March, 1985] Bull. Chem. Soc. Jpn., 58, 881—884 (1985) 881

# Solvent Extraction of Mercury(II) from Hydrochloric Acid with 1,2-Bis(hexylthio)ethane

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(Received August 6, 1984)

Solvent extraction of mercury(II) from hydrochloric acid with 1,2-bis(hexylthio)ethane (=BHTE=$\bar{S}$) in 1,2-dichloroethane has been studied at 30 °C. Mercury(II) was found to be extracted into pure 1,2-dichloroethane without extractants, which is due to the physical partition of the neutral species, $HgCl_2$. The partition coefficient, $K_D$, was evaluated as $K_D=0.314$. It was clarified that the extraction mechanism with BHTE can be explained in terms of solvation by BHTE and that 1:1 metal: the ligand complex is formed in the organic phase as follows.

$$\bar{S} + HgCl_2 \rightleftharpoons \overline{HgCl_2 \cdot S} \qquad K_e$$

The extraction equilibrium constant, $K_e$, was evaluated as $K_e=1.61\times10^3\ dm^3\ mol^{-1}$.

Solvent extraction of metal ions is one of the effective, energy-saving and nonpolluting processes for hydrometallurgy and/or the treatment of the wastewater containing heavy metals. The most important factor in the solvent-extraction processes is the extractants selective to the specified metal ions to be recovered.

So far, a number of commercial extractants have been developed and used extensively in hydrometallurgy. The majority of them are those of the O or N atom donating ligand type. Those possessing sulfur as a donor atom are relatively few. These are interesting extractants since they have a high selectivity to special metals which are classified as "soft acids" such as copper(I), silver, mercury, gold and platinum-group metals through a so-called soft-soft interaction. Among the sulfur-possessing extractants, there have been many studies of those possessing one sulfur atom such as dialkyl sulfides and dialkyl sulfoxides acting as neutral monodentate ligands.[1–3,5] However, relatively few studies have been carried out on those possessing more than two sulfur atoms acting as polydentate ligands except for *O,O*-dialkyl hydrogenphosphorodithioate.[4]

Some Soviet investigators[6–8] studied the extraction properties of bis(alkylthio)alkanes, the bidentate neutral extractants possessing two sulfur atoms, and found that these are very selective to silver, mercury, gold, palladium and platinum although their works were merely qualitative. Ohki *et al.*[9] have conducted an investigation of the extraction of copper(I), silver(I), and gold(III) by 1,2-bis(hexylthio)ethane. They found that copper and silver are extracted as 1:2 metal:reagent complexes in the extraction from perchlorate media though a 1:1 complex becomes predominant in the region where the reagent concentration is not sufficient for silver. The same was also suggested by Artyukhin *et al.*[8] for palladium extraction from hydrochloric acid.

The present authors have conducted a quantitative investigation on the distribution equilibrium in the extraction of mercury(II) from hydrochloric acid with 1,2-bis(hexylthio)ethane in 1,2-dichloroethane in this paper to clarify the composition of the extracted species and to evaluate the extraction equilibrium constant.

## Experimental

*Reagents.* 1,2-Bis(hexylthio)ethane (BHTE) was synthesized from 1-hexanethiol and 1,2-dibromoethane using a conventional method according to the following reaction.

$$2n\text{-}C_6H_{13}SH + CH_2BrCH_2Br + 2KOH \longrightarrow (n\text{-}C_6H_{13}S\text{-}CH_2\text{-})_2 + 2KBr + 2H_2O$$

The product was purified by vacuum distillation (bp 169—170 °C/5 mmHg (1 mmHg=133.322 Pa)). The identification of this product was carried out using IR and NMR spectra. The purity was verified to be about 97% by gas chromatography. The purified product was diluted using GR-grade 1,2-dichloroethane, the most polar diluent, to a required concentration in order to increase the solubility of the complex to be formed in the organic phase. The initial mercury concentration in the hydrochloric acids was adjusted to 0.005 mol dm$^{-3}$.

