EFFECT OF VARIOUS ADDITIVES ON COAL EXTRACTION WITH CARBON DISULFIDE / *N*-METHYL-2-PYRROLIDINONE MIXED SOLVENT

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INTRODUCTION

We have reported (1) that the extraction yield with carbon disulfide / *N*-methyl-2-pyrrolidinone (CS2 / NMP) mixed solvent (1:1 by volume), which gave very high extraction yields for bituminous coals at room temperature (2), increases by the addition of a small amount of tetracyanoethylene (TCNE) to the solvent. The yield of the room temperature extraction of Upper Freeport coal with the 1:1 CS2 / NMP mixed solvent increases from 59 wt% (daf) to 85 wt% (daf) by adding only 5% (based on coal) of TCNE to the mixed solvent. *p*-Phenylenediamine(PDA) is also an effective additive for the mixed solvent extraction (3).

We have also found (4) that when the extracts obtained with the CS2/NMP mixed solvent were fractionated with pyridine to yield pyridine insoluble (PI) and soluble fractions, part of PI became insoluble in the mixed solvent. The addition of a small amount of TCNE, tetracyanoquinodimethane (TCNQ) or *p*-phenylenediamine to the mixed solvent, PI became soluble in the mixed solvent.

While, swelling and viscoelasticity behaviors of coal shows that coal has a kind of macromolecular network structure. The changes of this network structure were often quoted to explain the changes of reactivity and product selectivity of coal by heat or solvent treatment. But the nature of the macromolecular network structure are still unknown. Although covalently connected crosslinking structures are often assumed,the evidencces for them are not enough. Recent works, including our results, suggest that for some bituminous coals, large associates of coal molecules i.e., non-covalent (physical) network are a better network model, than the covalent one. Coal extracts and coal-derived liquids are known to readily associate between themselves to form complex associates (5-8).

Solubility limit of coals, i.e., how high extraction yields can be obtained without the breaking of covalent bonds is one of the key points to clarify a kind of network bonds, i.e., covalent or non-covalent (physical) networks. If coal consists of highly developed covalent networks and low molecular weght substances occuluded in them, coal extractability is low, as observed in the extraction with conrentional solvents such as pyridine. However, 85wt% of the extraction yield obtained for CS2 / NMP / TCNE solvent system described above suggests that Upper Freeport coal has little covalent networks. The reversibility of the effect of TCNE on the solubility increase for coal extracts (PI) was observed, indicating that no covalent bond breakings occur during this extraction(8).

In this study the effect of electron acceptors and donors on extraction yield of coal, and solubility of the extract component (PI) in the mixed solvent was studied. Formation of charge-transfer complex of TCNE with coal extracts was also investigated. Mechanisms for the enhancement of the extraction yield and the solubility by the additives are discussed.

EXPERIMENTAL

Extraction of coals with CS2 / NMP mixed solvent

Six Argonne coals were used. The as-received coal samples (2.5 g) were extracted with 60 ml CS_2 / NMP mixed solvent (1:1, volume ratio) and an electron donor under ultrasonic irradiation for 30 min at room temperature (2). PDA, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA), aniline and melamine were used as an electron donor. The quantity of electron donor was 10 – 100 mg/g-coal. For exhaustive extraction the extraction was repeated (usually 3 times) until the color of the extract solution almost disappeared. Extraction yields were determined from the amount of the residue, after the correction for water content in the coals.

Solubility of PI in CS2 / NMP Mixed Solvent

The extracts obtained by the extraction of Upper Freeport (Argonne Premium coal, 86.2 wt% C(daf)) and Zao Zhuang (Chinese coal, 87.8 wt% C(daf)) coals with the CS2 / NMP mixed solvent were fractionated to acetone soluble (AS), pyridine soluble/acetone insoluble (PS) and pyridine insoluble (PI) fractions, with acetone and pyridine, respectively (2). The yields of PI are about 30 and 40 wt% (daf coal base), for Upper Freeport and Zao Zhuang coals, respectively.

