18. Effect of Tetrabutylammonium Acetate Addition on the Aggregation of Coal Soluble Constituents

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Abstract
The effect of tetrabutylammonium acetate (TBAA) addition on the aggregation of heavy coal extract component, pyridine insoluble (PI) from the extraction of Upper Freeport (UF) coal with carbon disulfide-N-methyl-2-pyrrolidinone (CS₂-NMP) mixed solvent (1:1 by volume) was investigated. PI is partially insoluble in the mixed solvent, but the addition of a small amount of TBAA, the almost entire PI molecules become soluble in the mixed solvent. Recovered PI (PI-1) obtained by the removal of CS₂, NMP and TBAA from the solution was found to become almost completely soluble in the mixed solvent and NMP. The dissolution mechanism was discussed from the change of the aggregation state of PI at solution and solid states.

Introduction
Petroleum and coal derived materials are known to readily aggregate, and the aggregation state influences their solubility in organic solvents. CS₂-NMP mixed solvent has been found to give high extraction yield for some bituminous coals. We have reported that the addition of a small amount of tetracyanoethylene (TCNE) in the extraction of UF coal with CS₂-NMP mixed solvent greatly increased the extraction yield. Moreover, in the early study we found that pyridine insoluble extract component (PI) which came from the extracts of coals with CS₂-NMP mixed solvent (1:1 by volume) became partially insoluble in the CS₂-NMP mixed solvent. Addition of a small amount of TCNE or TBAA to the mixed solvent, PI became soluble again. Although the extraction yield enhancement of coals by adding some additives (TCNE or TBAA) has been found for a long time, but the mechanism is still not clear. In this paper, the influence of TBAA addition on the solubility of PI in CS₂-NMP mixed solvent and NMP is investigated, and the effect of additive on the aggregation of PI and the mechanism for solubility enhancement of PI are discussed.

Experimental Section
Upper Freeport coal (Argonne Premium Coal, <150μm) was exhaustively extracted with CS₂-NMP mixed solvent (1:1 by volume) under ultrasonic irradiation (38 kHz) at room temperature. The extraction yield of UF coal was 60.5 % (daf). The extract obtained was fractionated with acetone and pyridine, respectively, to give aceton soluble (AS), pyridine-soluble (PS) and pyridine-insoluble (PI), the amount of AS, PS and PI were 7.6, 24.3 and 24.5 wt% (db), respectively, the procedure was performed in the same way as that described elsewhere.

0.2g of PI was dissolved in 50ml CS₂-NMP mixed solvent at room temperature under ultrasonic irradiation with TBAA (5×10⁻⁵ mol to 0.2g PI). After the filtration with 0.8μm filter and removal of CS₂ and NMP from the PI solution in the CS₂-NMP mixed solvent with TBAA, the recovered PI was washed with water-acetone mixed solvent (4:1 by volume) to remove TBAA, then dried under vacuum for 12 h at 353
K. The resultant substance is hereafter referred to PI-1. Further solvent treatments of PI-1 were carried out by the procedures shown in Figure 1.

Results and Discussion
Effect of TBAA addition on the solubility of PI. Table 1 shows the results of the solvent treatments of PI in the CS$_2$-NMP mixed solvent (1:1 by volume) and NMP with or without TBAA. 31.4 wt% and 47.2 wt% of PI became insoluble in the CS$_2$-NMP mixed solvent and NMP, respectively, though PI is a part of the mixed solvent extracts. With the addition of a small amount of TBAA (0.25mmol/g-PI), the almost entire PI became soluble in the mixed solvent and NMP. PI-1 obtained by removal of CS$_2$, NMP and TBAA from the solution was found to be dissolved in the mixed solvent and NMP almost completely. The FT-IR spectra show that the peak at 2950 cm$^{-1}$ due to TBAA disappeared for PI-1, indicating little TBAA was retained in PI-1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Solubility, wt% db</th>
<th>Fractionation, wt% db</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CS$_2$-NMP</td>
<td>CS$_2$-NMP/TBAA</td>
</tr>
<tr>
<td>PI-1</td>
<td>68.6</td>
<td>99.2</td>
</tr>
<tr>
<td>PI-2</td>
<td>98.0</td>
<td>--</td>
</tr>
<tr>
<td>PI-3</td>
<td>63.1</td>
<td>99.2</td>
</tr>
<tr>
<td>PI-4</td>
<td>74.6</td>
<td>99.3</td>
</tr>
</tbody>
</table>

a: pyridine soluble.