*Measurements of Extraction Equilibrium.* Prior to the measurement of the extraction equilibrium, preliminary experiments were carried out in order to examine the contact time required for the attainment of equilibrium in this system

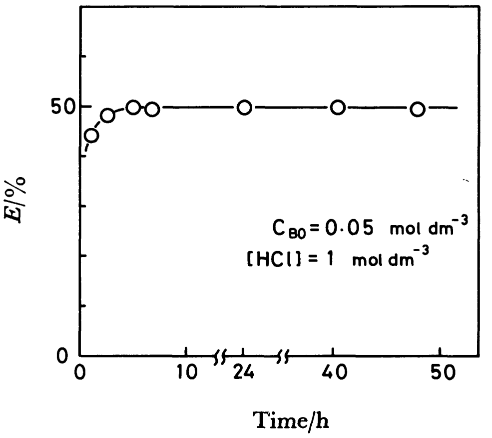

Fig. 1. Relation between the extent of extraction of mercury (II) and the contact time.

and to assure the stability of the extractant and the complex extracted into the organic phase. Figure 1 shows a typical example of the relation between the extent of extraction of mercury and the contact time. From this result, it is obvious that the extraction equilibration is attained within 5—6 h and that the extractant and the extracted complex in the organic phase are stable, at least, for 48 h. Consequently, the contact time in this system was determined as 24 h, also taking account of the convenience of the experimental operation.

Equal volumes (30 cm$^3$) of the aqueous and organic phases were shaken in a stoppered glass flask for 24 h at 30±0.1 °C. After equilibration, the two phases were separated and analyzed for mercury content in both phases. The mercury concentration in the aqueous phase was determined by titration with EDTA in the presence of an excess of Mg–EDTA using eriochrome black T(BT) as an indicator. That in the organic phase was determined by atomic absorption spectrochemical analysis using a Nippon Jarrell-Ash model AA-782 spectrophotometer after stripping with a 1 mol dm$^{-3}$ aqueous ammonium thiocyanate solution.

## Results and Discussion

*Extraction of Mercury with Pure Diluent.* First of all, mercury was found to be extracted into pure 1,2-dichloroethane without extractants as shown in Fig. 2. The extraction mechanism of mercury from a hydrochloric acid solution is considered to be caused by the physical partition of the neutral species, HgCl$_2$, as follows.

$$\mathrm{HgCl_2} \rightleftharpoons \overline{\mathrm{HgCl_2}} \tag{1}$$

$$K_\mathrm{D} = \frac{[\overline{\mathrm{HgCl_2}}]}{[\mathrm{HgCl_2}]} \tag{2}$$

In this case, the distribution ratio of mercury, D, is expressed as follows.

$$\mathrm{D} = \frac{[\overline{\mathrm{HgCl_2}}]}{C_{\mathrm{Hg\,aq.}}} = \alpha_2 \cdot K_\mathrm{D} \tag{3}$$

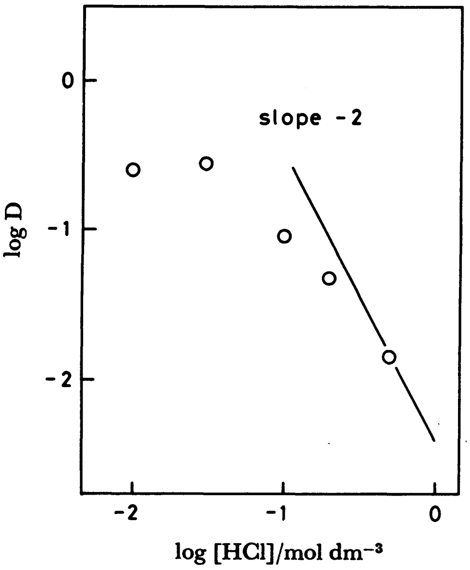

Fig. 2. Equilibrium distribution of mercury (II) from hydrochloric acid solutions with 1,2-dichloroethane.

