

Dependence of Solvent Swelling on Coal Concentration: A Theoretical Investigation

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An empirical equation for the dependence of coal concentration on coal solvent swelling was theoretically investigated on the basis of the associated structural model of coal. Swelling results of previously reported concentration dependence were analyzed by following this theory. It was reasonably derived that coal molecules are physically associated, and the covalently cross-linked macromolecular model is questionable. The swelling ratios of high-molar-mass fractions were larger than those of low-molar-mass fractions. This was interpreted as intermolecular association is superseding intramolecular association, and that the size of molecules in associated complexes is a determining factor for swelling ratios. The average molar mass of coal is apparently comparable to those of high-molar-mass fractions in coal extracts. The average molar mass of coal decreases with an increase in the rank of coal. Extraction and swelling kinetics follow the first-order process, and are controlled by the solvation of associated sites.

Introduction

Coal has been one of the main energy resources since the Industrial Revolution in the 18th century. It is needless to say that the structure of any material should be well understood if optimal utilization is desired. The structure of coal is, however, still unknown despite its usage for more than two and a half centuries. Since coal is the most abundant fossil fuel on earth, coal will continue to be valuable. As for the structure of coals, three factors, (1) high-molar-mass mixtures, (2) amorphous nature, and (3) limited extractability, have made the characterization of coal extremely difficult.

A cross-linked, three-dimensional macromolecular model, model A in Figure 1, has been widely accepted since van Krevelen proposed the polymeric character of coal in 1961.¹ Cross-links in model A are covalent bonds. It was, however, recognized that intra- and intermolecular interactions, so-called noncovalent bonds, play an important role for coal structure.^{2–9} Noncovalent bonds in coal include ionic forces, charge-transfer interactions, and interactions due to π -electrons in polycyclic aromatic compounds.⁴ The abundance of these interactions is highly rank-dependent. These interactions are believed to be stronger than hydrogen bonds and dispersion forces, and to only partially be solvated even with one of the best known solvents, pyridine.³ It has been suggested that significant sites are cross-linked by these noncovalent bonds and behave as if they

are covalently cross-linked.^{4–8} The structure of coal with noncovalent bonds is illustrated as model B in Figure 1. The actual structure of coal may be a mixture of models A and B. The extent to which coal molecules may be model A and/or model B is unknown. However, several lines of evidence for model B were obtained from the studies of solvent swelling of coal in 1992 and 1993.^{4–8} These were (1) irreversibility of swelling,⁵ (2) dependence of swelling on coal concentration,⁶ and (3) larger swelling of coal residue than coal extract.⁷

A volumetric swelling method using a glass tube is commonly used. Swelling ratios Q are calculated by the differences between heights or volumes before and after swelling and may reach as much as 2–3. Since Q values change with the bulk density (BD) of powder samples, the specific swelling ratio Q' defined in eq 1 should be used.⁶

$$Q' = Q/BD \quad (1)$$

The value Q' corresponds to the swollen volume (mL) of a 1 g sample.

The dependence of coal concentration on swelling has been found by careful measurements. Solvent swelling is significantly enhanced at low coal concentrations. This indicates that associated coal complexes dissociate at low concentrations. An empirical eq 2 was proposed for the dependence of coal concentration on specific swelling ratios,⁶

$$Q' = [Q'] \left(\frac{C}{S} \right)^{-n} \quad (2)$$

where C/S is the coal/solvent mass ratio, and $[Q']$ and n are constants. Since the molar mass of coal is not known and concentration in a coal-solvent system cannot be clearly defined, C/S was used as an index of concentration. $[Q']$ is defined as the intrinsic swelling

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(2) Nishioka, M.; Larsen, J. W. *Energy Fuels* **1990**, *4*, 100.

(3) Nishioka, M. *Energy Fuels* **1991**, *5*, 487.

(4) Nishioka, M. *Fuel* **1992**, *71*, 941.

(5) Nishioka, M. *Fuel* **1993**, *72*, 997.

(6) Nishioka, M. *Fuel* **1993**, *72*, 1001.

(7) Nishioka, M. *Fuel* **1993**, *72*, 1719.

