December, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 3835—3839 (1986)* 3835

Extraction Equilibria of Mercury(II) from Hydrochloric Acid with Trialkylphosphine Sulfides

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(Received June 5, 1986)

The extraction of mercury(II) from hydrochloric acid was compared using five kinds of sulfur-containing extractants. Mercury(II) was extracted most effectively by trialkylphosphine sulfides. Subsequently, the distribution equilibria of mercury(II) from hydrochloric acid with triisobutylphosphine sulfide (TIBPS=$\overline{S}$) and trioctylphosphine sulfide (TOPS=$\overline{S}$) in toluene have been measured at 303 K in order to clarify the concentration dependencies of the reactant species. It was found that mercury(II) is extracted according to the solvation reaction by TIBPS or TOPS as a mercury(II): extractant 1:2 complex, $HgCl_2S_2$, in the range of low loading ratio of mercury(II) to the extractants, and as a 1:1 binuclear complex, $(HgCl_2)_2S_2$, in the region of high loading ratios, as follows:

$$HgCl_2 + 2\overline{S} \rightleftharpoons \overline{HgCl_2S_2} \qquad K_e$$

$$2HgCl_2 + 2\overline{S} \rightleftharpoons \overline{(HgCl_2)_2S_2} \qquad K_e'$$

The extraction equilibrium constants, K_e and K_e', were evaluated as $K_e=4.0\times10^5$ $(dm^3\ mol^{-1})^2$ and $K_e'=2.0\times10^8$ $(dm^3\ mol^{-1})^3$ for TIBPS and as $K_e=7.2\times10^6$ $(dm^3\ mol^{-1})^2$ for TOPS.

Thus far, the solvent extraction of mercury(II) has been investigated using various kinds of extractants: trioctylphosphine oxide (TOPO),[1,2] tributyl phosphate (TBP),[2] trioctylamine,[3] and trioctylmethylammonium chloride (Aliquat 336).[4] However, these extractants, containing nitrogen or oxygen as a donor atom, have only poor selectivities to mercury(II) over other metals. On the other hand, it is well-known that the extractants containing sulfur as a donor atom, such as dialkyl sulfides[5,6] and trialkyl thiophosphate,[7] are very powerful and selective extractants for mercury(II). From this point of view, in a previous work[8] we studied the extraction equilibrium of mercury(II) with 1,2-bis(hexylthio)ethane, which contains two sulfurs as donor atoms.

Recently, the American Cyanamid Co. has developed a new commercial extractant, CYANEX 471, the active species of which is triisobutylphosphine sulfide, as a selective extractant for palladium(II) and silver(I).[9] Hitchcock et al.[10] reported that tributylphosphine sulfide (TBPS) completely extracted mercury(II) from 0.1 mol dm^{-3} hydrochloric acid; however, they did not succeed in finding an effective aqueous solution for stripping. Further, no detailed studies of the extraction of mercury(II) with trialkylphosphine sulfides have been carried out to date.

In the present investigation, the authors have conducted a detailed and quantitative investigation of the distribution equilibrium of mercury(II) in extraction from hydrochloric acid with two kinds of trialkylphosphine sulfides: triisobutylphosphine sulfide and trioctylphosphine sulfide.

Prior to the detailed study of the extraction equilibrium, preliminary experiments were carried out in order to compare qualitatively the extraction behavior of trialkylphosphine sulfides with that of other sulfur-containing compounds for mercury(II).

Experimental

Reagents. Two kinds of trialkylphosphine sulfides, possessing different alkyl chains-triisobutylphosphine sulfide and trioctylphosphine sulfide-were used as the extractants. These will be abbreviated to TIBPS and TOPS respectively and denoted by S hereafter. The TIBPS was purified from a commercial extactant, CYANEX 471, donated by the American Cyanamid Co., by recrystallization from a water-ethanol mixture. The purity of the purified reagent was confirmed by elemental analysis to be as follows: Found: C, 61.34; H, 11.48%. Calcd: C, 61.49; H, 11.61%. The TOPS, which was kindly supplied by the Nippon Chemical Industry Co., was used as delivered, without further purification. The purity of this reagent was also confirmed by elemental analysis to be as follows: Found: C, 71.95; H, 12.64%. Calcd: C, 71.64; H, 12.64%. Among the extracting reagents used in the preliminary experiment for the sake of comparison, 1,2-bis(hexylthio)ethane and 2-(butylthio)dodecanoic acid were synthesized and purified in the manners reported in previous papers,[8,11] while dihexyl sulfide was used as delivered from the Daihachi Chemical Co., Ltd. These reagents will be abbreviated as BHTE, 2-BTDA and DHS respectively hereafter. An organic phase was prepared by diluting these extractants with toluene of an analytical grade on a gravimetric basis. An aqueous phase was prepared by dissolving mercury(II) chloride in hydrochloric acid.

