

EXTRACTION EQUILIBRIA OF MERCURY(II) FROM ACIDIC CHLORIDE SOLUTIONS WITH TRIOCTYLAMINE

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Distribution equilibria of mercury(II) between trioctylamine–hydrochloric acid salt in xylene and acidic solution containing high or low chloride ion concentrations were measured at 298 K.

Mercury(II) is extracted as the complexes $(RH)_3HgCl_5 \cdot H_2O$ and $(RH)HgCl_3$, which are formed respectively by the reactions of $HgCl_4^{2-}$ and $HgCl_3^-$ with the amine salt, from aqueous solution with high chloride ion concentration. In the extraction from 0.1 mol/dm³ hydrochloric acid solution, it is considered that $HgCl_2$ also reacts with the amine salt and then forms the complex $(RH)_2HgCl_4 \cdot H_2O$. The formation constants for their respective reactions were determined.

Introduction

Solvent extraction with high-molecular weight amines was successfully applied to the purification of nuclear fuel,³⁾ and then the amines were found to be efficient extractants for the separation and purification of metals. In recent years, as environmental contamination and the exhaustion of resources have become serious problems, considerable interest has been directed to the examination of solvent extraction techniques with the amines as an energy-saving separation process in the fields of hydrometallurgy and industrial waste water treatment.

From this point of view, we have studied the extraction mechanism of uranium(VI) and cadmium(II) with high-molecular weight amines.^{7,8)} Solvent extraction of mercury(II) with high-molecular weight amines has been investigated by Chapman *et al.*,²⁾ Tandon *et al.*,^{10,11)} and others,^{4,9)} but the equilibrium relation for the mercury(II) extraction has not yet been adequately clarified.

In the present study, the extraction equilibria of mercury(II) with trioctylamine (TOA) were investigated. Mercury(II) distribution equilibria between xylene solutions of TOA–hydrochloric acid salt and acidic solutions containing high or low chloride ion concentrations were measured. In addition, water co-extracted into the organic phase together with mercury(II) was determined.

1. Experimental

All the experiments were performed by the batch-wise method. A known volume of an aqueous

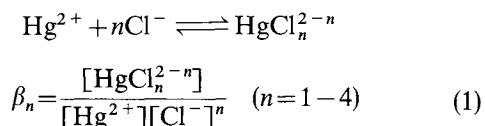
mercury(II) solution was equilibrated with an equal volume of an organic solution in an Erlenmeyer flask with a stopper by shaking the two phases in an air bath maintained at 298 K.

The organic phase was prepared by diluting TOA–hydrochloric acid salt prepared by the ordinary method⁶⁾ in xylene of commercial GR grade. The aqueous phase was prepared by dissolving mercury(II) chloride, hydrochloric acid and sodium chloride of commercial GR grade in deionized water saturated with xylene.

The concentration of mercury(II) in the aqueous phase was determined by chelate titration with a 0.01 mol/dm³ EDTA standard solution in the range of high concentration and by the cold vapor atomic absorption method in the range of low concentration. The concentration of mercury(II) in the organic phase was obtained from the mass balance. The initial concentration of the amine salt was analyzed by titrating with sodium hydroxide solution. The water content in the organic phase was determined by the Karl Fisher method.

2. Basic Equation of Equilibrium Relation

Mercury(II) forms chloride complexes by the following reaction in the aqueous chloride solution.

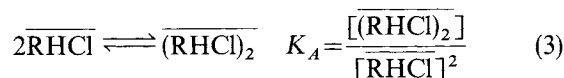


The concentration C_M of mercury(II) in the aqueous phase is described by

$$C_M = \left(1 + \sum_{i=1}^4 \beta_i [Cl^-]^i \right) [Hg^{2+}] \quad (2)$$

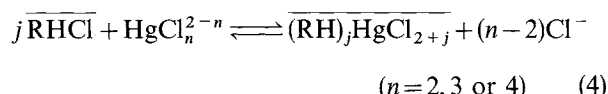
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An amine-hydrochloric acid salt exists as a monomer and a dimer in the organic phase according to the dimerization reaction¹²⁾:



where the overbar refers to the organic phase.