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

symbol	sample	H ₂ O	ash	element (daf)			
				C	H	N	S
ND	North Dakota (lignite)	32.2	6.6	72.9	4.8	1.2	0.9
IL	Illinois No. 6 (hvb)	8.0	14.3	77.7	5.0	1.4	5.7
PITT	Pittsburgh No. 8 (hvb)	1.7	9.1	83.2	5.3	1.6	2.4
UF	Upper Freeport (mvb)	1.1	13.0	85.5	4.7	1.6	2.7

ratio, which is independent of coal concentration.

$$[Q] = \lim_{\log(C/S) \rightarrow 0} Q \quad (3)$$

The dependence of coal concentration on swelling is an essential characteristics to elucidate the structure of coal. In this paper, eq 2 is theoretically investigated and previously reported data are further analyzed.

Experimental Section

All data investigated in this paper have been reported in earlier papers.⁷⁻⁹ The results for coals, obtained from the Premium Coal Sample Bank at Argonne National Laboratory, are investigated.¹⁰ The proximate analysis of these coals are summarized in Table 1. Coal symbol names in Table 1 are used in this paper. PS and PI refer to pyridine extract and pyridine extracted coal prepared with Soxhlet extraction, respectively, and all experimental procedures of coal swelling are described in earlier papers.⁵⁻⁸

Results and Discussion

Theoretical Investigation. Consider the simplest assumptions that the average number of associated sites determines the average molar mass per cross-link, which is a function of the number of the solvated sites. The isolation of molecules from associated complexes by solvation is ignored. The average molar mass per cross-link M_c after solvation can be expressed with the average molar mass M , the number of the ultimate solvation points N_0 , and the number of the solvated points N_s as follows:

$$M_c = \frac{M}{N_0 - N_s} \quad (4)$$

$$= \frac{M}{N_0 \left(1 - \frac{N_s}{N_0}\right)} \quad (5)$$

$$= M_0 \left(\frac{1}{1 - f_s}\right) \quad (6)$$

where $M_0 = M/N_0$, and f_s is the fraction of solvation.

While, the average molar mass per cross-link is provided by the following Flory-Huggins equation:¹¹

$$M_c = \frac{\frac{1}{3}\rho_2 V V_2}{-\ln(1 - V_2) - V_2 - \chi V_2^2} \quad (7)$$

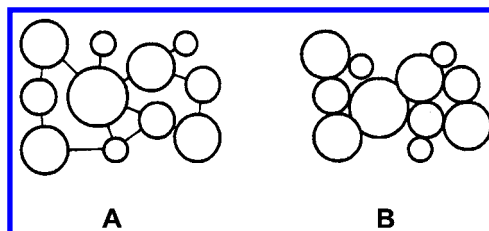


Figure 1. A, covalently cross-linked and B, physically associated models of coal structure.

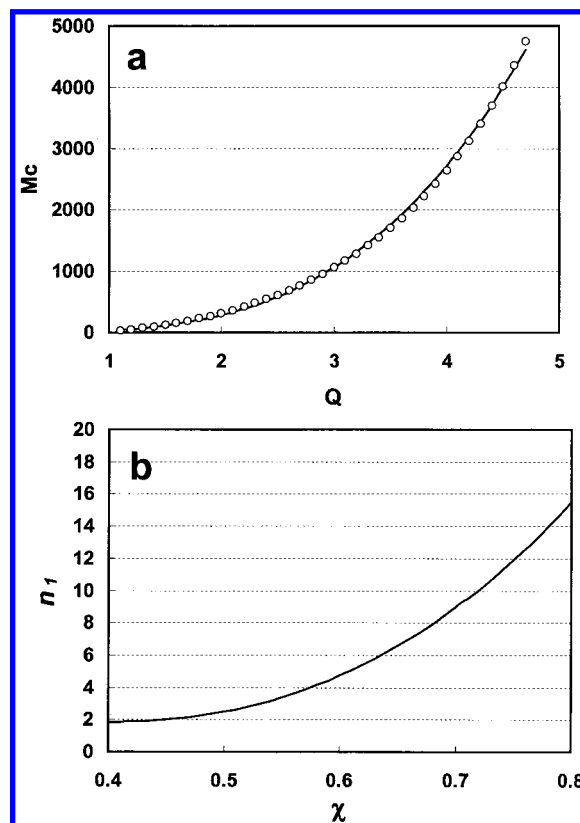


Figure 2. (a) Comparison of calculations by Flory Huggins equation (eq 7) and by approximated equation (eq 9). (b) The relationship between n_1 and χ is determined by the calculation of eqs 7 and 9.

