EFFECT OF VARIOUS ADDITIVES ON SOLVENT EXTRACTION OF COALS

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INTRODUCTION

The extraction of bituminous coals with carbon disulfide / *N*-methyl-2-pyrrolidinone (CS2 / NMP) mixed solvent (1:1 by volume) was found to give very high extraction yields at room temperature (1). We have also found that the addition of a small amount of various additives such as tetracyanoethylene (TCNE) and *p*-Phenylenediamine(*p*-PDA) to the mixed solvent increases the extraction yields greatly(2,3). For example, 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(2). Recently inorganic salts of chloride and fluoride are found to be also effective for the increase of the extraction yields.

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 (PS) fractions, part of PI became insoluble in the mixed solvent, though it is a part of the extracts with the mixed solvent. By the addition of a small amount of the additives such as TCNE, tetracyanoquinodimethane (TCNQ) or *p*-phenylenediamine to the mixed solvent, PI became soluble in the mixed solvent.

While, swelling and viscoelasticity behaviors of coal show that coal has a kind of macromolecular network structure. The changes of reactivity and product selectivity of coal by heat or solvent treatment were often explained by the changes of this network structure. 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 extractions with conventional 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.

In this presentation the effect of various additives on extraction yield of coal, and solubility of the extract component (PI) in the mixed solvent was reviewed including recent results. 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

The coals used in this study are shown in Table 1. A coal was extracted with CS_2 / NMP mixed solvent (1:1, volume ratio) under ultrasonic irradiation repeatedly at room temperature (1) with or without an additive. The extract obtained was fractionated with acetone and pyridine, respectively, to give acetone-soluble(AS), pyridine-soluble and acetone-insoluble(AI/PS), and pyridine-insoluble(PI) fractions. Solubility of PI in the mixed solvent was examined at room temperature under ultrasonic irradiation with or without an additive.

RESULLTS AND DISCUSSION

Effect of Additives on Extraction Yields of Coals

Tables 2 - 4 show the yields of the extractions of Upper Freeport coal with the CS_2/NMP mixed solvent with electron acceptors, donors (aromatic amines), and halogenide salts, respectively. Table 2 shows the effect of an electron acceptors, together with their electron affinity, which is a measure of the electron acceptability of electron acceptor. Table 2 shows that only TCNE and TCNQ gave high extraction yieldsas expected from their high electron affinities. However, other electron acceptors used here do not show the extraction yield enhancements. Table 3 also shows that the effectiveness of electron donors is not an order of their electron donatability, since *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA), which is the strongest electron donor, gave much lower yield than other donors. The results for halogenide salts in Table 4 indicate that a kind of halogenide anions affects the extraction yields, i.e., the yields increased in the order; F>Cl>Br>I, and little change between Li and tetrabutylammonium cations.

Table 5 shows the effect of the addition of tetrabutylammonium fluoride (TBAF) on the extraction of various coals. Upper Freeport, Lower Kittanning, and Stigler coals incresed their extraction yields with the CS_2 / NMP mixed solvent by the addition of TBAF, but for Pttsburgh No.8, Illinois No.6 coals the yields did not increase. For the addition of TCNE the same tendency of the extraction yields were obtained for the five coals above (2).

Effect of Additives on Fraction Distribution of Extracts

Table 6 shows the fraction distribution of the extracts obtained from the extraction of Upper Freeport coal with TCNE, *p*-PDA, and TBAF. Table 6 indicates that the increase in the extraction yields is mainly due to the increase of the heaviest extract fraction, i.e., PI, and little increase in the lighter fractions of AS and AI/PS.

Effect of Additives on Solubility of Extract Fraction

Tables 7 and 8 show the effect of electron acceptors and donors (aromatic amines) on the solubility of PI in the CS_2 / NMP mixed solvent, respectively. Table 7 shows a similar tendency as the effect of electron acceptors on the extraction yiellds (Table 2), i.e., only TCNE and TCNQ are effective for the increase in the solubility of PI. Table 8 shows that aniline and *p*-PDAincreased the solubility of PI greatly, and especially *p*-PDA is as effective as TCNE and 25mg (0.23mmol)/g-PI increased about 40% of the solubility.

