Studies on the Removal and Recovery of Organic Sulfur Compounds in Hydrocarbon Oils by Liquid-Liquid Extraction (IV)*

—The Solvent Extraction of Tetrahydrothiophene with Aqueous Bromo-Copper(II) Complex Solutions—

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Summary: In order to develop a new method for removing the sulfur compounds in hydrocarbon oils, the extraction behavior of tetrahydrothiophene (THS) with an aqueous copper (II) bromide solution was investigated with special reference made to the mechanism of extraction and the factors which influence the extraction ability of copper complexes.

Bromo-copper(II) complexes exhibited excellent extraction efficiency for THS that was more than 50 times as great as that of cupric ion itself. CuBr^+ , among the bromo complexes, was mainly concerned with the extraction of THS and it formed a white solid complex having a composition of $[\text{Cu(I)Br THS}]$. This solid complex was redissolved in the presence of excess amounts of Br^- ion and/or CuBr_2 ; and, thus, THS was extracted into the aqueous phase as water soluble complexes; i.e., copper(I) complex ions, $[\text{Cu(II)Br}_n\text{THS}]^{(n-1)-}$ ($n=2,3$) and/or mixed valance polynuclear complex ions, $[\text{Cu(II)-Br}_{n-1}\text{-Cu(I)THS}]^{(2-n)+}$ ($n=1,2$), respectively. The role of Br^- ion as an auxiliary ligand was also discussed.

1 Introduction

For establishing a new method to remove organic sulfur compounds in hydrocarbon oils by liquid-liquid extraction, a series of basic studies has been made with aqueous metal ion solutions^{1)~4)}. In the case of alkyl sulfides, it was revealed that both extraction efficiency and extraction rate can be controlled by adding halide salts to the aqueous phase^{3),4)}. The most effective results were obtained, among the combinations of several kinds of metal ions and halide ions, when copper(II) ion was used with bromide ion.

Extraction of sulfides with metal salt solutions^{5)~9)} such as Hg(II) acetate and Zn(II) chloride solution was previously reported, but the mechanism of extraction was not elucidated in detail.

The present investigation was undertaken in order to make clear the mechanism of extraction of tetrahydrothiophene(THS) with bromo-copper(II) complexes with special reference made to study the chemical species containing THS in the aqueous phase.

Compared with usual desulfurization methods such as catalytic hydrodesulfurization and the classic extraction techniques with sulfuric acid etc., extraction with a copper(II) bromide solution has potential advantages. For example, the method does not need any hydrogen; it can be operated at room temperature with simple extractors and it is possible to recover the sulfur compounds in hydrocarbon oils. Thus, if the recovered sulfur compounds could be used as a starting materials for new organic syntheses, the proposed extraction method will be pregnant with significance and of great value.

2 Experimental

9 ml of organic solvent (*n*-heptane) containing 60 μl of tetrahydrothiophene(THS) and internal reference (toluene) and the equal volume of an aqueous solution of bromo-copper(II) complexes were shaken for 1 hour in a 40 ml stoppered test tube. After separation of phases, the concentration of THS in the organic phase was determined with a Yanagimoto-G 8 model gas chromatograph. The ultraviolet spectra of bromo-copper(II) complex ions were measured by a Hitachi model 124 double-beam spectrophotometer equipped with 1 mm quartz cells. The concentration of metal ion was determined by the usual chelatometric titration with ethyl-

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enediamine-tetraacetic acid(EDTA). The concentration of copper(II) ion after extraction was determined by the bathocuproine method¹⁰. Polarograms of THS (0.01 M) and bromide ion (0.01 M) were measured in an anhydrous N, N-dimethylformamide (DMF) solution with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Dissolved oxygen in the solution was removed by passing nitrogen gas through it for about one hour. Under these conditions, values of the half-wave potential, $E_{1/2}$ (v.s. S. C. E.), for bromide and THS were +1.10 volt and +1.15 volt, respectively.

3 Results

3.1 Extraction of THS with Cupric Salts Solutions

Extraction efficiency of THS was measured with aqueous cupric salts (Br^- , Cl^- and NO_3^- salts) solutions as a function of salt concentrations. The results shown in Fig. 1 indicate that the efficiency was strongly influenced by the nature of anion in the solution and it increased in the following order: $\text{NO}_3^- < \text{Cl}^- < \text{Br}^-$. In the case of chloride and nitrate salts, THS was extracted as water soluble complexes in the aqueous phase under all conditions shown in Fig. 1. In the case of bromide salts, however, a white complex was formed at the boundary of the two phases under conditions where the concentration of cupric bromide was less than 2.25 M, and when it was more than 2.25 M, the white solid complex disappeared and THS was extracted as water soluble complexes.