where ρ_2 is the original density of the coal, V is the molar volume of the solvent, V_2 is the molar volume fraction of the coal, and χ is the interaction parameter. For convenience, consider an approximation by eq 8 for eq 7:

$$M_c \cong K_1 (1/V_2)^{n_1} \quad (K_1, n_1: \text{constants}) \quad (8)$$

$$= K_1 (Q)^{n_1} \quad (9)$$

Figure 2a shows an example of approximated calculations by eq 9. The values shown with open circles were calculated by eq 7 where 0.55, 1.3 (g/cm³), and 80.56 (cm³/mol: pyridine) were used for χ , ρ_2 , and V , respectively. The solid line was calculated by eq 10:

$$M_c = 28.928 Q^{3.276} \quad (10)$$

It is seen that eq 7 is numerically approximated by eq 9. If eq 9 is calculated for various χ values, the relationship between n_1 and χ is available as shown in Figure 2b. When the value of χ is assumed as in the

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(11) Larsen, J. W.; Kovac, J. In *Organic Chemistry of Coal*; Larsen, J. W., Ed.; American Chemical Society: Washington, DC, 1978; Chapter 2.

following equation using %C in coal,¹²

$$\chi = 0.0116(\%C) - 0.4901 \quad (11)$$

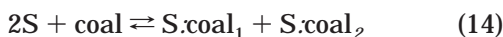
n_1 is between 2 and 3.5 when χ is between 0.4 and 0.55.

From eqs 6 and 9, Q is

$$Q = K_2 M_c^{1/n_1} \quad (K_2: \text{constant}) \quad (12)$$

$$= K_2 \left(\frac{1}{1 - f_s} \right)^{1/n_1} \quad (13)$$

Consider the simplest assumptions that solvation is determined by solvent or coal concentration and the probability of possible solvation and solvated sites. The dynamic equilibrium between solvent S and coal is



The rate of solvation v_1 is proportional to both a solvent concentration, [S], and the probability that two solvent molecules will find sites,¹³

$$v_1 = k_s [S] \{N_0(1 - f_s)\}^2 \quad (15)$$

where k_s is the rate constant for solvation between solvent and coal. The rate of coal association v_2 is proportional to both a coal concentration, [C], and the frequency of encounters of solvated sites of coal,

$$v_2 = k_a [C] (N_0 f_s)^2 \quad (16)$$

where k_a is the rate constant for the association of coal. The condition for these two rates to be equal leads to the following equation:

$$k_s [S] \{N_0(1 - f_s)\}^2 = k_a [C] (N_0 f_s)^2 \quad (17)$$

\therefore

$$1 - f_s = \frac{1}{1 + K_3^{1/2} [S/C]^{1/2}} \quad \left(K_3 = \frac{k_s}{k_a} \right) \quad (18)$$

Therefore, from eq 13:

$$Q = \left\{ \frac{1}{1 + K_4 [C/S]^{-1/2}} \right\}^{-1/n_1} \quad (K_4: \text{constant}) \quad (19)$$

if $1 \ll K_4 [C/S]^{-1/2}$, then

$$Q = K \left(\frac{C}{S} \right)^{-n} \quad (K: \text{constant}) \quad (20)$$

where $n = 1/2n_1$, and n is between 0.14 and 0.25 when n_1 is between 2 and 3.5. If K is replaced by $[Q]$, eq 2 is obtained. Since a mole concentration of coal is not available, coal/solvent mass ratio was used for eq 2 in the previous papers.

