

THE INCREASE OF THE EXTRACTION YIELD OF COALS BY THE ADDITION OF AN ELECTRON ACCEPTOR

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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 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 (PS) 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, the aggregation state of coal molecules and its change with heating or contact with solvent and reagent play an important role in structure and reactivity of coal, but the details on them are still unknown. Coal extracts and coal-derived liquids are known to readily associate between themselves to form complex aggregates(5-7). The effect of TCNE on the extraction yields above mentioned can be explained by its breaking ability of noncovalent bonds through which the aggregates form(1). However, another explanation is possible, i. e., covalent bonds in coal such as ether bonds break after electron transfer from coal to TCNE, which is a strong electron acceptor. Solubility limit of coals, i. e., maximum extraction yield without the breaking of covalent bonds is one of the key points to clarify a kind of cross-linking bonds, i. e., covalent or non-covalent (physical)cross-links. If coal has developed covalent cross-links, its extractability is low, as observed in the extraction with conventional solvents such as pyridine which gave the yields less than 30-40wt% (daf) of coal. So, 85wt% of the extraction yield for CS₂-NMP-TCNE solvent system suggests that Upper Freeport coal has little covalent cross-links, if no covalent bond breakings occur during this extraction.

In this study the effect of various electron acceptors on solubility of PI in the mixed solvent and also the effect of TCNE retained in PI on the solubility of PI were investigated. The mechanisms for the enhancement of the extraction yield of coal and solubility of PI by electron acceptors are discussed.

EXPERIMENTAL

Upper Freeport(Argonne Premium coal, 86.2 wt% C(daf)) and Zao Zhuang(Chinese coal, 87.8 wt% C(daf)) coals were extracted with the 1:1 CS₂-NMP mixed solvent repeatedly at room temperature (2). The extract obtained was fractionated with acetone and pyridine, respectively, to give acetone-soluble(AS), pyridine-soluble and acetone-insoluble(PS), and pyridine-insoluble (PI) fractions, as shown Figure 1. Solubility of PI in the CS₂-NMP mixed solvent was examined using 0.4g of PI and 50ml of the mixed solvent at room temperature under ultrasonic irradiation with or without an electron acceptor such as TCNE. The quantity of an electron acceptor added is 8×10^{-5} mol to 0.4g of PI. This quantity corresponds to 2.5wt% (10wg) of TCNE to 0.4g of PI.

RESULTS AND DISCUSSION

The Effect of Electron Acceptors on the Solubility of PI

Table I shows the solubility of PI in the mixed solvent when an electron acceptor was added, together with its electron affinity, which is a measure of the electron acceptability of electron acceptor. Table I shows that only TCNE and TCNQ gave high solubility as expected from their high electron affinities. However, other electron acceptors used here do not show the solubility enhancements. So, it is not clear whether charge-transfer (donor-acceptor) interactions is responsible for the solubility enhancement by the addition of TCNE and TCNQ, or not.

The Effect of TCNE Retained in PI on the Solubility of PI

Figure 2 shows the result of the repeated dissolution experiments of PI(PI-1 in Figure 2) from Zhao Zhuang coal in the 1:1 CS₂-NMP mixed solvent with or without TCNE. 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). Figure 1 shows that PS(PS-2) and AS(AS-2), in addition to PI(PI-2), were also obtained from PI-1 in the yield of 9.2% and 5.0%, respectively, probably due to the change of the aggregation state, as described later. PI-2 was well washed with pyridine to remove PS. It was reported that most of TCNE retained in PI could be removed by its washing with pyridine (1). In fact, from Figure 3, which shows that the FT-IR spectra of soluble and insoluble fractions of PI in the CS₂-NMP-TCNE solvent, PI-2, and PS-2, the peak at 2200cm⁻¹ due to TCNE (nitrile group) was almost disappeared in PI-2 (Figure 3-c), compared to soluble fraction (Figure 3-a) and PS-2 (Figure 3-d), indicating the removal of TCNE retained in PI-2 by washing with pyridine. PI-2 was then tried to redissolve in the CS₂-NMP mixed solvent and again a considerable part(31.6%) of PI-2 became insoluble, and 99.0% of PI-2 was dissolved in the mixed solvent containing TCNE, as shown in Figure 2. Fractionation of PI soluble in CS₂-NMP-TCNE solvent gave again 9.1% of PS+AS. A similar result was obtained for the PI from Upper Freeport coal, as shown in Figure 4.