The effect of bromide ion concentration on the extraction of THS was also examined with 0.1 M cupric bromide solutions containing various amounts of calcium bromide (Fig. 2). The extraction efficiency was almost zero for 0.1 M cupric bromide solution itself and it increased with the increase in calcium bromide concentration up to 2.5 M and, at higher concentrations, it decreased again. In Fig. 2, the formation of the white solid compound was also observed at calcium bromide concentrations lower than 3.0 M.

3.2 Extraction Efficiency Diagram for THS

Based on these preliminary experiments, an extraction efficiency diagram for THS was established as a function of cupric bromide and calcium bromide concentrations. A solubility curve of these mixture was determined by the

Fig. 1 Extraction of Alkylsulfides with Copper(II) Salts Solutions

Fig. 2 Effect of CaBr_2 Concentration on the Extraction Efficiency ($[\text{CuBr}_2]=0.1 \text{ M}$)

usual chelatometric titration with EDTA; then, the extraction efficiency of THS was measured with the mixtures under the curve (Fig. 3).

The diagram (Fig. 3) was divided into three regions, A, B and C, based on the nature of Cu-THS complexes and the extraction efficiency of THS. In C region, extraction efficiency for THS was effectively zero. In B region, a white solid complex was formed at the boundary of the two phases. And in A region, water soluble Cu-THS complexes were formed in the aqueous phase. The A region was further divided into three sub-regions, i.e., A_1 region where THS was quantitatively extracted into the aqueous phase, A_2 region where extraction efficiency for THS was 90~100%, and A_3 region where the efficiency decreased with increasing calcium bromide concentration.

This kind of diagram is not only useful to find the optimal condition for practical application of this system to sulfur removal but also useful to understand the extraction mechanism and the role of bromide ion and copper complexes in the extraction process. A diagram for *n*-butylsulfide was also obtained (Fig. 3').

3.3 Composition of the White Solid

○: A₁ (100%), ◐: A₂ (90~100%), ⊙: A₃ (50~80%), ●: B (0~90%), ⊗: C (0%)

Fig. 3 Extraction Efficiency Diagram for THS

A₁ (100%), A₂ (90~100%), A₃ (50~80%), B (0~90%), C (0%)

Fig. 3' Extraction Efficiency Diagram for *n*-Butylsulfide (*n*BS)

Complex

The white solid formed at the **B** region in **Fig. 3** [$\text{Cu(II)Br}_2 = 1.0 \text{ M}$ and $\text{CaBr}_2 = 0.5 \text{ M}$] was separated by suction and was analysed after drying in a silica-gel desiccator overnight. The results obtained are shown in **Table 1** together with the results of the similar white solid formed in the $\text{CuBr}_2\text{--CaBr}_2\text{--}(\text{CH}_3)_2\text{S}$ system. Thus, the results seem to indicate that the white solid material contained the predomi-

Table 1 Composition of White Solid Complexes

	[Cu]	[Br]	[Sulfur Ligand]
$\text{CuBr}_2\text{--CaBr}_2\text{--}(\text{CH}_3)_2\text{S}$ System	1.0	0.97	0.87
$\text{CuBr}_2\text{--CaBr}_2\text{--THS}$ System	1.0	1.2	0.83

Curve 1: Cu^{2+} , 2: CuBr^+ , 3: CuBr_2 , 4: CuBr_3^- , 5: CuBr_4^{2-}

Fig. 4 Mole Fraction of Copper(II) Species in $\text{CuBr}_2\text{--CaBr}_2$ Solution

nantly solid complex of composition Cu(THS)Br . Stoichiometry and white color of the complex suggested that Cu(II) was reduced to Cu(I) in the complex.

4 Discussion

4.1 Extraction Mechanism of THS with Bromo-Copper(II) Complex Solutions

4.1.1 Formation of the White Solid Complex

As discussed in the previous paper, the extraction efficiency (D) and the extraction rate constant (k) of cupric salts for dimethyl sulfide were remarkably influenced by the nature of anions in the system as follows³⁾:

