

Communications

Investigation of Association in Coal Extract Solution by the Measurement of Relative Viscosity

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Received February 21, 2001

A large portion of coal does not dissolve even in good solvents, but swells in many organic solvents. Swelling ratios of coal are constant within experimental errors regardless of coal/solvent ratios, if coal/solvent mass ratios (C/S) are more than 10%. However, when coal concentrations are decreased to less than 10%, swelling ratios increase as illustrated in Figure 1.¹ The result in this figure was obtained by the volumetric method using a glass tube. With this method, the initial height before swelling often differs even though the amount of samples is constant. This is attributed to the different bulk density of coal powder. The difference in the initial height leads to significant errors for volumetric swelling ratios. This is particularly true when a small amount of coal must be examined. Swelling volume (Q') per bulk density (BD) is, therefore, used in Figure 1 instead of the conventional swelling volume ratios. The Q' value corresponds to a swollen volume (mL) of 1 g sample.

The dependence of solvent swelling on coal concentration is not coincident with the three-dimensionally cross-linked model, because the number of cross-links changes with coal concentration. Exposure to lower C/S values results in increased solvation of strongly interacted sites, or larger swelling. Although solvent swelling is the characteristics of cross-linked macromolecules, physically interacted sites may contribute to cross-links in addition to covalently cross-linked chemical bonds for coal. The dependence of solvent swelling on coal concentration is the result of associative equilibria for coal insoluble fractions. The same associative equilibria may also be observed for coal soluble portions.

Association in polymeric material solutions is often observed. Solutions are uniform under a low degree of association, whereas phase separation such as precipitation and colloidal formation may be observed under a high degree of association. In fact, colloidal formation^{2,3} and change in measured molecular mass⁴ were found for coal soluble fractions. However, these phenomena have been interpreted as the results of chemical reactions. Thus, the possibility of association must be carefully considered for the analysis of molecular mass and phase separation.

Precipitation from a pyridine extract solution was

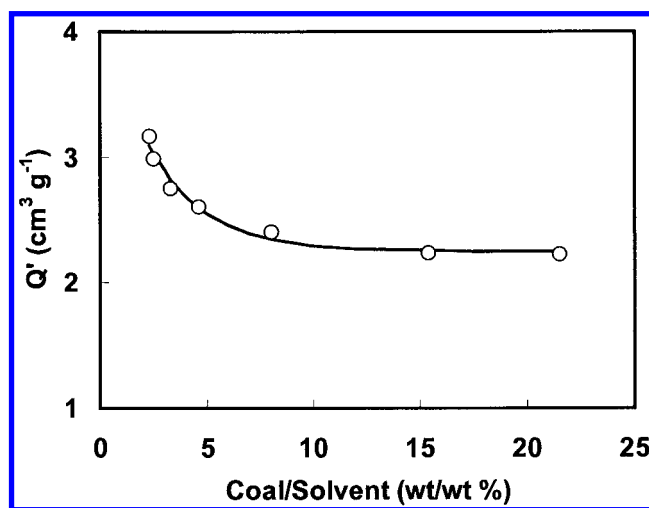


Figure 1. Swelling ratios of a coal insoluble portion in pyridine as a function of coal/solvent ratio.¹

reported by Dormans and Krevelen.⁵ Pyridine extracts from coals of less than 87% C did not form precipitates after 240 h, while those from coals with more than 87% C yielded precipitates amounting to between 10 and 30 wt % of extracts. Pyridine extracts from lower rank coals did not precipitate, but did when their solutions were concentrated.⁶ These results may be interpreted as the change in associative equilibria controlled by coal rank and concentration.

Association is a critical factor to determine molecular mass and its distribution of coal solubles. Vapor pressure osmometry (VPO) is usually used to measure a number average molecular mass. Molecular mass is obtained by extrapolating observed values to zero concentration to minimize the effect of concentration, whereas gel permeation chromatography (GPC) has been used to obtain a molecular mass distribution of coal at relatively high concentrations.^{7,8} Care must be taken in the analysis of a molecular mass distribution.