Concentration Dependence of Swelling. Figure 3 compares the specific swelling ratios of the PIs of four coals in pyridine with those calculated by eq 2. The determined n values are also shown in the figure. Since

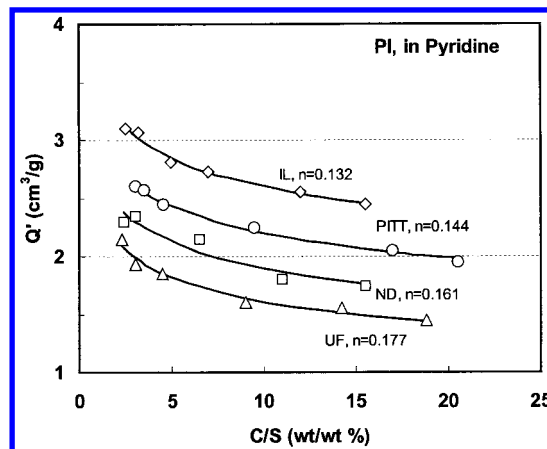


Figure 3. Specific swelling ratios Q' of PI from four coals in pyridine vs coal/solvent mass ratios C/S . Refer to eq 2 and Table 1 for n values and coal symbols, respectively.

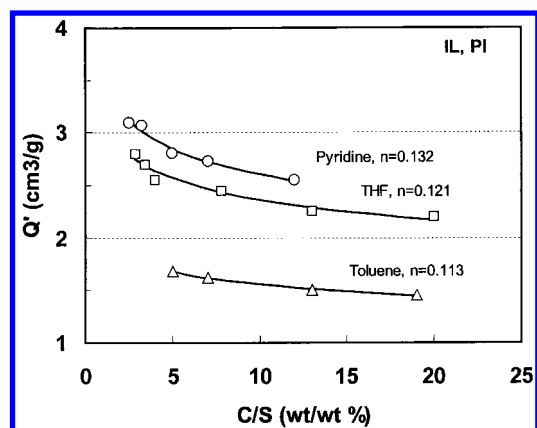


Figure 4. Specific swelling ratios Q' of PI from IL coal in pyridine, tetrahydrofuran (THF), and toluene as a function of coal/solvent mass ratios C/S . Refer to eq 2 for n values.

North Dakota (ND) coal swells slowly in pyridine, its swelling after 24 h is presented. The other coals promptly swell in pyridine, and swelling at the initial stage is reported. A notable point is that coals from four different ranks, ranging from lignite to medium-volatile bituminous coal, amazingly show similar dependence of coal concentration on the specific swelling ratios. The agreement between calculated and observed values is quite good. The n values are also within the approximate range predicted in the previous section.

If PI is a covalently cross-linked macromolecular network, the dependence of coal concentration on solvent swelling is deemed thermodynamically impossible. It was proposed in the previous paper⁶ that such dependence of solvent swelling implied that the dissociation and swelling of PI increased at low concentrations. This proposition has now been rationalized by the comparison of observed values with the theoretical analysis of model B.

Figure 4 shows the specific swelling ratios of PI from the Illinois No. 6 (IL) coal in three solvents. When compared to pyridine, the poorer the solvent, the smaller the n value. This apparently stems from a difference in the value of χ . A further systematic study will be necessary to evaluate the relationship between the solvent and its n value.

Swelling of Fractionated Samples. When the solvent swelling of fractionated samples such as PS is

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(13) Atkins, P. W. In *Physical Chemistry*; W. H. Freeman and Company: New York, 1990; Chapter 29.

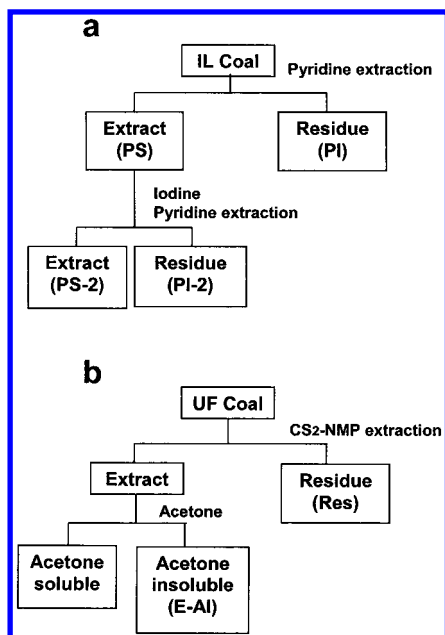


Figure 5. Fractionation scheme of (a) IL and (b) UF coals.