If the solubility increase by TCNE addition is caused by the covalent bond breaking through the electron transfer from coal to TCNE, the insolubilization of PI in the mixed solvent after the removal of TCNE from the PI, just described above, should not be observed. So, the solubility increase of PI by TCNE is considered to be caused by the breaking of noncovalent bonds in the aggregates among coal molecules and the new associates with TCNE is more soluble than the original aggregates, as shown in Figure 5. In Figure 5, two kinds of noncovalent bonds, weak and strong, are assumed. The CS₂-NMP mixed solvent can break the weak bonds, but not the strong bonds, and the mixed solvent containing TCNE, which has strong interaction with coal molecules, can break even the strong bonds. The interaction between TCNE and coal molecules may be charge-transfer (donor-acceptor) and/or other interactions. The solvents such as pyridine and THF seem not to break easily even the weak noncovalent bonds, resulting in low extraction yields. The mechanism shown in Figure 5 can also explain the reason why the extraction yield increased by TCNE addition.

Figures 2 and 4 show that lighter fractions such as AS and PS formed from PI by the treatment with CS₂-NMP mixed solvent containing TCNE. This suggests that they are included in PI due to the formation of the aggregates which are not soluble in pyridine nor acetone and became soluble in those solvents by the change of the aggregation state. So, the fraction distribution obtained here is considered to be a reflection of not only solubility of coal molecules themselves, but aggregation state among coal molecules.

TCNE is very efficient for the extraction yield enhancement of Upper Freeport coal. 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 *f*_a and degree of aromatic ring condensation for Upper Freeport coal reported by Solum et al.(8), 0.05g of TCNE per 1g of coal is calculated to correspond to 1 molecule of TCNE per about 8 aromatic clusters of the coal.

These results obtained strongly suggest that at least some bituminous coals, which gave high extraction yields with the CS₂-NMP-TCNE 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 effect of various electron acceptors on the solubility of pyridine-insoluble extract fraction (PI) in the CS₂-NMP mixed solvent was investigated. The other electron acceptors than TCNE and TCNQ do not show the solubility enhancement. So, it is not clear whether the solubility enhancement by TCNE and TCNQ is ascribed to their charge-transfer interactions with coal molecules or not. The results obtained for the effect of TCNE retained in PI on solubility of PI suggest that the solubility increase by the electron acceptors is caused by the breaking of noncovalent interaction in aggregates of coal molecules.

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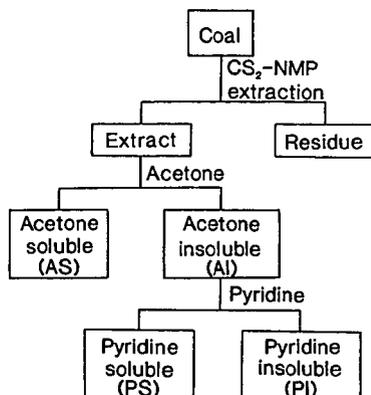


Figure 1 Extraction and fractionation procedures

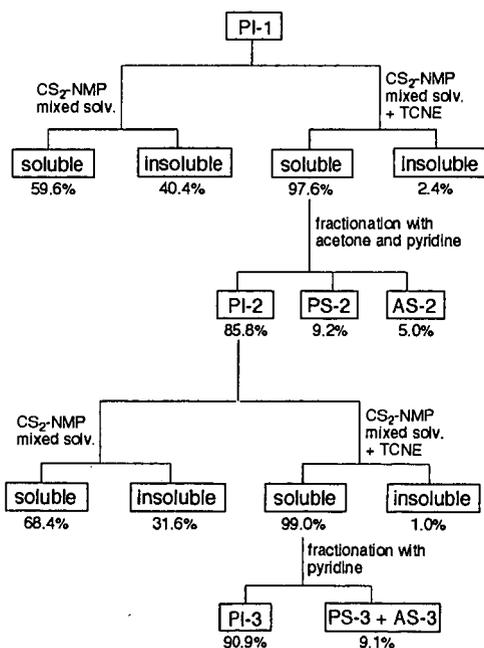


Figure 2 Repeated solubility experiments for PI from Zao Zhuang coal in the CS₂-NMP mixed solvent with or without TCNE (2.5 wt% based on PI).