Solubility of PI in the mixed solvent with or without an electron acceptor was determined using 0.4g of PI and 50ml of the mixed solvent at room temperature under ultrasonic irradiation. The quantity of an electron acceptor added is 8×10^{-5} mol to 0.4g of PI. This quantity corresponds to

2.5wt% (10mg) to 0.4g of PI for TCNE. After the irradiation a centrifugation and filtration of the mixture were carried out, and the amount of the insoluble PI was determined. In the solubility experiments under nitrogen atmosphere all the procedures before a centrifugation were carried out in a glove box filled with nitrogen. The CS_2/NMP mixed solvent were also deaerated by passing nitrogen gas before use. While, solubility of PS and PI in THF or the mixed solvent with and without PDA were examined using 0.2 g of fraction and 50 ml of solvent at room temperature under ultrasonic irradiation. The amount of PDA added is 25 mg/g-PS.

Synthesis of Pyridinium 1,1,2,3,3-pentacyanopropenide (PPCP)

Pyridinium 1,1,2,3,3-pentacyanopropenide (PPCP) was synthesized from TCNE with water in the presence of a base (pyridine) in acetone at - 50 ℃ (9).

RESULLTA AND DISCUSSION

Effect of a Kind of Electron Acceptors on Solubility of PI

Table 1 shows the solubility of PI from Zao Zhuang coal in the mixed solvent when various electron acceptors were added, together with their electron affinities, which are a measure of their electron acceptabilities, i.e., the degree of charge-transfer (donor-acceptor) complex formation with an electron donor. Table 1 shows that only TCNE and TCNQ gave high solubility as expected from their high electron affinities.The three electron acceptors which contain chlorine atom, i.e., DDQ, *p*-chloranyl and 2, 6-dichloro-*p*-benzoquinone shows much lower solubilities than those expected from their electron affinities. It could not clarify from this experiment whether charge-transfer interactions are responsible for the solubility enhancement by the addition of TCNE and TCNQ or not.

IR Study on Interaction of PI with TCNE

Figure 1 shows the result of the solubility experiments of PI from Zao Zhuang and Upper Freeport coals in the 1:1 CS2 / NMP mixed solvent with or without TCNE. For Zao Zhuang coal a part (40.4%) of PI becomes insoluble in the mixed solvent, though PI is a part of the mixed solvent extract, but almost completely (97.6%) soluble in the mixed solvent containing TCNE, as already reported (4). For Upper Freeport coal (the data shown in the parenthesis in Figure1) a similar result was obtained.

Figure 2 shows that FT-IR spectra of soluble and insoluble fractions of PI from Zao Zhuang coal in the CS2 / NMP / TCNE solvent indicate the peak at 2200cm^{-1} due to nitrile group of TCNE. The peak is much greater for the soluble PI than the insoluble PI. We also reported that the peak was almost disappeared by washing with pyridine(1). The removal of TCNE retained in the soluble PI, by washing with pyridine, resulted in the insolubilization in the CS2 / NMP mixed solvent again i.e., 31.6% of PI became insoluble, but by the addition of TCNE 99.0% of PI became again dissolved in the mixed solvent (8).

The peak at 2200cm^{-1} is considered to be that due to a charge-transfer complex of TCNE with the aromatic rings of coal (10, 11). Flowers et al. (11) proposed the formation of TCNE (and TCNQ) - coal complex in which TCNE accepts an electron from cooperated delocalized state of structure,not from individual independent aromatic structures of coal, since the shift of the nitrile peak from pure TCNE, about 36cm^{-1} is unusually large, compared to that for TCNE - model aromatic compounds complex such as phenanthrene.

Figure 3(a) shows IR spectra of the solid obtained by the filtration of the mixture of PS with TCNE in acetone. Figure 3(a) shows the peak at 1500cm^{-1} in addition to that at 2200cm^{-1}, as indicated in the literature (10). When this sample was washed several times with acetone, acetone soluble component was obtained. Its IR spectrum (Figure 3(b)) shows that the two peaks at 1500cm^{-1}and 2200cm^{-1} became predominant, suggesting that they come from some stable compound, which is not a charge transfer complex, since the peaks due to PS appeared in Figure 3(a) drastically decreased in Figure 3(b). Figure 3(c) shows that synthesized pyridinium 1,1,2,3,3-pentacyanopropenide (PPCP) has a similar spectrum as that of Figure 3(b). According to Middleton et al. (9), the hydrate of free PPCP acid, i.e., 1,1,2,3,3-pentacyanopropene dihydrate is a strong acid with pKa of 1.9, and has also the peaks at 1500cm-1and 2200cm-1 like PPCP. Although pyridine and water which need to get PPCP from TCNE are usually present in coal, we can not deny the possibility that other derivatives of PPCP has a similar peaks at 1500cm-1and 2200cm-1.

