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Investigation of Associated Structure of Upper Freeport Coal by Solvent Swelling

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Upper Freeport (Argonne Sample) coal was extracted with carbon disulfide−*N*-methyl-2-pyrrolidinone (CS_2−NMP) mixed solvent at room temperature. The swelling behaviors for the raw coal, heavy extract fractions, and extraction residue were investigated in several organic solvents. The swelling ratio of the raw coal was lower than those of the extract fractions and residue, independent of the kind of solvents used. For both acetone-insoluble extract fraction and extraction residue, swelling ratio in THF increased with decreasing the sample/solvent weight ratio. The extract fractions and residue also showed similar swelling behaviors on effects of swelling time and temperature. These results suggest that the extraction residue has a similar cross-link structure as that for the extract fractions, i.e., a strongly associated structure among coal molecules through several noncovalent interactions, since the extract fractions seem to have little covalently bound cross-link structure as they are soluble in a better solvent such as the CS_2−NMP mixed solvent. So, Upper Freeport raw coal also consists of mainly associated structure of coal molecules.

Introduction

Coals are known to swell in organic solvents, indicating that coals have a cross-link structure. Extraction yield of coals with usual organic solvents is usually less than 20 wt % if bond scissions do not occur in coals. This agrees with the concept of "two phase model";[1,2] i.e., coal consists of solvent-insoluble covalently bound cross-linking network structure and a relatively small amount of low molecular weight constituent trapped in the network. While a carbon disulfide−*N*-methyl-2-pyrrolidinone (CS_2−NMP) mixed solvent has been found to give high extraction yield, 45−78 wt % (daf) for bituminous coals under mild condition as at room temperature,[3−6] no significant chemical reaction has been indicated to occur during the solvent extraction.[4] Moreover, recently it was found that the addition of tetracyanoethylene (TCNE) in the extraction of Upper Freeport coal with CS_2−NMP mixed solvent greatly increased the extraction yield from 60 wt % (daf) to 85 wt % (daf),[7,8] suggesting that TCNE dissociates the association between coal molecules, resulting in the increase in the extraction yield. These results indicate associated structure of coals and little existence of solvent-insoluble covalently bound cross-link structure. The associated nature in coal structure was also indicated from the results of solubility[9−11] and molecular weight distribution of coal molecules,[12] and calculation of energy-minimum structure for coal molecular models.[12] Significant contributions of noncovalent interactions (hydrogen bonds,[13,14] charge transfer interactions,[8,15,16] π−π interactions,[17,18] etc.) to coal association have been also reported.

Coal extract has been reported[19−21] to swell in organic solvents like extraction residue. One explanation for this swelling is an existence of strong associates by several noncovalent interactions,[21] although no evidence for the cooperative mechanism that couples these weak interactions together in coal structures has yet been provided. Phase separation of the extract−solvent

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system is another explanation.[22] The acetone-insoluble (E-AI) fraction of the coal extract with the CS_2−NMP mixed solvent was little soluble in methanol or benzene and swelled to a significant extent in those solvents.[21] Some portion of the E-AI fraction was soluble and gave a high swelling ratio in pyridine. Extractability, solubility, and swellability of coal depend on the affinity between the coal and solvent used. Swelling is a behavior observed by dissolution of solvent into coal cross-links. The order of affinity among the solvents above is methanol, benzene < pyridine < CS_2−NMP. Methanol or benzene would not be able to dissociate the strong associates in the heavy extract constituent. Recently, the correlation of the coal swelling with the heat of immersion of coal in various solvents was reported by Suuberg et al.,[23] and the dissociation of noncovalent cross-links was described to be an important factor of the coal swelling process.

The volumetric swelling measurement using a glass tube has been widely used.[24-26] One of the problems for this method is a dissolution of coal soluble portions in the solvent used, resulting in a change in the chemical potential of the solvent. It can be avoided by using the extraction residue, although the cross-link structure of the residue may be different from that of the raw coal. When a raw coal is used as a swelling sample, the solvent/coal weight ratio of more than 10 is needed to neglect the effect of solubles.[27] Nishioka has reported[28] that at lower coal concentration, i.e., more than 20 of solvent/coal weight ratio, swelling ratios for both raw coal and the pyridine-extracted coal were significantly enhanced, probably due to the dissociation of coal associates at low concentration. Thus, attention should be given to the measurement procedure of swelling ratio and the explanation of the results.