In mercury(II) extraction with the amine salt from the aqueous chloride solution, mercury(II) chloride HgCl_2 and anion complexes HgCl_3^- , HgCl_4^{2-} are extracted into the organic phase, and the extraction reaction is generally expressed as follows:



The equilibrium relation for the above reaction is given by

$$K_{e,j,n} = \frac{[\overline{(\text{RH})_j\text{HgCl}_{2+j}}][\text{Cl}^-]^{n-2}}{[\overline{\text{RHCl}}]^j[\text{HgCl}_n^{2-n}]} \quad (5)$$

Equation (5) is transformed by use of Eqs. (1) and (2).

$$K_{e,j,n} = \frac{[\overline{(\text{RH})_j\text{HgCl}_{2+j}}]}{q_H^j f_n([\text{Cl}^-]) C_M} \quad (6)$$

where $q_H (= [\overline{\text{RHCl}}])$ is the concentration of amine hydrochloride monomer and

$$f_n([\text{Cl}^-]) = \frac{\beta_n [\text{Cl}^-]^2}{1 + \sum_{i=1}^4 \beta_i [\text{Cl}^-]^i} \quad (7)$$

From Eq. (6), the concentration q_M of mercury(II) in the organic phase is expressed as:

$$q_M = \sum_j [\overline{(\text{RH})_j\text{HgCl}_{2+j}}] = \sum_j K_{e,j,n} f_n([\text{Cl}^-]) C_M q_H^j \quad (8)$$

The total concentration Q of amine in the organic phase is obtained from Eqs. (3) and (8).

$$Q = \sum_j \{ j K_{e,j,n} f_n([\text{Cl}^-]) C_M q_H^j \} + 2 K_A q_H^2 + q_H \quad (9)$$

3. Results and Discussion

3.1 Effect of initial concentrations of hydrochloric acid and sodium chloride on distribution

The effects of the aqueous initial concentrations of hydrochloric acid and sodium chloride on the distribution equilibria of mercury(II) were examined for a total amine concentration of 0.1 mol/dm^3 and initial mercury(II) concentrations of 0.01 and 0.025 mol/dm^3 . The results are shown in Fig. 1.

The distribution coefficient K_D decreases with increasing initial concentrations of hydrochloric acid and sodium chloride, and the effect at higher initial concentration of mercury(II) becomes larger than

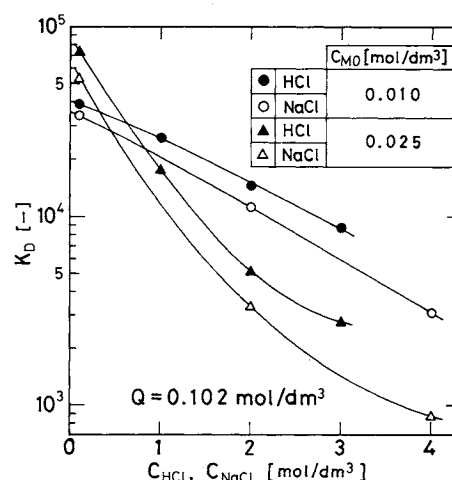


Fig. 1. Effect of initial concentration of HCl or NaCl on distribution coefficient K_D .

that at lower concentration. However, the lowest distribution coefficient is about 900 under the present experimental conditions and mercury(II) is thus extracted efficiently from the aqueous solution containing a high concentration of chloride ion.

3.2 Distribution from the aqueous solution containing high chloride ion concentration

Mercury(II) forms several chloride complexes in the aqueous chloride solution. Figure 2 represents the fraction of each mercury(II) complex at various chloride ion concentrations. This result was calculated from Eq. (1), using the values of the stability constant for the formation of mercury(II) chloride complex in the ionic strength of 0.5 to 3 mol/dm^3 reported by Hepler *et al.*⁵⁾ Only a little Hg^{2+} and HgCl^+ are formed and therefore they are not presented in the figure. In the range of high chloride ion concentrations, it is adequate to consider only the two complexes HgCl_4^{2-} and HgCl_3^- .