where

$$\alpha_2 = \frac{\beta_2[\mathrm{Cl^-}]^2}{1+\sum_{1}^{4}\beta_i[\mathrm{Cl^-}]^i}\ * \tag{4}$$

The logarithm of Eq. 3 gives the following equation.

$$\log \mathrm{D} = \log \alpha_2 + \log K_\mathrm{D} \tag{5}$$

Figure 3 shows log-log plots of D against $\alpha_2$ on the basis of Eq. 5, where the values reported by Hepler[10] were used as the stability constants of chloro complexes, $\beta_i$. The plotted points in Fig. 3 lie on a straight line of slope 1 as expected from Eq. 5. From the intercept of the straight line with the ordinate in Fig. 3, $K_\mathrm{D}$ was evaluated as $K_\mathrm{D}$=0.314.

*Extraction of Mercury from Aqueous Hydrochloric Acid Solutions with BHTE in 1,2-Dichloroethane.*

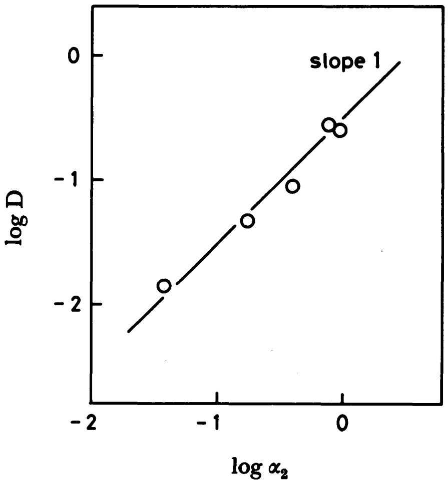

Fig. 3. Relation between logD and log$\alpha_2$ for extraction of mercury(II) with 1,2-dichloroethane.

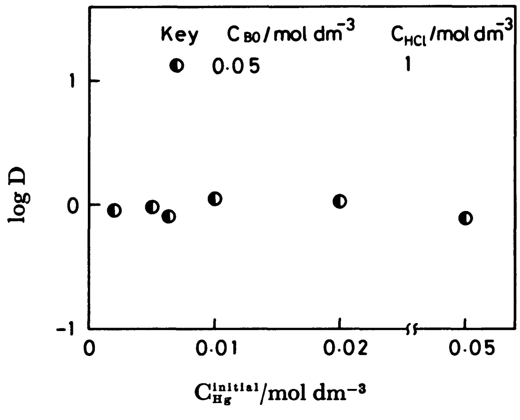

Fig. 4. Effect of the initial mercury concentration in the aqueous phase on the distribution ratio of mercury (II).

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* The dimerization constant ($K_\mathrm{d}$) of mercury(II) chloride in aqueous solution was reported as $K_\mathrm{d}$=0.3 at 25 °C by Linhart (*J. Chem. Soc.*, **37**, 258 (1915)). This value is so small as to neglect the dimerization of mercury(II) chloride in hydrochloric acid compared with monomeric chloride complexes.

In order to investigate the species of mercury existing in both phases, the effect of the concentration of mercury on the distribution of mercury was examined. The distribution ratio was found to be independent of the mercury-ion concentration in the aqueous phase over the concentration range ($2\times10^{-3}$—$5\times10^{-2}$ mol dm$^{-3}$) examined as shown in Fig. 4. This indicates that only monomeric complexes are formed in the organic phase. Figure 5 shows the effect of a hydrochloric acid concentration in the aqueous phase on the distribution ratio of mercury, where the difference between the total concentration of mercury in the organic phase and concentration of mercury extracted only by the diluent was used for the calculation of the distribution ratio. As is evident from Fig. 5, the distribution ratio decreases with an increase in the hydrochloric acid concentration. Mercury is considered to be extracted from aqueous chloride solutions according to the reaction described by

$$HgCl_2 + \bar{S} \rightleftharpoons \overline{HgCl_2 \cdot S} \qquad K_e \qquad (6)$$

$$K_e = \frac{\overline{[HgCl_2 \cdot S]}}{[HgCl_2][\bar{S}]} \qquad (7)$$

where $\bar{S}$ denotes the extractant in 1,2-dichloroethane.