In this paper, cross-link structures of Upper Freeport raw coal and its extract fractions and extraction residue which were obtained from CS_2−NMP extraction at room temperature are discussed based on the swelling behaviors in several organic solvents.

Experimental Section

Extraction and Fractionation. Upper Freeport coal (Argonne Sample, <150 μm) was exhaustively extracted with the CS_2−NMP mixed solvent (1:1 by volume) under ultrasonic irradiation (38 kHz) at room temperature.[5] The extract obtained was fractionated with acetone into acetone-soluble (E-AS) and acetone-insoluble (E-AI) fractions, and the E-AI fraction was further fractionated with pyridine into pyridine-soluble (E-PS) and pyridine-insoluble (E-PI) fractions as shown in Figure 1. The residue, E-PS, and E-PI were washed with acetone, while E-AS was washed with acetone−water (2:8) solution under ultrasonication to remove the retained solvents. All fractions were dried in a vacuum oven at 80 °C overnight. The extraction yield was calculated from the weight of residue on a dry-ash free basis. The extraction yield and the fraction distribution are shown in Table 1.

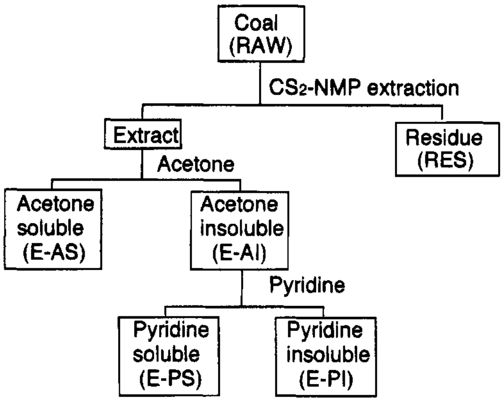

Figure 1. Extraction and fractionation procedures.

Table 1. Extraction of Upper Freeport Coal with the CS_2−NMP Mixed Solvent and Fractionation of the Extract

extraction yield (wt % (daf))	residue (RES) (wt % (db))	extract fraction (wt % (daf))		
		E-AS	E-PS	E-PI
59.4	48.4	7.3	22.1	30.0

Solvent Swelling. A disposable Wintrobe glass tube (Fisher Scientific, Pittsburgh) of 3 mm inner diameter and 115 mm in length was used. Upper Freeport raw coal, its extract fractions, and extraction residue were passed through the screen of −100 mesh (<150 μm). A styrene−divinylbenzene copolymer with 8% cross-linkage (BIO-BEADS S-X8, Bio-Rad Laboratories) was also used as a swelling sample. The weighed sample put in the glass tube was centrifuged for 5 min (3600 rpm). Solvent was added to the sample in the tube, and the content was stirred with a thin stainless rod. The tube was again centrifuged for 5 min and the height of the sample layer was measured. The specific swelling ratio Q' (cm^3/g) is calculated by the following equation.

$$Q' = V_{\text{swell}}/W_{\text{init}} \tag{1}$$

V_{swell} is swollen coal volume (mL) and W_{init} is initial weight (g) of the sample. Ash in coal sample is considered not to swell and the ash content was corrected as the following equation.

$$Q'_{\text{ash-free}} = \frac{h\pi(d/2)^2 - W_{\text{init}}\text{ash}/2.7}{W_{\text{init}}(1 - \text{ash})} \tag{2}$$

h is the height of the swollen sample and d is the inner diameter of glass tube. ash is weight fraction of ash in the sample, and the average density of ash was assumed 2.7 (g/cm^3). Q' has the following relationship with Q (swollen coal volume/initial coal volume) using a bulk density (BD) of the sample.

$$Q' = Q/\text{BD} \tag{3}$$

The above procedure, from stirring to measuring the swollen height, was repeated until a constant height was attained.

Deashing of the extraction residue was carried out; i.e., 1 g of residue was mixed with 15 mL of hydrochloric acid, 5 mL of hydrofluoric acid, and 15 mL of distilled water, and then warmed at 95 °C under nitrogen gas for 3 h. The sample after filtration was washed with distilled water until its filtrate was neutral and dried in a vacuum oven at 80 °C overnight.