Table 1 The effect of the addition of electron acceptors on the solubility^{a)} of PI from Zao Zhuang coal in the CS₂-NMP mixed solvent at room temperature

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- <i>p</i> -benzoquinone(DDQ)	53.8	1.95
1,2,4,5-Tetracyanobenzene	47.7	0.4
<i>p</i> -Benzoquinone	44.1	0.77
2,6-Dichloro- <i>p</i> -benzoquinone	37.0	1.2
<i>p</i> -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 acceptor.

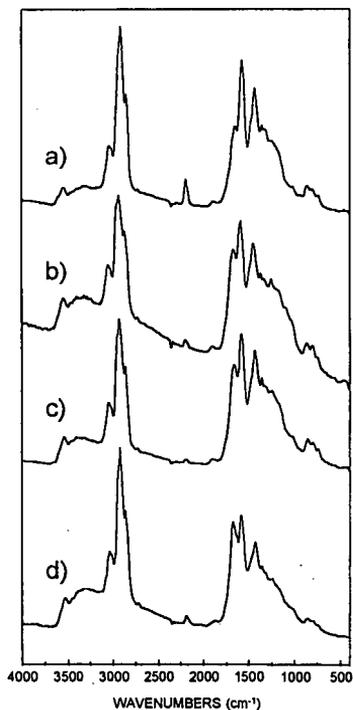


Figure 3 FT-IR spectra of soluble(a) and insoluble(b) fractions of PI-1 in the CS₂-NMP-TCNE solvent, PI-2(c) and PS-2(d).

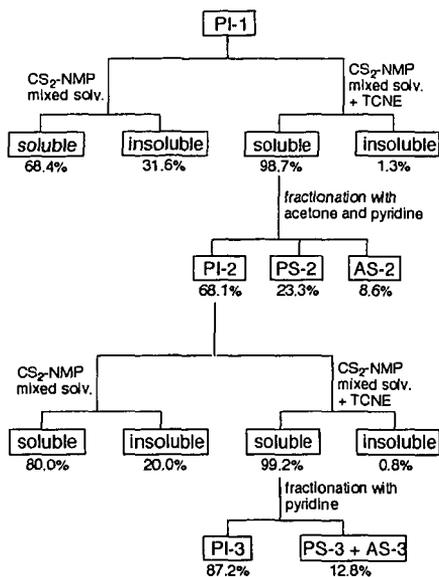


Figure 4 Repeated solubility experiments for PI from Upper Freeport coal in the CS₂-NMP mixed solvent with or without TCNE(2.5 wt% based on PI),

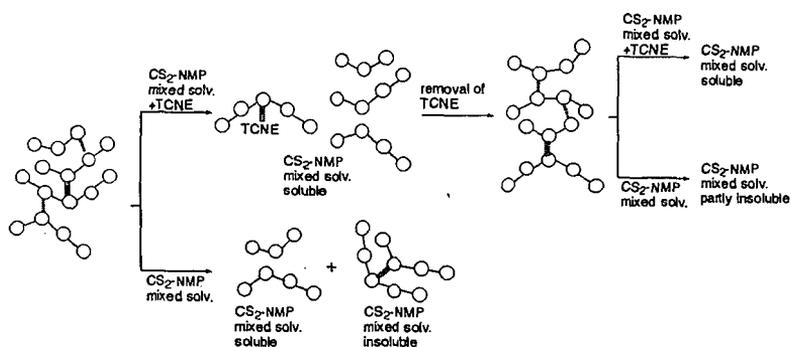


Figure 5 Solubilization mechanism of PI in the CS₂-NMP mixed solvent with or without TCNE. ○: aromatic cluster, —: covalent bond, |||||: non-covalent bond(strong), ||||: non-covalent bond(weak)