PPCP was found to have a similar enhancement effect on the solubility of PI as TCNE, as shown in Figure 4. At present we consider that PPCP or its acid is formed through interaction of TCNE with coal molecules, resulting in the solubility increase of coal molecules.

Effect of Oxygen on Solubility of PI in CS2 / NMP Mixed Solvent

Figure 4 shows that the removal of oxygen drastically decreases the solubility of PI, regardless of the presence of TCNE. Figure 4 further shows that the addition of PPCP increases the solubility to a similar degree as TCNE, and also decreases it under nitrogen atmosphere. Mechanisms of the enhancement of solubility by oxygen are not clear, but change of association state, i.e., change to smaller associates by the presence of oxygen, like TCNE, is conceivable. In

fact,oxygen is known to have charge transfer interaction with electron donors, and with strong donor oxygen radical anion forms. The occurrence of some chemical reaction such as covalent bond breaking by oxygen is unlikely, since PI was already in enough contact with oxygen during the extraction and subsequent solvent fractionation procedure through which PI was obtained, before this solubility experiment.

Effect of the Addition of Electron Donors on the Extraction Yield.
In Table 2, the yields of the exhaustive extraction of coals studied in the mixed solvent with and without PDA are given. It indicates that the addition of only 25 mg/g-coal of PDA increased extraction yield of Upper Freeport coal from 51.4% to 81.3%. The addition of PDA slightly increased the extraction yield of high-volatile coals. Increasing the amount of PDA to 100mg/g-coal did not increase the extraction yield.

In Table 3, the extraction yields of Upper Freeport coal when an electron donor added into the mixed solvent together with their ionization potentials are given. Table 3 indicates that there is no correlation between the ionization potential of the donors and the extraction yield. According to the ionization potential of TMPDA, it is expected to show higher extraction yield than those of PDA and aniline. However, it doesn't show a significant increase in the extraction yield.

Effect of PDA on the Solubility of Extract Fractions of Upper Freeport Coals.
The solubility of PS fraction of Upper Freeport coal increased 10% in the presence of PDA.PDA is also effective on the solubility of PI fraction of Upper Freeport coal. When we added only 5 mg / 0.2 g-PI of PDA into the mixed solvent, solubility of PI increased from 75.4 to 90.2%.

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Table 1. The effect of the addition of electron acceptors on the solubility [a] of PI from Zao Zhuang coal in CS_2/NMP mixed solvent at room temperatrue

Electron acceptor	Solubility of PI (wt%)	Electron affinity [b] (eV)
None	51.0	—
Tetracyanoethylene(TCNE)	99.5	2.2
7,7,8,8-Tetracyanoquinodimethane(TCNQ)	81.0	1.7
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone(DDQ)	53.8	1.95
1,2,4,5-Tetracyanobenzene	47.7	0.4
p-Benzoquinone	44.1	0.77
2,6-Dichloro-*p*-benzoquinone	37.0	1.2
p-Chloranil	34.8	1.37

[a] Wt% of PI soluble in the mixed solvent when 8×10^{-5} mol of an electron acceptor was added to 0.4g of PI in 50ml of the mixed solvent [b] Electron affinity of the electron acceptors

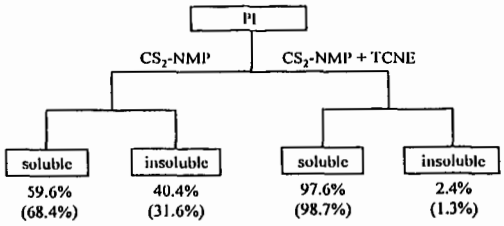

Figure 1. Solubility of PI from Zao Zhuang and Upper Freeport (shown in parenthesis) coals in CS_2/NMP mixed solvent with or without TCNE