Results and Discussion

Swelling of Raw Coal, Extraction Residue, and Extract Fractions in Methanol and Benzene. Table 2 shows the swelling ratios Q' of the raw coal, residue, and extract fractions in methanol and benzene. The

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Table 2. Swelling Ratios of Upper Freeport Raw Coal, Extraction Residue, and Extract Fractions in Methanol and Benzene

	swelling ratio, Q' (cm^3/g)	
sample	methanol	benzene
RAW	1.3	1.2
RES	1.8	2.1
E-AI	1.8	2.0
E-PI	2.0	2.1
E-PS	1.8	2.1

Table 3. Swelling Ratios of Upper Freeport Raw Coal, Extraction Residue, and Extract Fractions in Better Solvents

	swelling ratio, Q' (cm^3/g)				
sample	THF	pyridine	NMP	CS$_2$–NMP	TBAH-Py
RAW	1.3	1.3	–	nd[a]	nd[a]
RES	2.5	2.6	2.7	3.1	3.3[a]
E-AI	2.5	2.7[a]	nd[a]	nd[a]	nd[a]
E-PI	2.8	3.1	3.1	nd[a]	nd[a]
E-PS	2.8[a]	nd[a]	nd[a]	nd[a]	nd[a]

[a] Some dissolution occurred.

swelling ratio for raw coal is 1.2–1.3 and was much lower than those for the residue and extract fractions, which are 1.8–2.0 and 2.0–2.1 in methanol and benzene, respectively. For all fractions including the raw coal and residue, little solubles came out. The E-AI and E-PS fractions were all dissolved in the CS$_2$–NMP mixed solvent, while a part (45%) of the E-PI fraction was found to be insoluble in the mixed solvent,[8,29] although the E-PI has been obtained from the extraction with the same mixed solvent. It was noted that the addition of TCNE recovered solubility of the E-PI in the mixed solvent from 55 to 99%,[8] suggesting that the insolubilization of E-PI is due to the formation of association between the E-PI molecules themselves and the effect of addition of TCNE is to dissociate their associates.

It was reported[21] that the swelling ratio of the residue obtained from the CS$_2$–NMP extraction increased with increasing the extraction yield, that is, more removal of extracts reduced more the cross-link density. The addition of TCNE during the extraction of Upper Freeport coal with CS$_2$–NMP mixed solvent greatly enhanced the extraction yield from 60% (daf) to 85% (daf).[7] This result indicates that significant portions (at least 25%) of residue could be extracted (dissolved) when their associates have been dissociated.

Swelling in Better Solvents. Table 3 shows the swelling ratios of the raw coal, residue and extract fractions in THF, pyridine, NMP, CS$_2$–NMP, and tetra-*n*-butylammonium hydroxide (TBAH)–pyridine mixture (1:3)[30,31] which are better solvents than methanol or benzene. "nd" in Table 3 means that the measurement of the swelling ratios was impossible due to the dissolution in the solvent. The better the solvent that was used, the higher the swelling ratio that was obtained. In TBAH–pyridine, the swelling ratio of the residue was the highest value, i.e., 3.3, and some dissolution occurred. The swelling ratio of the residue increased as the affinity of solvent to coal increased, i.e., THF < pyridine < NMP < CS$_2$–NMP < TBAH–pyridine. This tendency was also observed for the extract fractions.

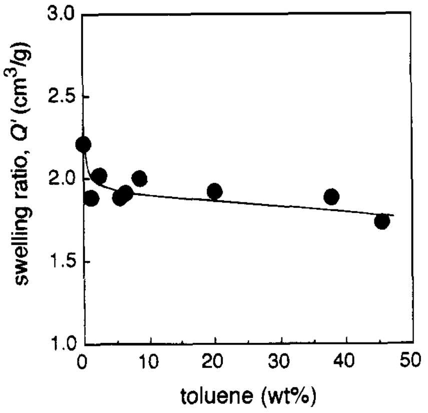

Figure 2. Effect of addition of toluene on the swelling ratio of styrene–divinylbenzene copolymer in THF.

To examine the effect of solubles on the swelling, toluene was added as the solubles to styrene–divinylbenzene copolymer–THF mixture. The swelling ratio of the copolymer versus the concentration of toluene added is shown in Figure 2. The swelling ratio without toluene was 2.2, and the ratio was decreased to 1.9–2.0 with addition of toluene of 1–10 wt %, indicating that an existence of dissolved component in the solvent lowered the swelling ratio of copolymer, probably due to lowering of chemical potential of the solvent.

