Behavior of additives on the coal solubility and aggregation

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Abstract

A very small amount of additives significantly increases the extraction yield of Upper Freeport coal in NMP/CS2 mixed solvent from 63% to 78~84%. Twenty additives were tested. The most effective ones are TCNE, TCNQ, PDA, 1,1,2,3,3-pentacyanopropenide (PCNP) and acetate anion. In addition, the effect of PCNP anion and acetate anion on the aggregation of coal extract was observed by Size Exclusion Chromatography. The result indicates that anions prevent the aggregation of the coal extracts.

Introduction

NMP/CS_2 mixed solvent has good extractability for some bituminous coals, e.g., ~60% for Upper Freeport coal and Zao Zhuang coal[1]. The purpose of adding additives into this mixed solvent is to further increase the coal solubility. Some of them increase the extraction yield of Upper Freeport coal from ~60% to ~80%[2,3]. Unfortunately, only a few additives are effective among the twenty additives we tested. In addition to their effect on coal extractability, some additives also prevent the aggregation coal molecules in solution, which was investigated by Size Exclusion Chromatography (SEC). The effect of TCNE on coal aggregation is hard to observe by SEC because of the strong interaction of TCNE with the polystyrene column[4]. Some anionic additives significantly increase coal extractability. They do not strongly interact with the column[5]. Their effect on coal aggregation was investigated by comparing the SEC eluted by NMP or NMP/anionic additive.

Experimental

Extraction of coal with NMP/CS_2 containing additive was carried out according to the method described in ref. 1. All the additives are commercial product except for NMP-1,1,2,3,3-pentacyanopropenide (PCNP), which was prepared by the author[3].

SEC was run on the polystyrene column (7.8_300mm, particle size 13μm, TOSOH Co., Japan) and eluted by NMP and additive modified NMP with a flow rate of 1.0ml/min.

The effect of anionic additives on pyridine-phenol hydrogen bond was observed by ^{1}H-NMR in $CDCl_3$.

Results and discussion

Table 1 presents the extraction yield of Upper Freeport coal extracted by NMP/CS_2 with or without additives. Some of these additives are strong electron acceptors or donors. In previous works, the charge-transfer interaction between coal and additive was considered to be responsible for breaking coal-coal interaction. However, the correlation of the electron acceptability or donate ability with coal extractability did not support this assumption[6]. In addition, TCNE was found converted to PCNP anion in NMP. This anion was as effective as TCNE, although it is not an electron acceptor[3]. The result rules out the formation of a charge-transfer complex between coal and TCNE as a main route to break coal-coal interaction.

TCNQ is another effective additive. The pathway of its interaction with coal is probably related to the interaction of TCNQ with solvent[7]. It is found that TCNQ forms radical anion in NMP but does not in THF and chlorobenzene. TCNQ is also effective in NMP but not in THF and chlorobenzene. TCNQ radical anion formed in NMP may have some relations with its effect on coal solubility. The mechanism is under investigation.

Aniline and *p*-dimethyl-aniline(PDA) are also very effective in increasing coal extractability as shown in table 1. Their electron donating ability with increased coal extractability was also not well correlated[8]. Instead, the hydrogen bonding formed between additive and coal was thought to be a factor. Comparing the effect of aniline and dimethylaniline; PDA and TMPDA, methylated amines are less effective. The result indicates that hydrogen bonding formation may affect the extraction of coal, because dimethylaniline and TMPDA have weaker ability to form hydrogen bonds with coal.

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Anion is an effective additive found recently [3,5]. The most effective ones are PCNP anion and acetate anion. They increase UF coal extractability from 62% to 78~84%. Hydrogen bonding with coal may also be a factor to break coal-coal interaction, which will be discussed later.