Procedure. Equal volumes of the aqueous and organic phases were shaken in a 0.1 dm^3 stoppered glass flask immersed in a thermostated bath maintained at 303 K—for 3 h or 1 h for TIBPS or TOPS respectively—in order to attain equilibrium. It was confirmed from a preliminary experiment that the equilibration could be attained within these times. The initial total concentration of mercury(II) was 1×10^{-3} or 5×10^{-3} mol dm^{-3} in all experiments. The total concentration of mercury(II) 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, or by atomic-absorption spectrochemical analysis

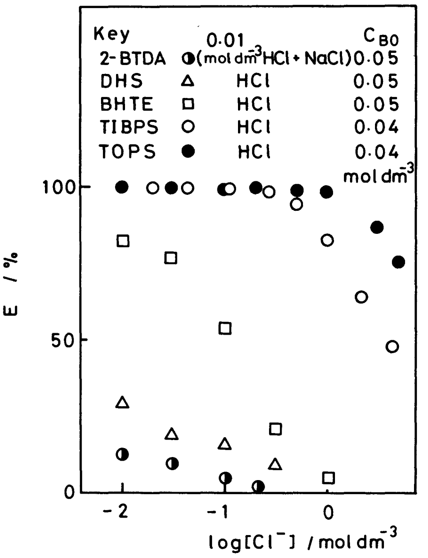

Fig. 1. Relation between % extraction of mercury(II) and log [Cl$^-$] (Initial concentration of mercury(II) is 5×10^{-3} mol dm^{-3}).

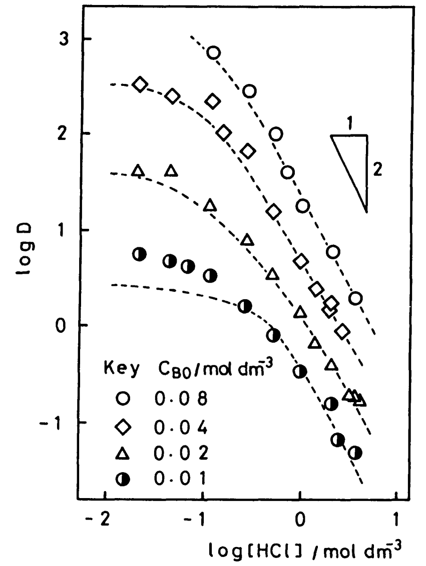

Fig. 2. Equilibrium distribution of mercury(II) from hydrochloric acid solutions with TIBPS in toluene (Initial concentration of mercury(II) is 5×10^{-3} mol dm^{-3}).

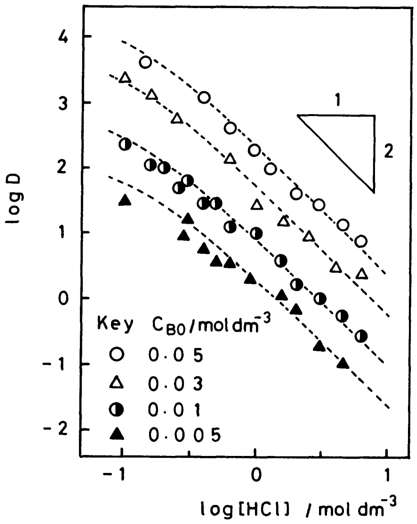

Fig. 3. Equilibrium distribution of mercury(II) from hydrochloric acid solutions with TOPS in toluene (Initial concentration of mercury(II) is 1×10^{-3} mol dm^{-3}).

using a Nippon Jarrell-Ash model AA-782 spectrophotometer. In the range of low loading ratios, the concentration of mercury(II) in the organic phase was determined by the methods described above after stripping with a 1 and a 2 mol dm^{-3} aqueous ammonium thiocyanate solution for TIBPS and TOPS respectively. In the range of high loading ratios, it was calculated from the difference between the initial and equilibrium concentrations of mercury(II) in the aqueous phase.