evaluated, the effect of solubles on swelling must be considered. If a solvent dissolves solubles, the solvent activity is not 1.0. A reduction in the solvent activity may change swelling ratios. The effect of this was investigated in the earlier paper.⁶ Swelling ratios only changed 0.1 or 5% even though samples contain 10% of solubles. The swelling ratio of a mixture of PS and PI was simply determined by the additive of each fraction as shown eq 21.

$$Q = f_{PS}Q_{PS} + (1 - f_{PS})Q_{PI} \quad (21)$$

where f_{PS} is the mass fraction of PS, and Q_{PS} and Q_{PI} are the swelling ratios of PS and PI, respectively. A whole coal was tested, which also followed the same relation.

Soluble fractions can be evaluated with solvents poorer than pyridine, because the effect of solubles on swelling is small. PS from the IL coal was further fractionated to PS-2 and PI-2 by mixing with iodine as shown in Figure 5a.⁷ For the Upper Freeport (UF) coal, two fractions were obtained with carbon disulfide-*N*-methyl-2-pyrrolidinone (CS₂-NMP) extraction, followed by acetone extraction as shown in Figure 5b.⁹ CS₂-NMP extractability was 59.4 wt % (@daf) and much larger than pyridine extractability. It should be recalled that PI from the UF coal contains solubles with CS₂-NMP mixed solvent.

Figure 6 shows the specific swelling ratios of these fractionated samples in tetrahydrofuran (THF). Four fractions from the IL coal (Figure 6a) demonstrate the same dependence of coal concentration on swelling. The dependence is compared with the results calculated by eq 2. The specific swelling ratios of both the original PS (Q_{PS}) and the fractionated PS-2 (Q_{PS-2}) are smaller than those of PI (Q_{PI}) and PI-2 (Q_{PI-2}). It is noted that the specific swelling ratios of PI and PI-2 obtained from PS are nearly identical. The specific swelling ratios of Res with this solvent is larger than that of PI (Figures 3 and 6b). Again, it is noted that the specific swelling ratios of Res (Q_{Res}) and E-AI (Q_{E-AI}) obtained from solubles with the mixed solvent are nearly the same.

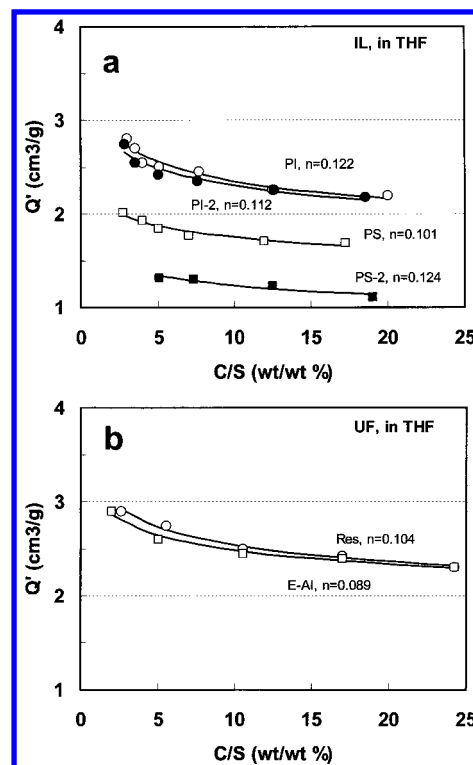


Figure 6. (a) Specific swelling ratios Q of PS, PI, PS-2, and PI-2 from IL coal in tetrahydrofuran (THF) vs coal/solvent mass ratios C/S . Refer to eq 2 and text for the n values and sample symbols. (b) Specific swelling ratios Q of Res and E-AI from UF coal in tetrahydrofuran (THF) vs coal/solvent mass ratios C/S . Refer to eq 2 and Figure 5 for n values and sample symbols.