The distribution equilibria of mercury(II) from 0.1 mol/dm^3 hydrochloric acid solution containing 4 mol/dm^3 of sodium chloride were measured by varying the amine concentration Q at mercury(II) concentrations of 0.01 and 0.025 mol/dm^3 . Figure 3 shows a plot of the distribution coefficient against Q . The distribution coefficients indicate different curves for each initial concentration of mercury(II) in the aqueous phase.

In this case, as is clear from Fig. 2, a large portion of mercury(II) in the aqueous phase exists as HgCl_4^{2-} . In the higher concentration range of Q in Fig. 3, where $Q \gg q_M$, K_D is nearly proportional to the third power of Q , and thus the following equilibrium relation obtained from Eq. (8) may be approximately applied.

$$K_D = \frac{q_M}{C_M} = \frac{[\overline{(\text{RH})_3\text{HgCl}_5}]}{C_M} = K_{e,3,4} f_4([\text{Cl}^-]) q_H^3 \quad (10)$$

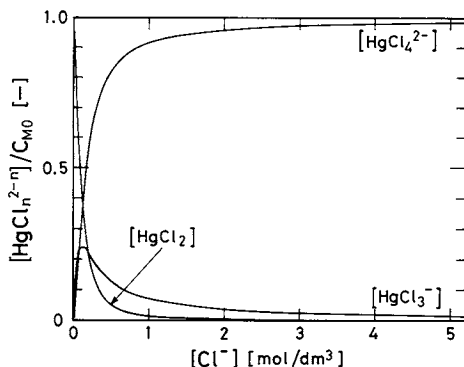


Fig. 2. Kinds of mercury(II) chloride complex existing in aqueous chloride media.

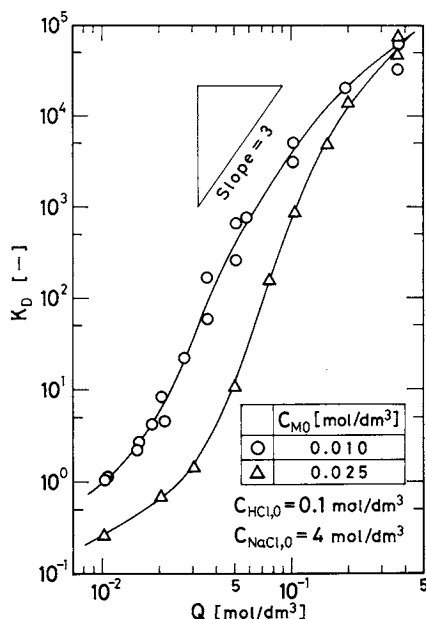


Fig. 3. Distribution coefficient K_D for total amine concentration Q .

The data of Fig. 3 at $C_{M0} = 0.01 \text{ mol/dm}^3$ in $Q > 0.05 \text{ mol/dm}^3$ are plotted against q_H calculated from Eq. (9) using a K_A value of $40 \text{ dm}^3/\text{mol}^{(12)}$ in Fig. 4. A linear relationship with a slope of 3 between K_D and q_H approximately holds. From the result and Eq. (10), a formation constant $K_{e,3,4}$ with a value of $4.6 \times 10^9 \text{ dm}^3/\text{mol}$ was obtained by assuming the chloride ion concentration $[\text{Cl}^-]$ to be constant at 4.1 mol/dm^3 .