Figure 2 also shows that the effect of toluene concentration on swelling was small when the concentration exceeded 10%. The synergistic effects of mixed solvent system on the swelling behavior of coal have been reported.[21,23,32,33] When the composition of the benzene–methanol mixed solvent was changed,[21] the highest swelling ratio (2.8–2.9) was obtained at 50–70 vol % benzene for the E-PI of Zao Zhuang coal, although each swelling ratio alone is 1.3 in methanol (100%) and 1.7 in benzene (100%). Hydrogen-bond breaking affinity of methanol and strong affinity of benzene toward coal aromatics may be the reasons for this synergistic effect of the mixed solvent. Suuberg et al.[23] have described that the swellability of coals in specifically interacting solvents is a strong function of the electron donatability of the solvents, and the solvents dissociate the noncovalent cross-links, resulting in the maximum extent of swelling.

Effect of Coal/Solvent Ratio. Figure 3 shows the swelling ratios of the residue and extract fractions against the coal/solvent weight ratio. When benzene was used as a solvent, no change was seen for the swelling ratio for both the residue and E-PI fraction. On the other hand, in THF, the swelling ratios of the residue and E-AI increased as the coal/solvent weight ratio was decreasing. For the pyridine-extracted coal, a similar behavior has been observed.[28] The swelling behavior of styrene–divinylbenzene copolymer, which is a covalent cross-linked polymer, is shown in Figure 4. The swelling ratios did not change in this case. THF is a more polar solvent and has a higher affinity for coal molecules than benzene. Association of coal-derived asphaltene has been reported to be less significant in

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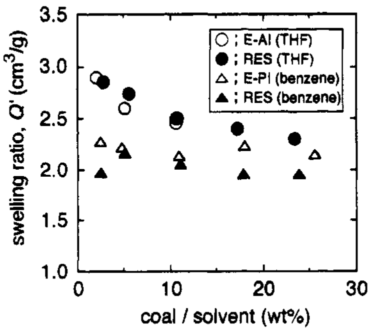

Figure 3. Swelling ratio of the residue and the extract fractions against the coal/solvent weight ratio: (○) E-AI (in THF); (●) RES (in THF); (△) E-PI (in benzene); (▲) RES (in benzene).

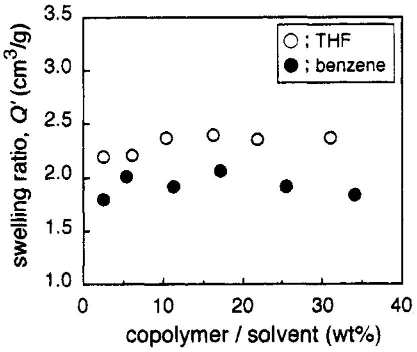

Figure 4. Swelling ratio of styrene–divinylbenzene copolymer against the copolymer/solvent weight ratio: (○) in THF; (●) in benzene.

THF than in benzene.[34] If several noncovalent interactions cooperatively form cross-links in the domains, THF dissociates some associates among coal molecules and dissolves some of coal molecules, leading to the decreases in cross-link density and the chemical potential of the solvent. Therefore, the increase in swelling ratio at low coal/solvent ratio in THF observed in Figure 3 may be due to the dissociation of associates among coal molecules or the apparent increase in the chemical potential of the solvent by adding more THF.

It should be noted that the evidence for formation of cross-links by noncovalent interactions is still poor, as suggested by Painter.[22] Recently, Suuberg et al. reported that the dissociation of such noncovalent cross-links in coals greatly influences the swelling process. Further study to make clear whether there exists the cooperative noncovalent cross-links or structural domains that provide mechanical integrity will be necessary.

Effect of Ash in Coal. Ash is concentrated in the residue in the CS_2–NMP extraction.[35] As described in the Experimental Section, ash constituents are not considered to swell in organic solvents and the swelling ratio was corrected for the ash content in the calculation. Here, the effect of ash present in the residue on swelling ratio was examined. Table 4 shows the change in swelling ratio by deashing treatment for the extraction residue. The ash content in the residue was decreased from 26.0 to 5.6% by the deashing. The swelling ratio of deashed residue was greatly decreased in both benzene and methanol. The decrease in spin concentrations in coals[36] and the decrease in extraction yield of coals[37] by deashing treatment have been reported. The removal of ash from coals decreases the swellability and extractability since it makes the coal molecules form strong interactions by access between the coal molecules. Mochida et al.[38] reported that the removal of bivalent Ca^{2+} by deashing treatment of low-rank coal increased liquefaction yields and described that this can be due to the breakage of cross-link by ionic interaction between the coal molecule and Ca^{2+}.

