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Mechanism of Coal Solubility Increase in NMP-CS₂ Mixed Solvents by Adding TCNE

by

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Abstract

The extraction yield of coal in N-methyl-2-pyrrolidinone (NMP)-CS₂ mixed solvents was greatly increased from 60% to 85% by adding a small amount of tetracyanoethylene (TCNE). The mechanism of TCNE interaction with coal to increase the coal extraction yield in solvent was investigated based on the spectrum properties of TCNE in NMP. It was found that TCNE does not exist as a neutral molecule in extraction solvent. Instead, TCNE forms 1,1,2,3,3-pentacyanopropenide anion in NMP. The 1,1,2,3,3-pentacyanopropenide anion might be responsible for the coal solubility increase.

Key Words : Coal, Extraction, TCNE, Spectrum

Introduction

N-methyl-2-pyrrolidinone (NMP)-CS₂ mixed solvent has the magic ability to dissolve coal up to about 60wt% based on daf coal¹. Looking for the powerful solvent to dissolve coal is what coal chemist expects both for coal structure investigation and its industrial utilization. After testing the effect of more than ten additives, TCNE was found to be the most effective one to increase coal extractability in 1:1 (v/v) NMP-CS₂ mixed solvents (up to 85% for Upper Freeport coal)^{2,3}. However, the mechanism of coal solubility increase by adding TCNE is not clear. Some researches pointed out that the effect of those additives with electron donor or acceptor ability should be related to charge-transfer complex formed between additives and coal⁴. However, the investigation based on the electron donor and acceptor theory was not very successful, since the solubility of pyridine insoluble (PI) does not well correlate with the electron accept-ability of the additives². On the other hand, TCNE is only effective in NMP but not so effective in pyridine³. These evidences forced us to reconsider the mechanism of the TCNE to increase coal extractability.

Our previous work showed that the coal containing TCNE deposited from NMP-CS₂ mixed solvents shows a pair of IR absorption at 2200cm⁻¹ and 1500cm⁻¹, which indicated that no neutral TCNE existed (ν_{CN} in natural TCNE appearing at 2260cm⁻¹)². The absorption at 2200cm⁻¹ was first assigned to the formation of charge-transfer complex between TCNE and coal. However, the 60cm⁻¹ shift of ν_{CN} is unusually large as compared to the charge-transfer complex of TCNE-aromatics

Received May 13, 1999

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(usually less than 10cm⁻¹ shift). The reaction product of TCNE with pyridine in presence of water i.e., pyridium 1,1,2,3,3-pentacyanopropenide (PPCNP), appears the same IR absorption at 2200cm⁻¹ and 1500cm⁻¹². PPCNP was found as effective as TCNE for the increase of PI solubility in the NMP-CS₂ mixed solvent. These results indicate that charge-transfer complex between TCNE and coal may not be responsible for the solubility increase of PI or coal.

PPCP was first considered to be a unique product of TCNE reaction with pyridine sites in coal molecules. Further investigation found that TCNE does not exist as a neutral TCNE in NMP, instead it forms NMP 1,1,2,3,3-pentacyanopropene salt (NPCNP) with NMP in presence of small amount of water. It means that TCNE does not directly interact with coal. NPCP may be responsible for the increase of coal solubility.

Experimental

UV spectral properties of TCNE in various solvents were carried out on HITACHI U2000 UV spectrometer with 1cm quartz cell. Anhydrous NMP was dehydrated by 5 Å molecular sieves. FTIR spectra of TCNE in various solvents were recorded on JASCO FT/IR-8300 spectrometer. The reaction of TCNE with NMP was examined at room temperature by adding TCNE acetone solution into NMP-H₂O mixture. The crude product was purified by re-crystallization in Diethyl ether. The product is yellow crystal, m.p. 60.5~61.5°C (found C, 59.18 ; H, 5.46 ; N, 26.78 ; O, 8.74. C₁₈H₂₀N₇O₂ requires C, 59.02 ; H, 5.29 ; N, 26.75 ; O, 8.78). Its structure was further identified by FTIR, UV, ¹³C-NMR.

Results and discussion

TCNE seems only effective in NMP-CS₂ mixed solvents. Although the high solubility of NMP-CS₂ mixed solvents may be one reason, the effect of solvent should also be considered. The interaction between TCNE and coal molecule was noticed and examined based on charge-transfer theory. However, less attention was paid to the interaction between TCNE and solvent.