The molecular mass distribution of a pyridine Soxhlet-extractable but room-temperature nonextractable fraction was measured.⁹ GPC results showed that there was a

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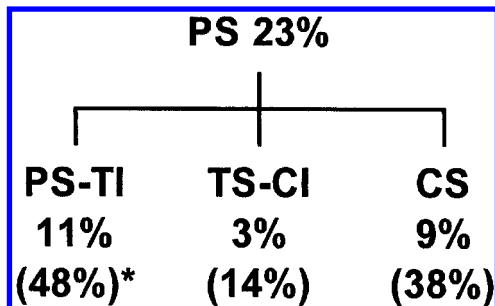
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Table 1. Elemental Analysis and Molecular Mass of Blind Canyon Coal and Its Extracts (wt %)

symbol	sample	H ₂ O	ash	element (daf)					H/C (atom/atom)	molecular mass
				C	H	N	S	O (diff.)		
DECS-16	Blind Canyon coal	5.2	13.2	81.0	5.9	1.5	0.6	11.0	0.87	
PS	pyridine-solubles			81.6	7.1	2.3	0.6	8.4	1.04	800
PS·TI	pyridine-solubles and THF-insolubles			78.2	6.5	2.4	0.4	12.5	1.00	1460
TS·CI	THF-solubles and chloroform-insolubles			79.0	5.9	2.3	0.4	12.4	0.90	1230
CS	chloroform-solubles			86.5	9.1	0.7	0.3	3.4	1.26	550

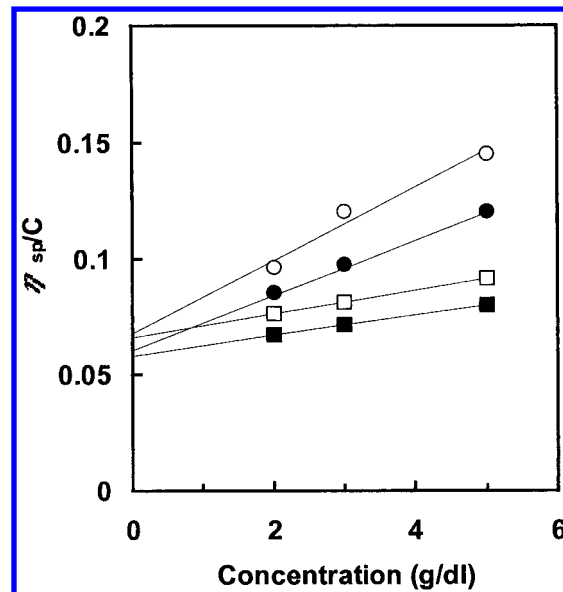
**Figure 2.** Yields (wt %) of fractionated samples (*values in parentheses denote yields in the PS fraction).

clear shift toward lower molecular mass at 70 °C compared to that at room temperature in pyridine. This demonstrated more association of coal extract in pyridine at room temperature. Iino et al.¹⁰ obtained 50–60 wt % extraction yields from medium-volatile bituminous coals using CS₂/*N*-methyl-2-pyrrolidinone (NMP) mixed solvent (1:1 by volume). A molecular mass distribution of the extract was measured in the mixed solvent by using GPC. The distribution was shifted toward lower molecular mass by adding small amounts of LiBr and anthracene.¹¹ It is seen from these results that the effect of association on the molecular mass distribution of coal is significant.

Although association of coal-derived material has been studied,¹² work done with coal extracts is very limited. Evaluation of association of coal solutions is essential for characterization of coal. An additional study is necessary to verify association of extracts. In this communication, coal molecular association in solution is evaluated by the measurement of relative viscosity of coal solutions.

Blind Canyon (DECS-16) coal was obtained from the DOE Coal Bank at Pennsylvania State University. Reagents and HPLC-grade solvents were obtained from Fisher Scientific (Pittsburgh, PA) and Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. The DECS-16 coal (10 g) was Soxhlet-extracted with pyridine for 72 h. The pyridine was removed with a rotary evaporator leaving a viscous sample (~10 mL). Approximately 300 cm³ of tetrahydrofuran (THF) was mixed with this sample and filtered. The recovered THF-solution was concentrated and treated with chloroform using the procedure described above. From this procedure, pyridine-soluble/THF-insoluble (PS·TI), THF-soluble/chloroform-insoluble (TS·CI), and chloroform soluble (CS) fractions were obtained in the amounts shown in Figure 2. A pyridine-soluble (PS) fraction was obtained for comparison.

An Ubbelohde viscometer (ASTM size 1) was used for viscosity measurements. The viscometer was immersed

**Figure 3.** The viscosity number in pyridine versus concentration for four fractions at 25 °C (○: PS·TI, ●: TS·CI, □: PS, ■: CS).

in a water bath controlled to ±0.1 °C. The measurements were carried out five times with average viscosity calculated after eliminating the extremes.

