ultimate toluene extractability of the dried coal was 0.8 wt % (daf), while that of the PS was 9.8 wt % (3 wt % (daf) of the coal). Extraction yields divided by ultimate extraction yields are shown in Figure 7. Results confirmed that extraction kinetics is essentially the same for these two samples. This means that the effect of solvent diffusion into a coal network during extraction is small. Results support the projected swelling process.

Concluding Remarks

The swelling mechanism during a sorption process has been used to analyze the swelling kinetics of coal in slurry without careful justification. The questionable structural model, a covalently cross-linked network, has also been assumed to propose a diffusion hypothesis. It is necessary to recognize that swelling kinetics in slurry and during vapor sorption are two physically different processes. Since the properties of material are a function of its structure, the swelling kinetics of coal must be evaluated on the basis of the appropriate structure of coal. Theoretical and experimental analyses in this paper confirmed that the solvation of intra- and intermolecular interactions is the rate-determining step for coal swelling in slurry. This mechanism is consistent with the associated structural model of coal.

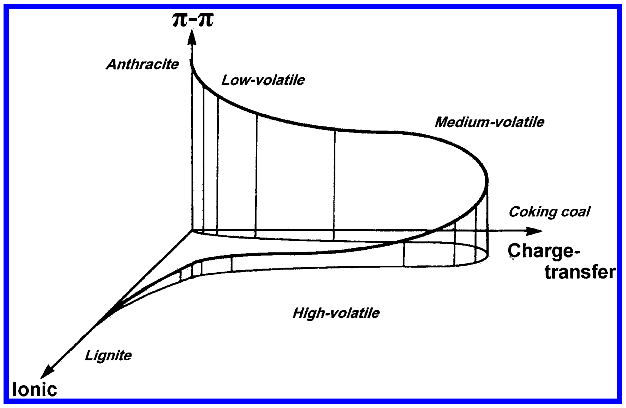

Figure 8. Proposed dependence of relatively strong intra- and intermolecular interactions on coal rank.[2]

Since the abundance of various intra- and intermolecular interactions is highly rank-dependent,[6] it is thought that swelling kinetics changes with the ranks of coal depending on conditions such as solvents, fractions (extract, residue, etc.), and coal treatments (drying, heating, exposure to solvents, etc). The concept of the rank dependency of relatively strong intra- and intermolecular interactions may be represented as shown in Figure 8.[2] Some changes in swelling kinetics caused by these interactions are summarized in Table 2. These changes cannot be explained by diffusion of solvents into coal molecules. Diffusion is one of several factors that control swelling kinetics, but it does not determine the rate-determining step of coal swelling in slurry. The following examples[3,9] can be reasonably interpreted on the basis of the solvation of intra- and intermolecular interactions.

The swelling rates of high-volatile bituminous coal are slower in poorer solvents. For example, equilibrium swelling ratios in toluene are too small in order to observe the time dependence of swelling. Swelling is larger in tetrahydrofuran which is a better solvent than toluene and increases with time. Pyridine is a much better solvent than tetrahydrofuran, thus when applicability is observed in pyridine, equilibrium swelling ratios are larger than in tetrahydrofuran, but due to the prompt swelling of the coal, it is difficult to observe the time dependence of the swelling. The better the solvents are, the better the solvation of intra- and intermolecular interactions is.

Swelling of lower ranks of coal in pyridine is the same at 25 and 70 °C. As the swelling of medium-volatile bituminous coal in pyridine is larger at higher temperatures ranging from 25 to 70 °C, the time dependence can be seen at higher temperatures. The time dependence of swelling may be different at temperatures depending on ranks of coal because the nature of intra- and intermolecular interactions is rank-dependent.

Although the time dependence of swelling in pyridine is not seen for lower ranks of coal, the dried coals slowly swell in pyridine. Ionic interactions have an important role for lower ranks of coal as shown in Figure 8. It is deduced that the swelling rate of raw coals is faster than that of dried coals because moisture in the coals is apparently beneficial to solvate ionic interactions. Once the ionic interactions are reduced by removing minerals via acid washing, it is observed that even the dried coals swell rapidly in pyridine.

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