These additive are also effective in increasing the solubility of PI fraction, which is a fraction from coal extract that dissolves in NMP/CS_2 but not in pyridine. Two PI fractions were prepared by different method. PI(1) was prepared by washing extract with pyridine under ultrasonic radiation at room temperature, while PI(2) was washed by pyridine with Soxhelt extraction, in which more pyridine solubles were removed(unfortunately, the accurate weight loss was not measured, roughly estimated about 10~20%). The solubility of the two PI in NMP/CS_2 is significant different as shown in table 2. The more pyridine solubles is removed the lower solubility is. It seems that the PI(2) becomes more associated. Both PI fractions are associated by non covalent bonding, but the effect of these additive on them is different. TCNE is always the most effective one. Over 90% of PI was dissolved in NMP/CS_2 with addition of TCNE for the two PI fractions. However, TCNQ, DDQ and others become less effective for PI(2). Some of them even cause stronger association of coal, and decrease the solubility of PI(2). The difference between PI(1) and PI(2) is that PI(1) still has more pyridine solubles which is difficult to remove at room temperature. In other words, PI(2) is heavier than PI(1). The major structure difference between PS and PI is that PI has higher heteoatom, OH content. Accordingly, PI(2) should have higher heteoatom, OH content and aromaticity, which may give rise to the stronger non-covalent interaction in PI(2). If the additive breaks the covalent bond to increase the coal solubility, their effect will not be so dependent on the lighter fraction(pyridine soluble) reminded in PI. These results demonstrate that additives break the non-covalent interaction but not the covalent bond in coal.

Based on the observation of the structure of additives listed in Table 1, the effective ones usually have symmetrical and delocalized structure. Most anionic additives are effective. Among those effective additive, TCNE, TCNQ and aniline, PDA were well discussed. Here, we force our interest on organic anion, e.g., PCNP anion and acetate anion.

The behavior of the two anionic additives on coal molecular aggregation was investigated by SEC. The use of NMP as an eluent minimized the sample adsorption on the polystyrene column[9-11]. The separation is mainly size based[10]. The SEC chromatogram of coal extract exhibits bimodal peaks. The first one appearing near exclusion limit of the column is assigned to those stronger aggregated molecules[5]. Another one resolved by the column eluting at longer retention time corresponds to the less aggregated portion[5]. Addition of small amount of PCNP or acetate anion into the NMP eluent results in the disappearance of the peak near exclusion limit of the column, but no effect on the peak at longer retention time. This change indicates the size of coal molecular aggregates decreased. The effect of anion on coal molecular aggregation depends on the nature of the anion. Addition of LiBr into NMP eluent shifts all the peaks to longer retention time, which was considered due to the decrease of solvent solubility because some precipitates appeared in NMP/LiBr[12]. Addition of PCNP anion and acetate anion increases the Upper Freeport coal solubility in NMP/CS_2 from 60% to 78% and 84%, respectively, but addition of same amount of LiBr does not increase coal solubility at all. Accordingly, the change of SEC behavior by adding PCNP and acetate anion is due to the disruption of the coal molecular aggregation. The reversible effect of additive on SEC was also found. Some materials eluted near exclusion limit still appear when injection of the sample containing anion additive onto the column eluted by NMP. The result indicates a partial reversible aggregation of coal extracts.

The mechanism of anion increasing coal extractability is under investigation. We are not very sure whether the new hydrogen bonds formed between coal molecules and anion will break the coal-coal interaction or not. The change of OH proton signal in NMR spectrum of pyridine-phenol mixture by addition of 0.1% PCNP anion may provide some information for better understanding the mechanism of PCNP anion increasing coal extractability. As described in figure 2, for the pyridine-phenol mixture, hydrogen bonded OH proton shows a broad peak in low field. Addition of 0.1% PCNP anion (NMP-1,1,2,3,3-pentacyanopropenide) shifts of this proton signal up field appearing as a sharp peak. The result indicates that the chemical environment of this proton changed. Pyridine-phenolic OH hydrogen bond is a major hydrogen bond in coal. NMR result

indicates that PCNP anion affects this hydrogen bond. If this is related to coal solubility increase is awaiting further investigation.