When the viscosity of solution and solvent are given as η and η_0 , respectively, specific viscosity (η_{sp}) is defined as eq 1:

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = (t - t_0)/t_0 \quad (1)$$

where t and t_0 represent flow times in the viscometer for solution and solvent, respectively. When solution concentration is given as c (g dL⁻¹), η_{sp}/c is called the viscosity number. The viscosity number at $c \rightarrow 0$ is called the limiting viscosity number and is expressed as $[\eta]$ (eq 2):

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/c \quad (2)$$

Elemental analyses of the fractions were conducted by Geochemical Testing (Somerset, PA). Molecular mass of the samples was determined in pyridine using VPO by Huffman Laboratories, Inc. (Golden, CO).

Table 1 shows the result of elemental analyses and molecular mass for the four fractions (PS, PS·TI, TS·CI, and CS) from the DECS-16 coal. It is observed that PS·TI and TS·CI fractions have higher molecular mass and higher oxygen content than PS and CS fractions, with the CS fraction containing the least amount of oxygen and nitrogen.

The dependence of concentration on specific viscosity was evaluated for the above four fractions in pyridine at 25 °C. The results are shown in Figure 3. Association of polymeric material in solution is generally enhanced at

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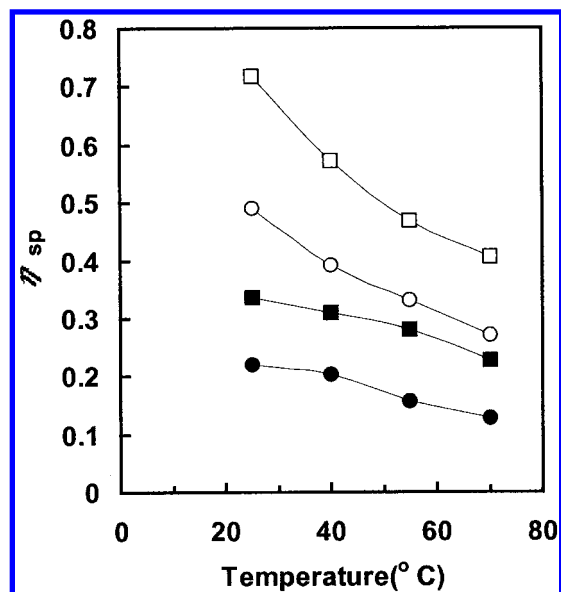


Figure 4. Specific viscosity in pyridine versus temperature for four fractions at concentration of 0.5 g dL⁻¹ (□: PS·TI, ○: TS·CI, ■: PS, ●: CS).

higher concentrations. The limiting viscosity number extrapolated to zero concentration is used to cancel the effect of concentration. The order of limiting viscosity numbers of these fractions was approximately the same within experimental errors, while the dependence of concentration on specific viscosity was larger for the PS·TI and TS·CI fractions than for the PS and CS fractions. It is interpreted that the PS·TI and TS·CI fractions with higher molecular mass associate in pyridine and their association is dependent on their concentration. On the other hand, the molecular mass of the PS fraction is larger than that of the CS fraction (Table 1), but the dependence of concentration on specific viscosity for the PS fraction is nearly equal to that of the CS fraction. This indicates that the degree of association and the effect of concentration on their association is similar for these two fractions.

From the results shown above and in Figure 1, it is seen that both soluble and insoluble fractions show associative equilibria in solvents and dissociate more at lower coal concentration. The dependence of coal swelling on coal concentration is the result for insoluble fractions, while the dependence of viscosity on coal concentration is the result for soluble fractions.

Next, specific viscosity of pyridine solutions for the four fractions from the DECS-16 coal was evaluated at concentration of 0.5 g dL⁻¹ between 25 and 70 °C. Figure 4 shows the results. The dependence of temperature on specific viscosity of the PS·TI and TS·CI fractions is larger than that of the PS and CS fractions. It is thought that the PS·TI and TS·CI fractions associate at lower temperatures than do the PS and CS fractions.