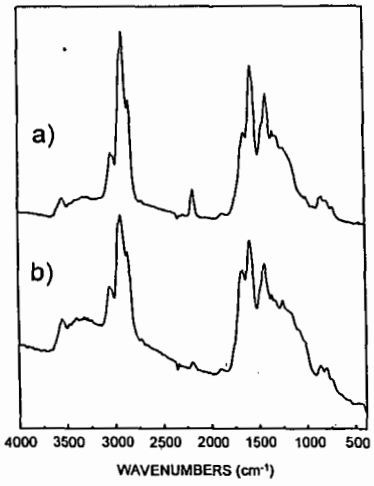

Figure 2. FT-IR spectra of soluble(a) and insoluble(b) fractions of PI from Zao Zhuang coal

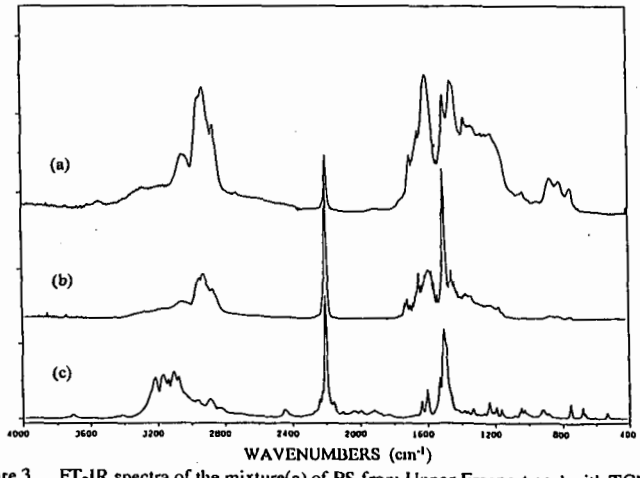

Figure 3. FT-IR spectra of the mixture(a) of PS from Upper Freeport coal with TCNE, its acetone soluble fraction (b),and Pyridinirm 1,1,2,3,3-pentacyanopropenide(c)

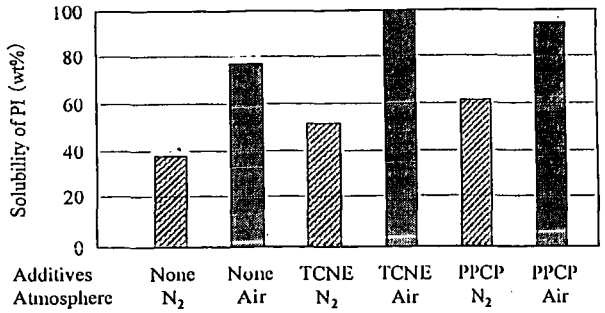

Figure 4. Solubility of PI from Upper Freeport coal in the CS_2/NMP mixed solvent under various conditions

Table 2. Effect of addition of *p*-phenylenediamine(PDA) on exhaustive extraction of Argonne coals with CS_2/NMP mixed solvent

coal[a]	PDA (mg/g-coal)	extraction yield (wt%,daf)
Upper Freeport	none	51.4
	25	81.3
Blind Canyon	none	36.3
	25	40.4
Lewiston-	none	24.6
Stockton	25	29.2
Pittsburgh No.8	none	41.5
	25	44.4
Illinois No.6	none	29.7
	35	34.8
Wyodak-	none	7.3
Anderson	50	11.9

[a]as received

Table 3. Effect of addition of electron donors[a] on single and exhustive extraction of Upper Freeport coal with CS_2/NMP mixed Solvent

electron donor	extraction yield (wt%,daf)		ionization potential (eV)
	single	exhaustive	
none	31.5	51.4	
PDA	61.2	81.3	6.87
aniline	32.5	72.3	7.7
TMPDA	42.3	61.4	6.5
melamine	62.6	-	-

[a] Amount of electron donors used is 25 mg/g-coal