In the lower concentration range of Q , it is predicted from Fig. 3 that a complex with one-molecule mercury(II) and one-molecule amine salt such as $(\text{RH})\text{HgCl}_3$ forms. Taking into account the formation of both the complexes $(\text{RH})_3\text{HgCl}_5$ and $(\text{RH})\text{HgCl}_3$, the distribution coefficient is expressed as follows from Eq. (8).

$$K_D = \frac{q_M}{C_M} = K_{e,3,4} f_4([\text{Cl}^-]) q_H^3 + K_{e,1,3} f_3([\text{Cl}^-]) q_H \quad (11)$$

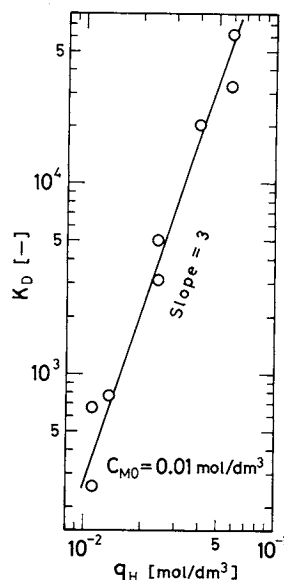


Fig. 4. Distribution coefficient K_D for monomer concentration q_H of amine-hydrochloric acid salt in the range of large q_H .

Figure 5 shows the result in which the K_D values of Fig. 3 are plotted against q_H obtained from Eq. (9). The solid line in the figure is the result calculated from Eq. (11) by using the above value of $K_{e,3,4}$ and adopting a $K_{e,1,3}$ value of 1.0×10^5 . The experimental data agree with the calculated values regardless of the initial concentration C_{M0} of mercury(II).

3.3 Distribution from the aqueous solution containing low chloride ion concentration

The distribution equilibria of mercury(II) from 0.1 mol/dm^3 hydrochloric acid solution were measured. In this case, three mercury(II) complexes, HgCl_4^{2-} , HgCl_3^- and HgCl_2 , exist in the aqueous phase. Assuming that HgCl_2 reacts with two molecules of the amine salt in addition to the extraction reactions for HgCl_4^{2-} and HgCl_3^- represented above,* the distribution coefficient is derived from Eq. (8).

$$K_D = \frac{q_M}{C_M} = K_{e,3,4} f_4([\text{Cl}^-]) q_H^3 + K_{e,2,2} f_2([\text{Cl}^-]) q_H^2 + K_{e,1,3} f_3([\text{Cl}^-]) q_H \quad (12)$$

Figure 6 is a plot of K_D against q_H , the values of which were evaluated from Eq. (9) by using the same values of K_A and $K_{e,3,4}$ as shown above and assuming a $K_{e,2,2}$ value of $1.0 \times 10^{10} (\text{dm}^3/\text{mol})^2$. In this calculation, the aqueous concentration $[\text{Cl}^-]$ of chloride ion is necessary to obtain the value of $f_n([\text{Cl}^-])$. The $[\text{Cl}^-]$ value was determined by Eq. (14) derived from Eq. (13), which describes the condition of electrical neu-

* We carried out a calculation similar to that shown below by assuming that HgCl_2 reacts with one or three molecules of the amine salt, but a good correlation between K_D and q_H was not obtained.

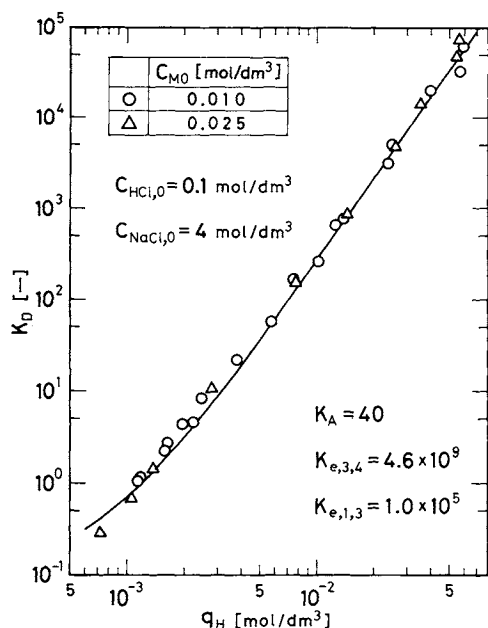


Fig. 5. Relation between distribution coefficient K_D and monomer concentration q_H of amine-hydrochloric acid salt.