Results and Discussion

Figure 1 shows the results of the preliminary experiment as the plot of the % extraction of mercury(II) by each extractant from chloride media against the chloride-ion concentration. Here, the % extraction is defined as the ratio of mercury(II) content in the organic phase after equilibration to the initial mercury(II) content in the aqueous phase. C_{B0} denotes the initial concentration of the extractants. From Fig. 1, mercury(II) is shown to be effectively extracted by TIBPS and TOPS in the range of low chloride-ion concentrations in particular; the % extractions are more than 50%, even in the high-chloride-ion-concentration region, which suggests that these extractants are very effective for the separation and recovery of mercury(II). On the other hand, DHS and 2-BTDA show only a poor extraction capacity for mercury(II) in chloride media, while BHTE shows an extraction capacity intermediate between the trialkylphosphine sulfides and DHS or 2-BTDA. Therefore, the present authors conducted a detailed and quantitative study of the extraction equilibria of mercury(II) with TIBPS and TOPS.

Figures 2 and 3 show the effects of the hydrochloric acid concentration on the distribution ratio of mercury(II) for various concentrations of the extractant in the extractions with TIBPS and TOPS respectively. As is evident from these figures, the distribution ratio, D, decreases with the increase in the hydrochloric acid concentration, which is similar to the extractions of mercury(II) from hydrochloric acid with 1,2-bis(hexylthio)ethane and 2-BTDA observed in the previous works.[8,12] Therefore, mercury(II) is considered to be extracted from hydrochloric acid according to the following solvation reaction for both the extractants:

$$\mathrm{HgCl_2} + n\overline{\mathrm{S}} \rightleftharpoons \overline{\mathrm{HgCl_2S}_n} \qquad K_e, \qquad (1)$$

where $\overline{\mathrm{S}}$ denotes the extractant species in the organic phase. The equilibrium constant, K_e, for the above reaction is given by Eq. 2:

$$K_e = \frac{\overline{[HgCl_2S_n]}}{[HgCl_2][\overline{S}]^n}. \qquad (2)$$

It is well-known that mercury(II) gives rise to chloro complexes in the aqueous chloride solution as follows:

$$Hg^{2+} + iCl^- \rightleftharpoons HgCl_i^{(i-2)-} \quad \beta_i\ (i=1\text{–}4) \qquad (3)$$

$$\beta_i = \frac{[HgCl_i^{(i-2)-}]}{[Hg^{2+}][Cl^-]^i}, \qquad (4)$$

where β_i is the stability constant of the ith chloro complex of mercury(II).[13] From Eqs. 3 and 4, the concentration of the neutral complex, $[HgCl_2]$, which takes part in the extraction reaction described by Eq. 1 is expressed as follows:

$$[HgCl_2] = \alpha_2 C_{Hgw}, \qquad (5)$$

where

$$\alpha_2 = \beta_2[Cl^-]^2/(1+\sum_{i=1}^{4}\beta_i[Cl^-]^i). \qquad (6)$$

In the region of high chloride-ion concentrations ($[Cl^-] > 1$ mol dm^{-3}), it can be approximated by Eq. 7:

$$[HgCl_2] = \alpha_2 C_{Hgw} \simeq (\beta_2/\beta_4[Cl^-]^2)C_{Hgw}. \qquad (7)$$

In Eqs. 5 and 7, C_{Hgw} denotes the total concentration of mercury(II) in the aqueous phase. From Eqs. 2 and 5, the distribution ratio is expressed by Eq. 8:

$$D = \frac{\overline{[HgCl_2S_n]}}{C_{Hgw}} = K_e\alpha_2[\overline{S}]^n, \qquad (8)$$

which is approximated by Eq. 9 in the regions of high concentrations of the chloride ion:

$$D \simeq K_e(\beta_2/\beta_4[Cl^-]^2)[\overline{S}]^n. \qquad (9)$$

The logarithm of Eq. 9 gives:

$$\log D = -\ 2\log[Cl^-] + a, \qquad (10)$$

where

$$a = \log(\beta_2/\beta_4) + n\log[\overline{S}] + \log K_e. \qquad (11)$$

In Eq. 11, the concentration of the unreacted extractant, $[\overline{S}]$, is nearly equal to its initial concentration, C_{B0}, in the region of low loading ratios.