The following conclusions are derived from the above results using fractionated samples:

First, solvation equivalently occurs for whole coal, because the n values of fractionated samples are nearly the same regardless of its solubility. Functional groups responsible for solvation may uniformly exist in coal. In other words, cross-links with noncovalent bonds are similarly distributed in both solubles and insolubles.

Second, covalently bonded cross-links in PI and Res are negligible because of $Q_{PI} \approx Q_{PI-2}$ and $Q_{Res} \approx Q_{E-AI}$. If cross-links of both covalent and noncovalent bonds are present in PI and Res, the n value of PI and Res must be smaller than those of the PI-2 and E-AI fractions under the condition of $Q_{PI} \approx Q_{PI-2}$ and $Q_{Res} \approx Q_{E-AI}$.

Finally, molecular size is a determining factor of swelling ratios, and swelling is controlled by intermolecular cross-links with noncovalent bonds. It is reasonably assumed that the average molar masses of PI and Res are larger than those of PS and solubles. Fractions with higher molar mass result in larger M_c and larger swelling. Thus, the relationship below is expected:

$$Q_{PI} > Q_{PS} \quad \text{and} \quad Q_{PI-2} \gg Q_{PS-2} \quad (\text{IL coal})$$

$$Q_{Res} > Q_{PI} \quad (\text{UF coal})$$

Intramolecular cross-links with noncovalent bonds may not be as important as intermolecular cross-links with noncovalent bonds.

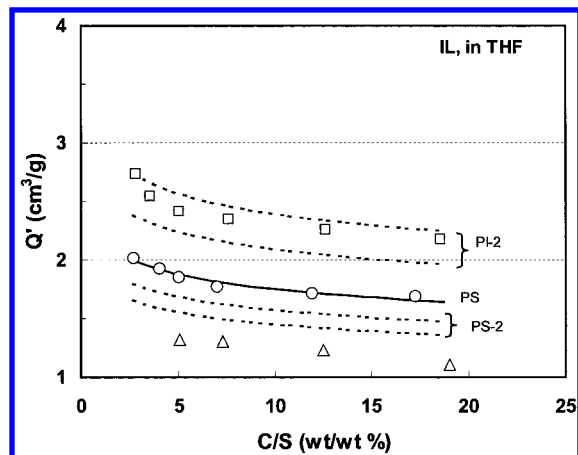


Figure 7. Specific swelling ratios Q' of PS (\circ), PS-2 (Δ), and PI-2 (\square), calculated PS-2 (dotted line), and calculated PI-2 (dotted line) from IL coal in tetrahydrofuran (THF) as a function of coal/solvent mass ratios C/S . Refer to Figure 5 for sample symbols.

Table 2. Molar Mass of Extracts from Blind Canyon Coal¹⁴

symbol	sample	average molar mass
PS	pyridine solubles	800
PS-TI	pyridine solubles and THF insolubles	1460
TS-CI	THF solubles and chloroform insolubles	1230
CS	chloroform solubles	550

It is suggested from the above investigation that the average molar mass per cross-link is nearly equal to the average molar mass of coal molecules.

$$M_c \approx M \quad (22)$$

Therefore, eq 23 is obtained from eqs 9 and 22.

$$Q_2 = Q_1(M_2/M_1)^{1/n_1} \quad (2 < n_1 < 3.5) \quad (23)$$

The specific swelling ratios of fractionated samples can be estimated by eq 23. Figure 7 shows calculated Q_{PS-2} and Q_{PI-2} from Q_{PS} and average molar masses of these fractions. Since the average molar masses of these fractions are not known, those of fractionated extract samples from Blind Canyon coal are used. These values are measured with vapor pressure osmometry and are shown in Table 2.¹⁴ For calculation, 550, 800, and 1500 were used for PS-2, PS, and PI-2, respectively. Although a systematic study will be necessary for the future, specific swelling ratios are approximately estimated by eq 23.