$$D_{\text{Br}^-} : D_{\text{Cl}^-} : D_{\text{NO}_3^-} = 32 : 2 : 1$$

$$k_{\text{Br}^-} : k_{\text{Cl}^-} : k_{\text{ClO}_4^-} = 360 : 13 : 1$$

A very similar anion effect was also observed in the case of THS as shown in **Fig. 1**. The above results suggest that the increase in the extraction efficiency is attributable mainly to the formation of copper(II)-anion complexes. Copper(II) ion reacts with bromide to form four kinds of bromo-copper(II) complexes with stability constants, $K_n = [\text{CuBr}_n] / [\text{CuBr}_{n-1}] [\text{Br}^-]$, and absorption maxima as follows: CuBr^+ ($K_1 = 0.23$, $\lambda_{\text{max}} = 285 \text{ nm}$), CuBr_2 ($K_2 = 0.052$, $\lambda_{\text{max}} = 285$ and 510 nm), CuBr_3^- ($K_3 = 0.031$, $\lambda_{\text{max}} = 510 \text{ nm}$) and CuBr_4^{2-} ($K_4 = 0.0066$, $\lambda_{\text{max}} = 510 \text{ nm}$), respectively^{11),12)}.

The data shown in **Figs. 4** and **5** indicate that monobromo- to tetrabromocopper(II) com-

Total concentrations of calcium Bromide (M) are
1: 0.1, 2: 0.4, 3: 0.8, 4: 1.0, 5: 2.0,
6: 2.25, 7: 2.50, 8: 3.0

Total copper bromide concentration is 0.1 M

Fig. 5 Absorption Spectra of Bromo-Copper(II) Complex Ions

plexes were formed successively in the solution, and aquo- and monobromo-copper(II) ions were predominant among them. Judging from the data in **Fig. 1** and **4**, it was most probable that the monobromo-copper(II) complex was mainly involved in the extraction of THS, because the aquo-copper(II) ion indicated but slight extraction power for THS. Thus, the white solid complex having a composition $[\text{Cu(I)THS Br}]$ was formed by the reaction of monobromo-copper(II) complex with THS, followed by reduction of Cu(II) to Cu(I).

Both in Cu(II)-Br^- and Cu(II)-THS systems, the decrease in the redox potential of the copper complex ($E_{1/2}$ for Cu(II) was -0.74 volt and that of Cu(II)-THS complex was -0.68 volt), but any spontaneous reduction of Cu(II) to Cu(I) was not observed. However, in the Cu(II)-Br-THS system, Cu(I) complex was formed (unfortunately, any well defined polarogram could not be obtained due to the serious interference of the bromide ion). This fact suggests that concerted electronic effects on the central Cu(II) ion of two kinds of ligands, bromo- and sulfur-ligands, resulted in the reduction of the redox potential of Cu(II) complex to such an extent that the cupric complex could accept an electron from a suitable reducing agent in the system. Unfortunately, the reducing agent in the system is not yet identified.

4.1.2 Formation of Water Soluble Complexes

By increasing the CuBr_2 concentration, extraction efficiency also increased and the white

Curve 1: f_{THS} (THS in org. phase), 2: f_{ppt} (THS in ppt.), 3: f_{sol} (THS in water soluble complex in aq. phase)

Fig. 6 Relationship between Mole Fraction of Tetrahydrothiophene (THS) Species and Total Concentration of CaBr_2 in the Extraction System

solid complex disappeared. Such dissolution of the white solid complex was explained by the formation of polynuclear species as follows:

The polynuclear complexes containing two kinds of oxidation states, such as $\text{Cu(II)-Br}_n\text{-Cu(I)}$, were also reported by Watkins et al.¹³⁾ and Doehleman et al.¹⁴⁾

The formation of water soluble complexes was also observed when the bromide ion concentration increased (**Fig. 3**, region A_3). In order to obtain further information about the role of bromide ion in the extraction, the mole fraction of THS in the solid complex and that in the water soluble complexes were estimated (**Fig. 6**). The total concentration of THS ($[\text{THS}]_{\text{total}}$) was given by Eq. (4) as the sum of concentrations of the chemical species in the two phases. Copper ion was expressed in the form of cuprous ion. The molar composition of the water soluble complex was assumed to be $\text{Cu} : \text{THS} = 1 : 1$, which has the same ratio as found in the white solid complex (**Table 1**).

$$[\text{THS}]_{\text{total}} = [\text{THS}]_o + [\text{THS}]_a + \sum_1^3 [\text{Cu(I)THS Br}_n]_a + [\text{Cu(I)THS Br}]_s \quad (4)$$

The subscripts s , o and a represent the solid

species, the species in the organic phase and that in the aqueous phase, respectively. The concentration of THS in the aqueous phase was very small compared with the other terms in Eq. (4) (distribution coefficient, $P_{\text{THS}} = [\text{THS}]_a / [\text{THS}]_o$, was well below 10^{-3}) thus, $[\text{THS}]_a$ can be neglected.