Mechanisms for the enhancement of the extraction yield and the solubility by the additives

The solubility increase of PI by TCNE addition, and also the increase in the extraction yield are considered to be caused by the breaking of noncovalent bonds in aggregates among coal molecules(8), since the effect of TCNE addition is reversible, i.e., PI', which is considered to be free of TCNE by washing the TCNE-solubilized PI by pyridine, is again partly insoluble in the mixed solvent, and it becomes almost completely soluble by the re-addition of TCNE. From similar behaviors of the other additives toward a kind of coals and fraction distribution of the extracts as TCNE they also solubilize coal by the same mechanism as TCNE.

The 1:1 CS2-NMP mixed solvent can break the weak non-covalent bonds which are not broken convensional solvents such as pyridine. The additive such as TCNE and *p*-PDA in the mixed solvent, which has strong interaction with coal molecules, can break even the strong noncovalent bonds. A kind of interactions between the additives and coal molecules are not clear, but the results here suggest that charge-transfer (donor-acceptor) interaction may not be a main interaction.

The additives such as TCNE, *p*-PDA, and TBAF is very efficient for the extraction yield enhancement of Upper Freeport coal. For example, the addition of TCNE more than 0.05g to 1g of the coal reached an almost constant extraction yield of about 85 wt% (daf). Using the structural parameters of fa and degree of aromatic ring condensation for Upper Freeport coal reported by solum et al.(9), 0.05g of TCNE per 1g of coal is calculated to correspond to 1 molecules of TCNE per about 8 aromatic clusters of the coal. The reasons why these additives are so effective, and the effectiveness is depend on a kind of coals are not clear, though all the coals which increase their solubility remakably by the additives contain much of the heaviest extract fraction, PI.

These results obtained strongly suggest that at least some bituminous coals, which gave very high extraction yields with the CS2/NMP/additive solvent, have chemical structure consisting of complex mixture of the aggregates among coal molecules, and having no giant covalently bound cross-linked network.

CONCLUSIONS

The effects of various additives on the extraction yield of coals and the solubility of extract fraction were investigated. The additives such as TCNE, *p*-PDA, and lithium and ammonium salts of fuloride and chloride are found to be very effective for the increase in the extraction yield and the solubility of the extract fraction. A mechanism that noncovalent bonds in the aggregates among coal molecules are broken by the additives is proposed.

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Table1. Analysis of coals

Coal	Ultimate analysis(wt%,daf)				Ash(wt%,db)
	C	H	N	O+S [a]	
Sewell'B'	88.4	5.3	1.4	4.9	4.6
Upper Freeport	86.2	5.1	1.9	6.8	13.1
Lower Kittanning	84.0	5.6	1.7	8.7	9.0
Lewiston Stockton	82.9	5.4	2.0	9.7	19.6
Pittsburgh No.8	82.6	5.5	2.1	9.8	8.7
Stigler	77.8	4.8	1.5	15.9	11.7
Illinois No.6	76.9	5.5	1.9	15.7	15.0

[a] By difference

Table 2. Effect of the addition of electron acceptors on extraction yields[a] of Upper Freeport coal together with their electron affinity

additive[b]	Ectraction yield (wt%)	Electron affinity (eV)
None	64.6	-
TCNE[c]	85.0	2.2
TCNQ[d]	80.0	1.7
DDQ[e]	49.8	1.95
1,2,4,5-Tetracyanobenzene	44.4	0.4
p-Benzoquinone	39.3	0.77
2,6-Dichloro-p-benzoquinone	49.7	1.2
p-Chloranil	45.5	1.37

[a] CS_2/NMP mixed solvent (1:1 by volume), room temperture

[b] 0.2mmol/g-PI of an election acceptor, [c] Tetracyanoethylene

[d] 7,7,8,8-Tetracyanoquinodimethane, [e] 2,3-Dichloro-5,6-dicyano-p-benzoquinone

Table 3.Effect of the addition of electron donors(aromatic amines)on extraction yields[a] of Upper Freeport coal together with their ionization potential

Additive[b]	Extraction yield (wt%,daf)	Ionization potential (eV)
None	51.4	
aniline	72.3	7.7
p-PDA[c]	81.3	6.87
TMPDA[d]	61.4	6.5
melamine	61.8	-