Table 4. Effect of Deashing on the Swelling Ratio of Residue

sample	swelling ratio, Q' (cm^3/g) methanol	swelling ratio, Q' (cm^3/g) benzene
RES	1.8	2.2
deashed RES	1.3	1.4

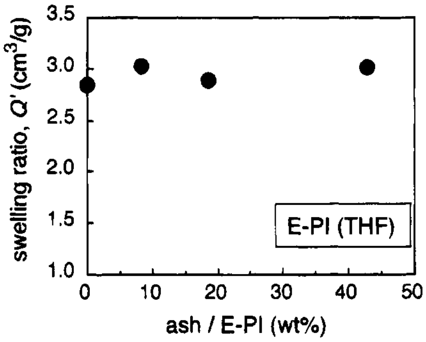

Figure 5. Effect of addition of ash on the swelling ratio of E-PI in THF.

Table 5. Time and Temperature Dependences of the Swelling Ratios in Toluene

time (h)	room temp RES	room temp E-PI	70 °C RES	70 °C E-PI
0	2.1	2.4	–	–
1	2.1	2.3	2.1	2.2
3	–	2.3	–	2.1
6	2.0	2.4	2.0	2.2
24	2.1	2.3	1.8	2.0
48	2.1	2.2	2.1	2.1
72	2.2	2.3	1.8	2.2

The ash component obtained from liquefaction process of Illinois No. 6 coal was added to the E-PI fraction, and the swelling ratio in THF is shown in Figure 5. No effect of addition of ash was seen on the swelling ratio, suggesting that the ash added does not influence on the swelling of organic components in coals; i.e., the ash added neither interacts with coal molecules nor penetrates the coal cross-links, unlike the effect of the ash that originally existed in the coal as described above.

Effect of Time and Temperature on Swelling Ratio. The time and temperature dependences of swelling ratios for the residue and the E-PI are shown in Tables 5 and 6. Table 5 shows the swelling ratios in toluene at room temperature and 70 °C. "Time 0" in Tables 5 and 6 means the value after the first centrifugation of coal sample with solvent. Time dependence at room temperature or at 70 °C was not seen for both the residue and the E-PI, indicating that a swelling

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Table 6. Time and Temperature Dependences of the Swelling Ratios in NMP

	RES	
time (h)	room temp	70 °C
0	2.9	–
1	2.8	2.7
3	–	–
6	2.7	2.8
24	2.9	2.7
48	2.8	2.8
72	2.7	2.7

equilibrium was reached as soon as the coal sample and solvent was mixed. The extent of sorption of pyridine on the coal cross-links has been reported to be similar for extract and residue from the pyridine–Soxhlet extraction.[39] Table 5 also shows that the residue gave a similar swelling ratio at room temperature and at 70 °C, and the swelling ratio of E-PI at 70 °C was a little lower than that at room temperature. The E-PI fraction which is the heaviest fraction of the extract obtained from the CS_2–NMP extraction has been reported[11] to undergo insolubilization by refluxing treatment (~115 °C) for 1 day with pyridine, and the swelling ratio after the refluxing treatment was decreased compared to that before the treatment. The pyridine treatment of bituminous coals at room temperature for 1 week also decreased the extraction yield.[11] The solubility of the E-PI was found to be enhanced by addition of a small amount of tetracyanoethylene (TCNE), tetracyanoquinodimethane (TCNQ), or *p*-phenylenediamine.[8,29] These results indicate that the increased mobility by the solvent treatment makes the strain and anisotropic structure[40–42] of raw coal a more stable conformation. The simulation of molecular structure for the solvent-solubles of coal showed that associated structures of coal molecules through noncovalent interactions are the most stable conformation.[12] Table 6 shows time and temperature dependences in NMP which is a better solvent than toluene. Higher swelling ratios than with toluene were obtained, but no temperature dependency suggests that the cross-link structure did not change at 70 °C. The occurrence of solubles was also hardly observed. Higher temperature may be needed to dissociate the associates among coal molecules formed through cooperative noncovalent interactions.