In the region of a lower loading ratio of mercury, the concentration of the unreacted extractant, $[\bar{S}]$, is nearly equal to its initial concentration, $C_{B0}$, and is constant. Moreover, in the region of higher chloride ion concentration ($[Cl^-]>1$ mol dm$^{-3}$), the concentration of neutral species of mercury in the aqueous phase, $[HgCl_2]$, can be approximated as follows.

$$[HgCl_2] = \alpha_2 \cdot C_{Hg\ aq.} \simeq (\beta_2/\beta_4[Cl^-]^2) \cdot C_{Hg\ aq.} \qquad (8)$$

Therefore, the distribution ratio is approximately expressed by Eq. 9 in this region from Eqs. 7 and 8.

$$\log D = -2\log[Cl^-] + a \qquad (9)$$

where

$$a = \log(\beta_2/\beta_4) + \log C_{B0} + \log K_e \qquad (10)$$

In Fig. 5, plotted points lie on straight lines of slope −2 in the higher concentration range of hydrochloric acid as expected from Eq. 9. The values of $a$, defined by Eq. 10, were evaluated from the intercepts of these lines with the ordinate for each value of $C_{B0}$ and plotted against $\log C_{B0}$ as shown in Fig. 6. As is evident from Fig. 6, the plotted points lie on a straight line of

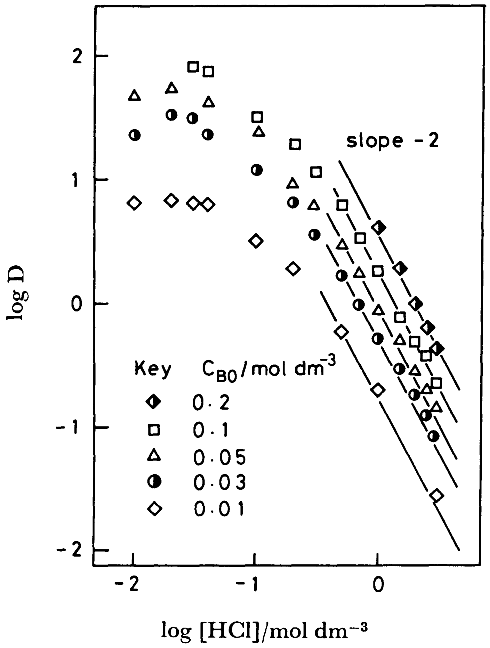

Fig. 5. Equilibrium distribution of mercury (II) from hydrochloric acid solutions with BHTE in 1,2-dichloroethane.

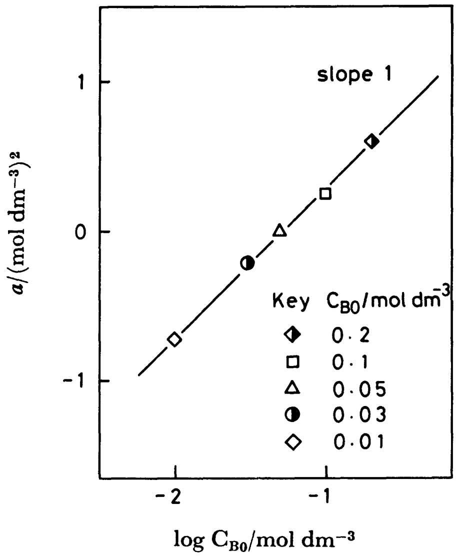

Fig. 6. Relation between $a$ and $\log C_{B0}$.