The total concentration of copper ion was given by

$$[\text{Cu}]_{\text{total}} = [\text{Cu}]_a + [\text{Cu(I)Br THS}]_s \quad (5)$$

where $[\text{Cu}]_a$ is the total copper concentration in the aqueous phase, which was determined spectrophotometrically using the bathocuproine method¹⁰. Thus, combining Eqs. (4) and (5) with the data on $[\text{Cu}]_{\text{total}}$, $[\text{Cu}]_a$ and $[\text{THS}]_o$ (determined by gas chromatography), the mole fraction of THS in the organic phase, $f_{\text{THS}} = [\text{THS}]_o / [\text{THS}]_{\text{total}}$, that in the water soluble complex, $f_{\text{sol.}} = \sum_1^3 [\text{Cu(I)THS Br}_n] / [\text{THS}]_{\text{total}}$, and that in the solid complex, $f_{\text{ppt.}} = [\text{Cu(I)THS Br}]_s / [\text{THS}]_{\text{total}}$ were calculated, respectively. The results are summarized in Fig. 6. The curve for $f_{\text{ppt.}}$ passed a maximal value around $[\text{CaBr}_2] = 1.75 \text{ M}$ and that for THS in the water soluble complexes, $f_{\text{sol.}}$, increased with the increase in the bromide ion concentrations.

Thus, the extraction behaviour of copper-THS system along the bromide concentration axis in Fig. 3 can be well understood by the following three reactions: for bromide concentration up to 2.0 M, the white solid complex formation was predominant (region D in Fig. 3),

for bromide concentration higher than 2.0 M, the water soluble complex was formed and THS was extracted into the aqueous phase efficiently (region B, A₁₋₃ in Fig. 3),

and in the presence of a large excess of bromide ions, a decrease in the extraction efficiency of THS took place (region C in Fig. 3, see also Fig. 2) due to the following displacement reaction of THS with bromide,

The driving force of the reaction (7) and (8) is attributed to the strong tendency of Cu(I) ion

to form stable bromo-complexes (cf. β_2 value of Cu(I) ion¹⁵), $[\text{Cu(I)Br}_2^-] / ([\text{Cu}^+][\text{Br}^-]^2)$ is $10^{5.04}$, whereas that for Cu(II) ion¹¹, $[\text{Cu(II)Br}_2] / ([\text{Cu}^{2+}][\text{Br}^-]^2)$ is only $10^{-1.84}$.

It was ascertained from these studies that CuBr⁺, among the copper(II) complex ions in Cu(II)-CaBr₂ system, was mainly concerned for the extraction reaction of THS to give the neutral complex $[\text{Cu(I)THS Br}]$, which reacted with the excess amount of bromide and/or copper(II) bromide to form the water soluble complexes as shown in the reaction (7) and (3), respectively.

4.2 The Role of Bromide Ion as an Auxiliary Ligand

As discussed above, the presence of a suitable auxiliary ligand such as bromide ion is essential for effective extraction of sulfide. The general order of extraction efficiency for THS (Fig. 1), DMS (dimethyl sulfide) and other sulfides⁹ was found to be

In this series, the order of $\text{Br}^- \gg \text{Cl}^-$ is just the reverse of the order of stability of their monohalogeno-Cu(II) complexes, that is $K_1^{\text{CuCl}^+} = [\text{CuCl}^+] / ([\text{Cu}^{2+}][\text{Cl}^-]) = 1.3 > K_1^{\text{CuBr}^+} = [\text{CuBr}^+] / ([\text{Cu}^{2+}][\text{Br}^-]) = 0.23^{16}$. Therefore, this fact indicates that the ligand which forms a more stable complex with the central metal ion does not necessarily act as a better auxiliary ligand for extraction of sulfide. On the other hand, the order in Eq. (9) is in good accordance with the order of softness of the base (ligand), which was proposed by Pearson¹⁷ in his "Soft and Hard Acid and Base" concept. Thus, it is found that the soft nature of the auxiliary ligand plays an important role in the formation of copper-sulfide bondings.

The extraction efficiency of alkylsulfide with CuBr₂ solution decreased in the following order: DMS(C₂) > DES(C₄) > nPS(C₆) > nBS(C₈) with increasing carbon number, and only 60% of n-butylsulfide(nBS) was extracted with a solution of CuBr₂ concentration as high as 5 M (Fig. 1). However, in the presence of 3 M of CaBr₂, a solution of relatively low CuBr₂ concentration such as 1.5 M can extract n-butylsulfide quantitatively (Fig. 3').

Thus, any extraction solution with desired extraction efficiency can easily be prepared by mixing CaBr₂ and CuBr₂ solutions based on the diagram shown in Figs. 3 and 3'.

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