The IR vibration of CN group (ν_{CN}) in TCNE was found shifting in some solvents. The list of ν_{CN} of TCNE in various solvents was shown in Table 1. It can be considered that there is almost

Table 1. List of ν_{CN} of TCNE in various solvents

Solvent	ν_{CN} (cm ⁻¹)
TCNE(solid state)	2260
Acetone	2257
THF	2257
Toluene	2252
NMP	2199

no change for TCNE in acetone and THF. The small shift of ν_{CN} in toluene is attributed to the formation of charge-transfer complex between TCNE and toluene. The large shift of ν_{CN} in NMP (used for extraction, not de-watered) indicates that TCNE may react with NMP and does not exist

as a neutral molecule in this solvent. Whether the unusual shift of ν_{CN} is related to the high efficiency of TCNE to increase coal solubility in NMP-CS₂ mixed solvents will be discussed below.

The UV-visible spectral property of TCNE-NMP mixture was also examined. Figure 1 shows the UV spectral properties of TCNE in NMP with different water content. TCNE-NMP π complex absorption at 298nm was observed in anhydrous NMP, while a pair of absorption assigned to some anion at 400 and 418nm appears when NMP contains a small amount of water. The absorption at 400 and 418nm were ascribed to 1,1,2,3,3-pentacyanopropenide (PCNP) anion was confirmed by the UV spectral character of a similar compound, pyridinium 1,1,2,3,3-pentacyanopropenide (PPCNP, as shown in Figure 1e), and the reaction of TCNE with NMP in presence of a small amount of water as discussed below. As the water content in NMP increase, the anion absorption at 400 and 418nm increase, but the absorption of TCNE-NMP π complex at 298nm decreases. In Figure 1(a), a pair of small peaks at 400 and 418nm can also be observed even in anhydrous NMP, which is probably due to the incomplete dewater of NMP. This result indicates that only a small amount of water is enough for TCNE to form anion in NMP. Since NMP is very easy to absorb water, it is quite possible that commercial NMP containing a small amount of water. It was also found that TCNE show the anion peaks in commercial NMP.

Does TCNE form PCP anion in NMP? If it is true the effect of TCNE should be related to PCP

Figure 1. UV-visible spectra of TCNE in NMP containing different amount of water (mg/mL NMP). a, 0; b, 15; c, 50. e, the UV spectrum of pyridinium 1,1,2,3,3-pentacyanopropenide (PPCNP) in NMP

anion. In order to clarify the assignment of the two peaks, the reaction of TCNE with NMP containing water was investigated under room temperature. The reaction product is a yellow crystalline product, which can be purified in Diethyl ether by re-crystallization. The yellow crystal shows the same UV spectrum as PPCP in methanol, as shown in Figure 2. Its FTIR spectrum in Figure 3 shows the feature of 1,1,2,3,3-pentacyanopropenide anion, i.e., strong absorption of ν_{CN} at 2203cm^{-1} and delocalization double bond at 1519cm^{-1} . The further structural identification by ^{13}C -NMR (see Fig. 4) indicates that the yellow crystal confirm the structure of NMP 1,1,2,3,3-pentacyanopropene salt (NPCNP). The structure of NPCNP was shown in Figure 4. The result demonstrates that

Figure 2. UV-visible spectra of pyridinium-1,1,2,3,3-pentacyanopropenide (PPCNP, upper) and NMP-1,1,2,3,3-pentacyanopropene salt (NPCNP, lower) in CH₃OH

Figure 3. FTIR spectrum of NMP-1,1,2,3,3-pentacyanopropene salt (NPCNP)

Figure 4. ^{13}C -NMR spectrum of NMP-1,1,2,3,3-pentacyanopropene salt (NPCNP)

TCNE exists as NPCP anion in NMP but not TCNE natural molecule. NPCNP may be responsible for the increase of coal solubility by adding TCNE in NMP. This anion with high polarizability may cause an induced dipole and break down the van der Waals interaction in coal. In addition, the break of hydrogen bonding may be another route to enhance coal solubility.

Acknowledgment

This work was supported by "Research for the Future" project of Japan Society for the promotion of Science (JSPS).

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