Next, the result, $Q_{PI} \approx Q_{PI-2}$, shown above, indicates that the average molar mass of PI is nearly equal to the average molar mass of high-molar-mass fraction in PS. Therefore, the average molar mass of coal may be smaller than previously expected. Information regarding the average chemical structure of coal may be obtained from the detailed characterization of extract rather than the coal itself, because coal is not soluble and its characterization is exceptionally difficult.

Similarly, the average molar mass of different ranks of coal may be estimated by eq 23. Figure 8 shows the intrinsic swelling ratios $[Q]$ of PI from four coals in

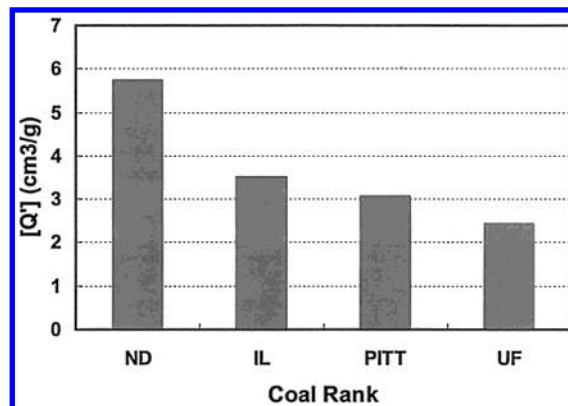


Figure 8. Intrinsic swelling ratios $[Q]$ of four coals in pyridine. Refer to Table 1 for coal symbols.

pyridine. Since ionic forces are predominant in lignite, $[Q]$ of the ND coal was obtained in tetrabutylammonium hydroxide/pyridine ($1/3$ v/v).⁸ The result indicates that the average molar mass of coal decreases with coalification. This proposition predicts that Q_{PI}/Q_{PS} for low rank coal is larger than Q_{PI}/Q_{PS} for high rank coal, because the average molar mass of PI from coal with high molar mass is estimated to be larger. The specific swelling ratios of PS and PI from O-methylated ND and IL coals were measured in THF at $C/S = 5\%$. The ND coal was O-methylated to reduce ionic forces in lignite. $Q_{PI}/Q_{PS} = 4.0/1.8$ for ND and $Q_{PI}/Q_{PS} = 2.5/1.8$ for IL were obtained.^{8,9} These results from this set of limited data support the above proposition.

Solvation Processes during Extraction and Swelling. If the structure of coal is represented by the physically associated structure, model B, the interaction of coal with solvents during extraction and swelling would then be controlled by the solvation of noncovalent bonds. Pyridine is one of the best solvents for coal, and an extractable portion of coal is promptly extracted or coal quickly swells in pyridine. Selected coal is, however, slowly extracted or swells. Even coal that is promptly extracted or swell is also slowly extracted or swell under certain conditions. These kinetics are easily measurable by use of regular procedures.

Ionic forces are known to be dominant noncovalent bonds in the lower ranks of coal.^{4,8} The process by which these ionic forces are solvated serves as the rate-determining step of swelling, during which water in the coal facilitates the solvation of these ionic forces. Dried lignite and subbituminous coal, in addition to their respective PI, swell very slowly in THF and pyridine.⁸ In this process, the dependence of time on swelling ratios is expressed by the following first-order equation as reported in the previous paper,⁸

$$\Delta Q = \Delta Q_{\infty} \{1 - \exp(-k_1 t)\} \quad (24)$$

where $\Delta Q = Q - Q_0$, $\Delta Q_{\infty} = Q_{\infty} - Q_0$, Q_0 and Q_{∞} are the initial and ultimate swelling ratios, and k_1 is the rate constant. Figure 9a shows the dependence of coal concentration on the specific swelling ratios of PI from ND coal in pyridine at the initial stage and again after 24 h. The specific swelling ratios of this sample is dependent on both coal concentration and time. Swelling kinetics is, therefore, diagrammatically shown in Figure 9b based on the results in Figure 9a, eqs 2 and 24.

(14) Nishioka, M. *Energy Fuels* **2001**, *15*, 1313.