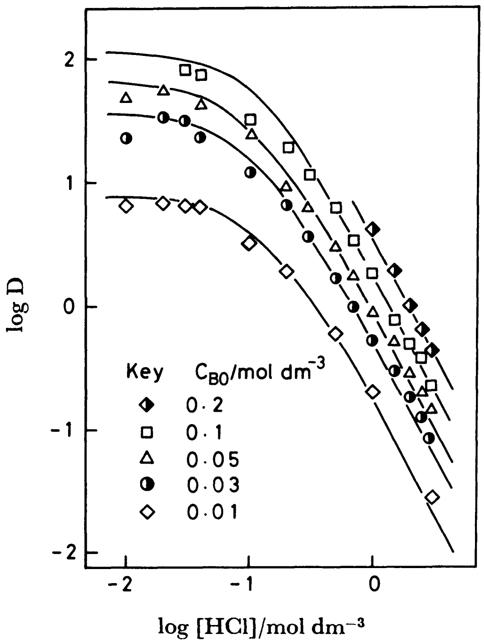

Fig. 7. Equilibrium distribution of mercury(II) from hydrochloric acid solutions with BHTE in 1,2-dichloroethane. The solid lines are the calculated results.

slope 1 as expected from Eq. 10. The extraction equilibrium constant, $K_e$, was evaluated from the value of the intercept of the straight line with the ordinate in Fig. 6 as $K_e=1.61\times10^3\ \mathrm{dm^3\,mol^{-1}}$.

Meanwhile, in the region of the higher loading ratio of mercury to the extractant, the mass balance of the extractant gives the concentration of the unreacted extractant, $\overline{[S]}$, as follows.

$$\overline{[S]} = \frac{C_{BO}}{1+K_e[HgCl_2]} = \frac{C_{BO}}{1+K_e\alpha_2 C_{Hg\,aq.}} \tag{11}$$

Substitution of Eq. 11 for Eq. 7 gives the following equation.

$$\log D = \log\alpha_2 + \log K_e + \log C_{BO} - \log(1+K_e\alpha_2 C_{Hg\,aq.}) \tag{12}$$

The solid lines in Fig. 7 are the calculated results obtained on the basis of Eq. 12 using the value of $K_e=1.61\times10^3\ \mathrm{dm^3\,mol^{-1}}$. The calculated results agree satisfactorily with the experimental ones.

*Infrared Spectrum of the BHTE–$HgCl_2$ Complex.* The low-frequency infrared spectrum of the crystalline BHTE–$HgCl_2$ complex was measured in order to identify the bond between the metal and the reagent or that between the metal and chlorine. The crystalline complex was prepared as follows. The complex of white slime was precipitated by a dropwise addition of $HgCl_2$ in 0.01 mol dm$^{-3}$ hydrochloric acid to BHTE dissolved in ethanol under intense agitation. It was purified by recrystallizing three times from aqueous ethanol solution to obtain the crystalline complex.

As a result, a single sharp band is observed at 273 cm$^{-1}$ ascribable to the Hg–Cl group, on which Coats *et al.*[11] observed $\nu$(Hg–Cl) at 288 s and 249 m cm$^{-1}$ for the $(CH_3CH_2S\text{-}CH_2\text{-})_2HgCl_2$ complex. Therefore, also taking account of the experimental results on the effect of mercury concentration on the distribution ratio mentioned earlier, the complex extracted into the organic phase is considered to be $(n\text{-}C_6H_{13}S\text{-}CH_2\text{-})_2HgCl_2$.

## Conclusion

Solvent extraction of mercury(II) with 1,2-bis(hexylthio)ethane(=BHTE) in 1,2-dichloroethane from hydrochloric acid was studied at 30 °C. It was concluded that mercury(II) can be extracted with 1,2-dichloroethane itself by the physical partition of $HgCl_2$ and that it is extracted with BHTE according to the following extraction reaction.

$$\overline{(n\text{-}C_6H_{13}S\text{-}CH_2\text{-})_2} + HgCl_2 \rightleftharpoons \overline{(n\text{-}C_6H_{13}S\text{-}CH_2\text{-})_2HgCl_2}$$

The authors are indebted to Professor M. Takagi of Kyushu University for his instruction in the synthesis of 1,2-bis(hexylthio)ethane.

The present work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

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