As is evident from Figs. 2 and 3, the plotted points lie on straight lines, with a slope of −2, in the high-concentration ranges of hydrochloric acid, as is to be expected from Eq. 10. The values of a, defined by Eq. 11, were obtained from the intercepts of these straight lines with the ordinate for each C_{B0} and for each extractant. In Fig. 4, they are plotted against $\log C_{B0}$ to evaluate n and K_e. As is evident from this figure, the plotted points lie on straight lines, with a slope of 2, which suggests that $n=2$ in Eq. 11; that is, mercury(II) is coordinately solvated by two molecules of TIBPS or TOPS in the organic phase. Therefore, the stoichiometric relation of these extraction reactions may be expressed as follows for both the extractants:

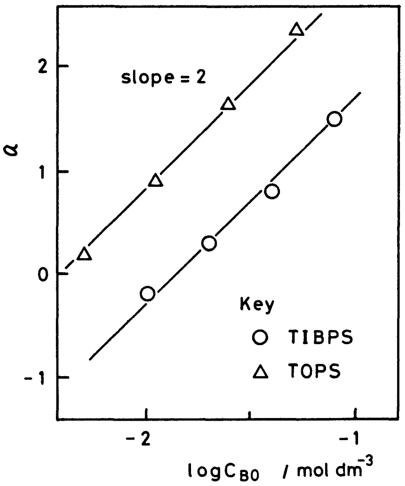

Fig. 4. Plot of a against $\log C_{B0}$ based on Eq. 11.

$$HgCl_2 + 2\overline{S} \rightleftharpoons \overline{HgCl_2S_2} \quad K_e \qquad (12)$$

On the basis of Eq. 11, the extraction equilibrium constant, K_e, was evaluated as $K_e = 4.0\times10^5$ (dm^3 mol^{-1})^2 for TIBPS, and as $K_e = 7.2\times10^6$ (dm^3 mol^{-1})^2 for TOPS, from the intercepts of the straight lines with the ordinate in Fig. 4.

Meanwhile, in the region of high loading ratios, the mass balances with regard to the extractant and mercury(II) should be taken into consideration. The initial concentration of the extractant (C_{B0}) in the organic phase and that of mercury(II)(C_{Hg0}) in the aqueous phase are expressed as follows:

$$C_{B0} = [\overline{S}] + 2\overline{[HgCl_2S_2]} \qquad (13)$$

$$C_{Hg0} = C_{Hgw} + \overline{[HgCl_2S_2]}. \qquad (14)$$

Equations 8 and 14 are then combined to give Eq. 15, taking into account the fact that $n=2$:

$$C_{Hgw} = C_{Hg0}/(1+\gamma[[\overline{S}]^2), \qquad (15)$$

where

$$\gamma = \alpha_2 K_e. \qquad (16)$$

The mass balance equation of the extractant in the organic phase expressed by Eq. 13 is reduced to the cubic equation expressed by Eq. 17 with respect to the unreacted extractant concentration ($[\overline{S}]$):

$$\gamma[\overline{S}]^3 + (2\gamma C_{Hg0} - \gamma C_{B0})[\overline{S}]^2 + [\overline{S}] - C_{B0} = 0. \qquad (17)$$

The distribution ratio is ultimately given by:

$$D = \frac{\overline{[HgCl_2S_2]}}{C_{Hgw}} = \frac{C_{Hg0}}{C_{Hgw}} - 1 = \gamma[\overline{S}]^2 \qquad (18)$$

The dotted lines in Figs. 2 and 3 show the results calculated from Eqs. 17 and 18. The calculated curves shown in Figs. 2 and 3 are in good agreement with the experimental results except for $C_{B0}=0.01$ mol dm^{-3} in the extraction with TIBPS in Fig. 2.

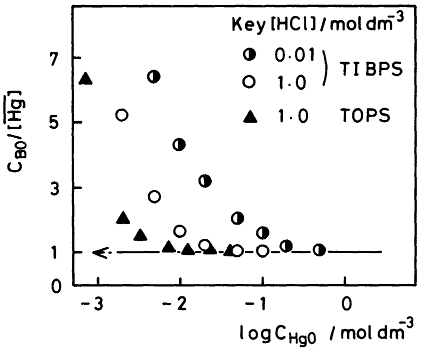

Fig. 5. Experimental results of the loading test (C_{B0}=0.01 mol dm^{-3}).

Since the calculated curve corresponding to C_{B0}=0.01 mol dm^{-3} in Fig. 2 deviates downwards from the experimental results as the mercury(II) concentration in the organic phase increases, the loading test was carried out for a constant initial concentration of the extractant in order to examine the mole ratio of mercury(II) extracted into the organic phase ($[\overline{Hg}]$) to the extractant under the conditions of excess concentrations of mercury(II), by varying the initial mercury(II) concentration (C_{Hg0}) in the aqueous phase.