Cross-Link Structures of the Raw Coal, Extract, and Residue. At least 85% of organic constituents of Upper Freeport raw coal has been found to consist of solvent-soluble molecules.[7,8] The stronger solvent was used as an extraction solvent; a higher extraction yield was obtained, indicating that many kinds of noncovalent bonds have a wide range of bond strength. The cross-link density of the raw coal is considered to be higher than those of the extract and residue, since the swelling ratio of the raw coal was low as shown in Table 2. Several cooperative noncovalent interactions, such as hydrogen bonding, π–π interaction, charge transfer interaction, and van der Waals interaction, are considered to form strongly associated structures among the coal constituents. Therefore, the cross-link structure of the raw coal is schematically shown in Figure 6a. The raw coal is considered to be anisotropically strained and of tight structure. The structure of raw coal largely consists of associates of solvent-soluble molecules through the noncovalent interactions since at least 85% of organic constituents were soluble. The CS_2–NMP mixed solvent is a powerful solvent for extraction of bituminous coal and would be able to disrupt some noncovalent interactions between coal molecules shown in Figure 6a, resulting in the high extraction yield. It can be difficult for weak solvents such as benzene and methanol to break the associates and to penetrate the inside of coal, resulting in the low swelling ratio (1.2–1.3). A stronger solvent such as THF or pyridine can disrupt some associates, extract much more solubles, and decrease the cross-link density, resulting in an increase in the swelling ratio as observed in this study. The swelling ratio of the residue has been reported to increase with the extent of removal of extract molecules, i.e., the extraction yield.[21] The cross-link structure of the residue is considered as Figure 6b. The residue has two types of noncovalent bonds, which existed originally and newly formed due to rearrangement of the coal molecules during solvent extraction. The former bonds would not been disrupted by the CS_2–NMP mixed solvent. Some significant pores can be formed in coal cross-links after solvent extraction since 60% of coal molecules have been removed from the inside of cross-links by the extraction. This concept agreed with the experimental result of a high swelling ratio for the residue.

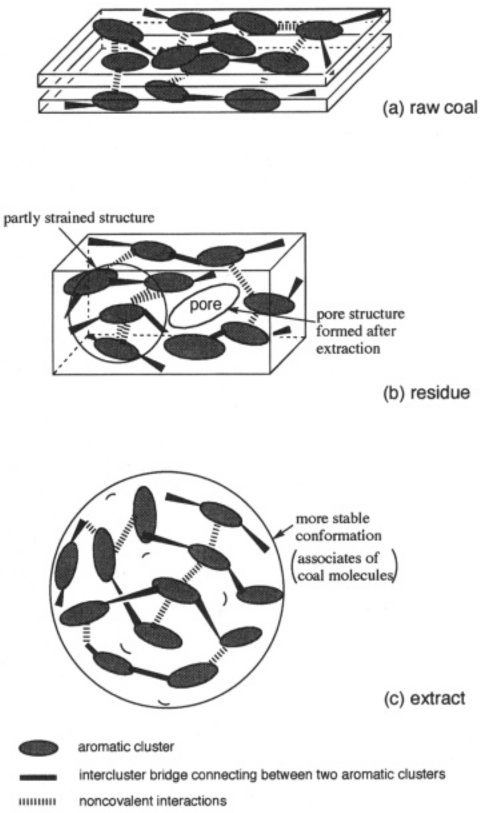

Figure 6. Cross-link structure of Upper Freeport raw coal (a), the extraction residue (b), and the extract (c) from the CS_2–NMP extraction.

The extract is associates of solvent-soluble molecules of various molecular weight. The molecular weight

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distribution for the E-PS and E-PI from some bituminous coals was composed of bimodal shape; i.e., one is a relatively low molecular weight region ($\sim10^3$) and the other is high molecular weight region ($\sim10^5$). It was found[12] that the region in high molecular weight was shifted to that in low molecular weight by addition of lithium bromide or anthracene in an eluent solvent, CS_2−NMP mixed solvent. This result is probably related to the existence of an association between coal molecules in the extract fractions. The associated structure of extract is formed by rearrangements of coal molecules during extraction. The structure of each coal molecule is relaxed in the solvent, and the energy-minimum conformation of coal molecules can be obtained. The cross-link structure of the extract is considered to be as shown in Figure 6c. There is little strained structure in the extract. The nature of the cross-links of the extract fractions is similar to that of the residue shown in Figure 6c, since a very similar swelling behavior was observed in this study.

Conclusion

Swelling behaviors of the extract fractions and residue obtained from the room-temperature extraction were investigated. It was found that the swelling ratios in THF for both the extract fraction and the residue increased with decreasing the coal/solvent weight ratio. They also showed similar swelling dependency on swelling time and temperature. This similarity of their swelling behavior suggests that they form strongly associated structures through several noncovalent interactions, not a covalently bound network structure. Thus, Upper Freeport raw coal itself is considered to be also associates of coal molecules, since the corresponding extract and residue have been obtained from the room-temperature extraction in which no breakage of covalent bond occurs.

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