Solvent treatment, i.e., dissolution, filtration, and removal of the solvents of PI-1 with the CS$_2$-NMP mixed solvent and NMP gave PI-2 and PI-3, respectively. PI-2 and -3 show low solubilities in the CS$_2$-NMP mixed solvent and NMP (63.1 wt% and 34.8 wt%, respectively), unlike PI-1, though they are considered to consist of the same components as PI-1 because of almost the complete dissolution (~ 98 wt% + loss) of PI-1 in the both solvents.

Table 1 shows that the addition of TBAA to PI-2 and -3 gave again high solubilities near 100%. Table 1 also shows that 30.9 wt% of PI-1 became soluble in pyridine, but original PI and PI-2 have only 0 wt% and 13.1 wt% of pyridine solubles, respectively.

All these results indicate that the addition of TBAA enhances the solubility of PI by changing the aggregation state, i.e., to a less aggregated state through the non-covalent bonds breaking among coal molecules.

Effect of temperature on solubility of PI in solution. PI-1 has a less aggregated state as mentioned above, and it can be almost completely dissolved in the CS$_2$-NMP mixed solvent without the presence of TBAA. Dissolving 0.05g of PI-1 in 50 ml CS$_2$-NMP mixed solvent, standing the PI-1 solution at different temperatures, the solubility changes of PI-1 with holding time were observed. The results are shown in Figure 2.

Figure 2 shows that after the standing at 50 °C for 1h, the PI-1 solution gave about 30 wt% of the insolubles, and further standing did not increase the insolubles much. This suggests that the aggregation state in PI-1 is not stable compared to a more extended aggregated state which makes the part of PI-1 insoluble. Addition of a small
amount of TBAA to PI-1 solution after standing at 50 °C for 1h, the amount of insoluble decreased from 30.5 wt% to 1.2 wt% due to the dis-aggregation by TBAA.

While, at 25 °C the change in the aggregation state is slow, and after 48h 32.8 wt% of PI-1 became insolubles, probably much more insolubles would be obtained for longer standing time. For PI-2 the amount of the insolubles in the mixed solvent is 36.9 wt% (Table 1), which is higher than 33.5 wt% of insolubles after PI-1 solution standing at 50 °C for 6.5h. This can be explained from the fact that PI-2 experienced about 2h at about 90 °C during the evaporation of NMP from PI-1 solution.

Mechanism of aggregation and dissociation of PI. Our present study indicates strongly that the aggregation state of PI influences its solubility with CS$_2$-NMP mixed solvent. The solubility of PI increase by TBAA addition is found to be caused by the breakage of non-covalent bonds between coal molecules. TBAA, which has strong interaction with coal molecules, can break even strong non-covalent bonds, and the new aggregates with TBAA are more soluble than the original aggregates. Washing the solid PI-1 with acetone-water mixed solvent to remove TBAA, PI-1 keeps the new aggregation state because the re-aggregation is very slow in the solid state, so it can be dissolved in the CS$_2$-NMP mixed solvent and NMP almost completely. The aggregation state of PI-1 is not stable, the re-aggregation of PI-1 is slow even in solution at room temperature, but this re-aggregation rate increases with temperature. PI-2 and PI-3 became partially insoluble again in the CS$_2$-NMP mixed solvent and NMP, respectively, by the change to more aggregated states during the NMP evaporation at about 90 °C for 2h.

Table 2 Peak area ratios of 3030 cm$^{-1}$ to 2920 cm$^{-1}$ from FT-IR spectra

<table>
<thead>
<tr>
<th>Samples</th>
<th>PI-2S</th>
<th>PI-2I</th>
<th>PI-3S</th>
<th>PI-3I</th>
</tr>
</thead>
<tbody>
<tr>
<td>3030 cm$^{-1}$/2920 cm$^{-1}$</td>
<td>0.19</td>
<td>0.35</td>
<td>0.20</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 2 is the results of FT-IR analysis for the peak area ratios of 3030 cm$^{-1}$ (assigned to aromatic ring C=C stretching) to 2920 cm$^{-1}$ (assigned to aliphatic C-H stretching). The ratio increase from the soluble to insoluble fractions, such as PI-2S (the soluble of PI-2 in the mixed solvent) = PI-2I (the insoluble of PI-2 in the mixed solvent), PI-3S < PI-3I. Insoluble fractions have more aromatic rings compared to soluble fractions. Aromatic π-π interactions may be one of the important non-covalent bonds in the aggregates.

References
Figure 1. solvent treatment procedure of PI from UF coal with the CS2-NMP mixed solvent and NMP with or without TBAA, and pyridine

Figure 2. Insolubles formed from PI-1/CS2-NMP solution vs. time at 25 °C (Δ) and 50 °C (□)