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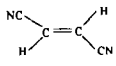
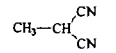
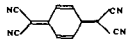
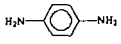
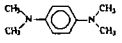
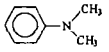
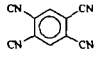
Table 1 Extraction yield of Upper Freeport coal from NMP/CS_2[a]

Additives[b]	Structure	Extraction yield wt%	Additives[b]	Structure	Extraction yield wt%
PCNP anion	 [c]	84.1			53.9
TCNE		81.3			60.2
TCNQ		80.0	TTF		61.9
PDA		78.6	TMPDA		60.4
Aniline		71.7			60.1
Acetate	 [d]	78.6		CH_3O [d]	61.8
	 [d]	75.0			49.7
	 [d]	69.5			49.8
	 [d]	68.0			39.3
	OH^- [d]	66.1			

[a]extraction yield with no additive added, 62.8%; [b]amount of additive, ~0.2mmol/g-coal; [c]from NMP-1,1,2,3,3-pentacyanopropenide [d] tetrabutlyammonium salt.

Table 2. Solubility of PI fraction in NMP/CS_2 with or without additive

Additive(~0.2mmole/g-coal)	Solubility of PI(wt%)	
	PI(1)	PI(2)
No	66.4	20.8
TCNE	99.5	89.5
TCNQ	94.3	52.9
DDQ	88.8	6.9
1,2,4,5-Tetracyanobenzene	71.2	10.5
Benzoquinone	76.1	10.2
2,6-Dichloro-*p*-benzoquinone	67.4	8.5

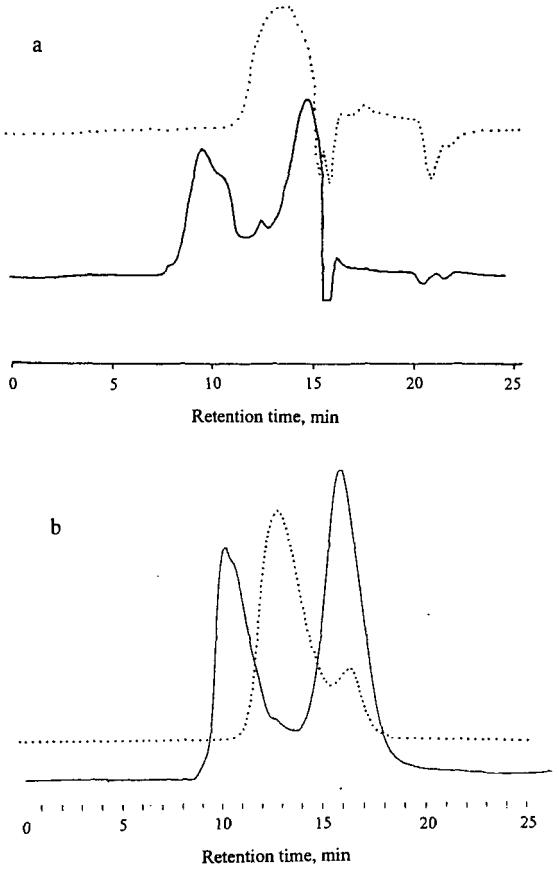


Figure 1. Size Exclusion Chromatograph of UF coal extract eluted by NMP(solid line) and NMP containing anion additive(dot line). (a) additive, 5mM NMP-PCNP; detected by RI detector; (b) additive, 10mM Tetrabutlyammonium acetate, detected by UV at 300nm

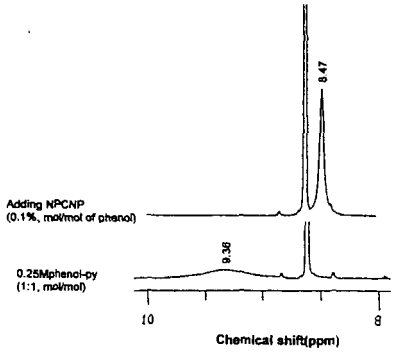


Figure 2. Shift of hydrogen bonded proton(phenol-pyridine) by adding NMP-PCNP. Solvent, $CDCl_3$