In Fig. 5, the experimental results are shown as plots of the mole ratio, $C_{B0}/[\overline{Hg}]$, against C_{Hg0}, which shows that the mole ratio asymptotically approaches unity for both extractants. From these results, it is evident that mercury(II) is extracted as a 1 : 1 metal : reagent complex in the region of high loading ratios. Consequently, it may be considered to be extracted as a binuclear complex according to the extraction reaction described by Eq. 19, taking the coordination number of mercury(II)(=4) into consideration and referring to the study by Mikhailov et al.[5] on the extraction of mercury(II) with dialkyl sulfides:

$$2HgCl_2 + 2\overline{S} \rightleftharpoons \overline{(HgCl_2)_2S_2} \qquad K_e' \qquad (19)$$

$$K_e' = \frac{[\overline{(HgCl_2)_2S_2}]}{[HgCl_2]^2[\overline{S}]^2} \qquad (20)$$

Taking account of the fact that mercury(II) is extracted according to the extraction reaction described by Eq. 19 in the region of high loading ratios, the calculated curves for the extraction with TIBPS in Fig. 2 were reconsidered. The distribution ratio, D, is described by Eq. 21 by taking account of the two reactions expressed by Eqs. 12 and 19:

$$D = \frac{[\overline{HgCl_2S_2}]+2[\overline{(HgCl_2)_2S_2}]}{C_{Hgw}} \qquad (21)$$

The substitution of Eqs. 2, 5, and 20 into Eq. 21 gives Eq. 22, taking into account the fact that n=2:

$$D = (K_e + 2K_e'C_{Hgw}\alpha_2)\alpha_2[\overline{S}]^2 \qquad (22)$$

Further, the total concentration of the extractant in the organic phase, C_{B0}, and the initial concentration of mercury(II) in the aqueous phase, C_{Hg0}, are expressed as follows:

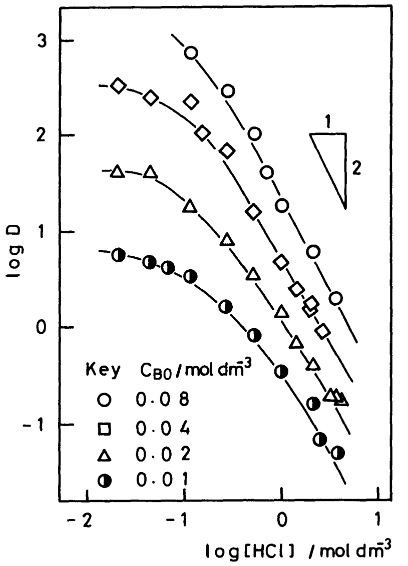

Fig. 6. Equilibrium distribution of mercury(II) from hydrochloric acid solutions with TIBPS in toluene.

$$C_{B0} = [\overline{S}] + 2[\overline{HgCl_2S_2}] + 2[\overline{(HgCl_2)_2S_2}] \qquad (23)$$

$$C_{Hg0} = C_{Hgw} + [\overline{HgCl_2S_2}] + 2[\overline{(HgCl_2)_2S_2}] \qquad (24)$$

The subtraction of Eq. 24 from Eq. 23, followed by the substitution of Eq. 8 and taking into account the fact that n=2, yields the following quadratic equation with respect to the unreacted extractant concentration ($[\overline{S}]$):

$$K_e\alpha_2C_{Hgw}[\overline{S}]^2 + [\overline{S}] - C_{B0} + C_{Hg0} - C_{Hgw} = 0 \qquad (25)$$

The equilibrium constant for the extraction reaction described by Eq. 19, K_e', was evaluated, using the least-squares method so as to minimize the deviations between the observed and calculated results from Eqs. 22 and 25, as K_e'=2.0×10^8 (dm^3 mol^{-1})^3. The solid lines in Fig. 6 are the calculated results obtained from Eqs. 22 and 25 using the values of K_e=4.0×10^5 (dm^3 mol^{-1})^2 and K_e'=2.0×10^8 (dm^3 mol^{-1})^3. For all of the extractant concentrations, the calculated curves are in good agreement with the experimental results.

The authors are deeply indebted to American Cyanamid Co. for supply of the sample of CYANEX 471.

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