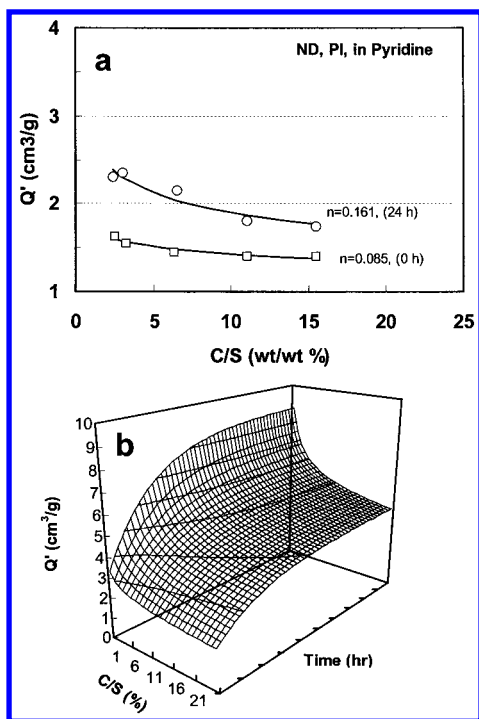


Figure 9. (a) Specific swelling ratios Q' of PI from ND coal in pyridine as a function of coal/solvent mass ratios C/S . Refer to n values for eq 2. (b) Schematic diagram of specific swelling ratios as functions of coal/solvent mass ratios C/S and time.

It was reported that extraction kinetics follow the same first order eq 25 as eq 24,³

$$E = E_{\infty} \{1 - \exp(-k_2 t)\} \quad (25)$$

where E is the extraction yield at time t , E_{∞} is the ultimate extraction yield, and k_2 is the rate constant. High-volatile bituminous coal is promptly extracted with pyridine and also instantly swells in the solvent. We note that it is difficult to accurately compare actual extractability with eq 25. Approximately 1 day was sufficient time to extract 95 wt % of the extractable materials from the coals, whereas more than 7 days were required to get the same 95 wt % extraction from medium- and low-volatile bituminous coals.³ For the latter case, it was found that extractability follows eq 25. Extraction is a process between solubles and insolubles, while swelling is a process for the entire coal fractions. Both Equations (24) and (25) demonstrate that the procedures of coals with solvents are controlled by the solvation of intra- and intermolecular interactions or noncovalent bonds regardless of whether the fraction is soluble.

Concluding Remarks. The structure of coal is represented by model B in Figure 1. The average molar mass of coal is estimated to be a few thousand, and decreases with an increase of the rank of coal. The average molar mass of PI is comparable to those of the high-molar-mass fractions of PS. Although these conclusions have not been proved, the experimental results and the theoretical investigation were all consistent.

The volumetric swelling method employed is relatively simple. Coal samples used are standard and obtainable by the entire community. Further systematic experiments with this method is desired. Other currently used analyses applicable for polymer solutions are also recommended to analyze coal structure. However, the average molar mass of coal may not be as high as previously expected, and should be noted to conduct these analyses. Why are most portions of coal not extracted with any solvents? We are still not ready to provide an answer, but it should be reiterated that coal is polyfunctional high-molar-mass material. There is no reason to expect that most portions should be readily extracted even if coal is not covalently cross-linked.¹⁵ Indeed, PI fractions are generally dissolved in pyridine to a small extent, even though coal has been exhaustively extracted. A soluble portion is easily visible. Before the discovery of CS_2 -NMP mixed solvent, pyridine was the best solvent for medium-volatile bituminous coal. The mixed solvent is, however, much more extractable for the coal than pyridine.

The volumetric swelling method using a glass tube is not an ideal procedure to measure swelling ratios, because the lower limit of C/S is practically 2–3%, and a mixture of coal and solvent is not continuously mixed. Is the swelling of coal significantly enhanced at very low concentrations under an ideal procedure? It has been suggested that intermolecular association is more dominant than intramolecular association, and that the size of molecules in associated complexes is a determining factor for swelling ratios. Accordingly, coal complexes swell more due to solvation of noncovalent bonds at very low concentrations, but coal molecules may also dissociate from complexes. Larger swelling may not be expected even though the coal swelling is at very low concentrations measured under continuous mixing.¹⁶ A change in the total number of coal particles must be considered to calibrate the value of coal swelling.

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