[a] CS_2/NMP mixed solvent(1:1 by volume), room temperature
[b] 25 mg/g-coal of an electron donor
[c] *p*-phenylendiamine, [d] N,N,N',N'-tetramethyl-*p*-phenylenediamine

Table 4. Effect of the addition of halogenide salts on extraction yields[a] of Upper Freeport coal

Additive (mmol/g-coal)	Extraction yield (wt%,daf)	Additive (mmol/g-coal)	Extraction yield (wt%,daf)
None	56.4, 59.8	$(n\text{-butyl})_4NH_4F$ (0.25)	83.9
LiCl (0.24)	81.7	$(n\text{-butyl})_4NH_4Cl$ (0.25)	78.8
LiBr (1.0)	68.7	$(n\text{-butyl})_4NH_4Br$ (0.25)	61.8
LiI (1.9)	60.9	$(n\text{-butyl})_4NH_4I$ (0.25)	59.3

[a] CS_2/NMP mixed solvent(1:1 by volume), room temperature

Table 5. Effect of the addition of TBAF on the extraction yields[a] of various coals and fraction distributions of the extracts

Coal	TBAF	Extraction yield (wt%,daf)	Fraction distribution(wt%,daf)		
			AS	PS	PI
Upper Freeport	None	60.1	8.2	25.0	26.9
	0.25mmol/g-coal	82.4	11.5	12.7	58.2
Lower Kittanning	None	38.7	6.3	27.1	5.3
	0.25mmol/g-coal	63.7	9.4	17.9	36.4
Pittsburgh No.8	None	43.5	12.3	30.0	1.2
	0.25mmol/g-coal	39.9	11.8	23.4	4.7
Stigler	None	21.2	6.1	14.5	0.6
	0.25mmol/g-coal	62.4	6.4	17.2	38.8
Illinois No.6	None	27.9	7.8	19.1	1.0
	0.25mmol/g-coal	27.4	10.0	16.8	0.6

[a] CS_2/NMP mixed solvent(1:1 by volume),room temperature

Table 6. Fraction distribution of the extracts obtained from the extraction[a] of Upper Freeport coal with the additives

Additive	extraction yield (wt%,daf)	fraction distribution of the extract (wt%,daf)		
		AS	AI/PS	PI
none	60.1	8.2	25.0	26.9
TCNE	85.0	10.5	28.5	47.0
p-PDA	81.3	9.8	23.1	48.4
LiCl	83.6	10.2	16.1	57.3
TBAF	82.4	11.5	12.7	58.2

[a] CS2/NMP mixed solvent(1:1 by volume), room temperature

Table 7. Effect of the addition of electron acceptors on solubility[a] of pyridine-insoluble extract (PI)

Additive[b]	Solubility of PI (wt%)		Electron affinity (eV)
	PI from Upper Freeport Coal	PI from Zao Zhuang Coal	
None	66.4	51.0	-
TCNE[c]	99.5	99.5	2.2
TCNQ[d]	94.3	81.0	1.7
DDQ[e]	88.8	53.8	1.95
1,2,4,5-Tetracyanobenzene	71.2	47.7	0.4
p-Benzoquinone	76.1	44.1	0.77
2,6-Dichloro-p-benzoquinone	67.4	37.0	1.2
p-Chloranil	51.8	34.8	1.37

[a] CS_2/NMP mixed solvent (1:1 by volume), room temperture

[b] 0.2mmol/g-PI of an electron acceptor, [c] Tetracyanoethylene

[d] 7,7,8,8-Tetracyanoquinodimethane, [e] 2,3-Dichloro-5,6-dicyano-p-benzoquinone

Figure 8. Effect of the addition of electron donors (aromatic amine) on solubility[a] of pyridine-insoluble extract fraction (PI) from Upper Freeport

Additive[b]	Solubility of PI (wt%)	Ionization potential (eV)
None	55.1	-
aniline	85.4	7.7
o-PDA	91.8	7.2
m-PDA	85.1	7.1
p-PDA	96.5	6.9

[a] In CS_2/NMP mixed solvent(1:1 by volume), room temperature
[b] 25mg/g-PI of an additive