The PS fraction contains PS·TI and TS·CI fractions (62 wt %), but the degree of association does not change as much with the change in temperature as the PS·TI and TS·CI fractions. This suggests that the CS fraction may help dissociate associated complexes. This hypothesis is supported by the following: Sanokawa et al.¹³ fractionated samples extracted with a CS₂/NMP mixed solvent by using acetone and pyridine. Products involved acetone-

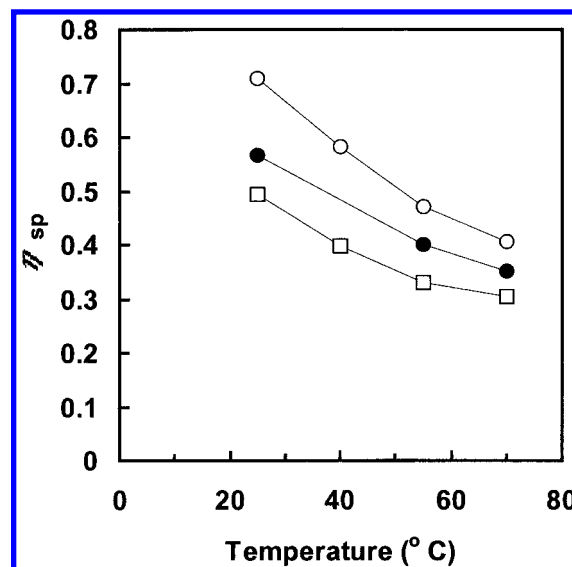


Figure 5. Specific viscosity of the PS·TI fraction versus temperature at concentration of 0.5 g dL⁻¹ (○: in pyridine, ●: in pyridine/triethylamine (95/5 v/v), □: in pyridine/NMP (95/5 v/v)).

soluble, acetone-insoluble, and pyridine-soluble, and pyridine-insoluble and CS₂/NMP mixed solvent soluble fractions. They found that 30–50 wt % of the pyridine-insoluble and CS₂/NMP mixed solvent soluble fraction became insoluble in the mixed solvent. The result showed that coexisting acetone- and pyridine-soluble fractions were necessary to dissolve the coal extract which was originally soluble in the mixed solvent.

Nitrogen and oxygen concentrations in the PS·TI and TS·CI fractions are higher than those of the CS fraction (Table 1). Solvent-induced associates contained higher contents of nitrogen and oxygen than the solubles.¹⁴ Nitrogen- and oxygen-containing compounds may affect solvent-induced association.¹⁴ Therefore, polar functional groups containing nitrogen and oxygen in the PS·TI and TS·CI fractions may be responsible for association in a solution. To confirm this proposition, 5 vol % of triethylamine and NMP was added in pyridine. The specific viscosity of the PS·TI fraction was measured at a concentration of 0.5 g dL⁻¹ between 25 and 70 °C. The results are shown in Figure 5. It was shown above that the PS·TI fraction shows the highest degree of association among the samples studied. Since the specific viscosity of this fraction visibly decreased after adding a small amount of triethylamine or NMP, it is thought that associative equilibria may have changed under the conditions imposed.

Pyridine is one of the best solvents for coal, but pyridine containing only 5 vol % of triethylamine is a much better solvent than pure pyridine for high-volatile bituminous coal.¹⁴ Amines are not good solvents as pyridine for bituminous coal. An increase in extractability was attributed to the better electron donor capability of amines than pyridine. The soluble wt % of the pyridine-insoluble and CS₂/NMP mixed-solvent-soluble fraction in the CS₂/NMP mixed solvent decreased after the fractionation as discussed above. This amount, however, significantly increased when adding less than 1 wt % of 7,7,8,8-tetracyanoquinodimethane or less than 5 wt % of *p*-

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phenylenediamine.¹³ The extractability of medium-volatile bituminous coal with this solvent also markedly increased after adding a few wt % of tetracyanoethylene (electron acceptor).¹⁵ These results support the above proposed mechanism on change in viscosity.

The dependence of coal swelling on coal concentration can be interpreted as the result of associative equilibria for coal insoluble fractions. In this communication, the same associative equilibria have also been observed for coal soluble fractions. The viscosity measurement using an Ubbelohde viscometer was confidently used to char-

acterize the association of coal soluble solutions. Extractable solubles showed association even in good solvents under the conditions used. The higher-molecular-mass fractions of PS·TI and TS·CI showed larger association in a solution. Association was dependent on temperature and concentration. The degree of association was reduced by adding small amounts of secondary solvents.

Acknowledgment. This work was partially supported by the U.S. Department of Energy under Contract No. DE-AC22-92PC91047. This author thanks my daughter, Yuzuka Nishioka, for clarifying my English.

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