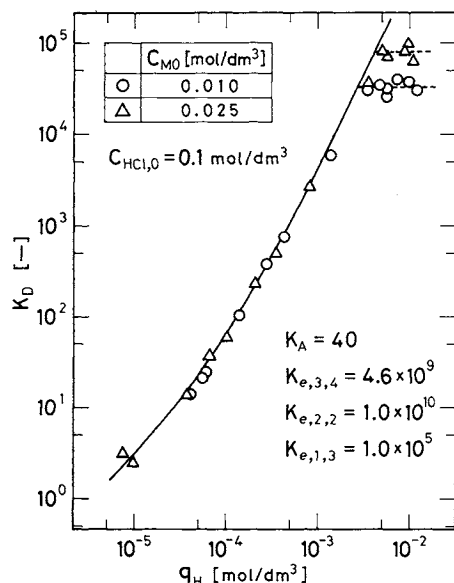


Fig. 6. Relation between distribution coefficient K_D and monomer concentration q_H of amine-hydrochloric acid salt.

trality in the aqueous phase.

$$\begin{aligned}
 &[\text{H}^+] + 2[\text{Hg}^{2+}] + [\text{HgCl}^+] \\
 &= [\text{Cl}^-] + [\text{HgCl}_3^-] + 2[\text{HgCl}_4^{2-}] \quad (13)
 \end{aligned}$$

$$\begin{aligned}
 &[\text{H}^+] = [\text{Cl}^-] \\
 &- \left(\frac{2 + \beta_1[\text{Cl}^-] - \beta_3[\text{Cl}^-]^3 - 2\beta_4[\text{Cl}^-]^4}{1 + \sum_{i=1}^4 \beta_i[\text{Cl}^-]^i} \right) C_M \quad (14)
 \end{aligned}$$

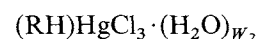
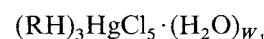
The solid line in the figure is the calculated result from Eq. (12). The calculated values are in satisfac-

tory agreement with the experimental data in the range of q_H less than 3×10^{-3} mol/dm³. The observed K_D values, however, become nearly constant when q_H is higher than 3×10^{-3} mol/dm³ and deviate from Eq. (12). Though a similar result has been reported by Chapman *et al.*,²⁾ it is necessary to investigate such a phenomenon further.

3.4 Combined water in the organic phase in extraction of mercury(II)

The water content combined with the amine salt produced by the reaction of the amine with hydrochloric acid was first measured. Figure 7 shows a plot of the water content q_W in the organic phase against the concentration Q of the amine salt. Xylene extracts water at 0.020 mol/dm³ at 298 K. q_W is the total water content minus the amount extracted by xylene in the organic phase, that is, the amount of water combined with the amine salt. A linear relationship with a slope of 1.0 between q_W and Q holds. It is inferred from the result that each molecule of the amine salt combines with one molecule of water and exists in the forms $\text{RHCl} \cdot \text{H}_2\text{O}$ and $(\text{RHCl} \cdot \text{H}_2\text{O})_2$.

Figure 8 shows the water content q_W for the mercury(II) concentration q_M in the organic phase observed in the distribution experiments of mercury(II) at $[\text{Cl}^-]$ of about 4.1 mol/dm³. Assuming that the extracted mercury(II) complexes exist in the following forms,¹⁾



the combined water concentration in the organic phase is expressed by

$$\begin{aligned}
 q_W = &Q + (W_1 - 3)q_M \\
 &+ (W_2 + 2 - W_1)[(\text{RH})\text{HgCl}_3 \cdot (\text{H}_2\text{O})_{W_2}] \quad (15)
 \end{aligned}$$

The slope of the solid line in Fig. 5 is nearly 3 in the range of higher q_H , so mercury(II) is extracted almost in the form of $(\text{RH})_3\text{HgCl}_5 \cdot (\text{H}_2\text{O})_{W_1}$. A value of W_1 may, therefore, be determined from the experiments at higher concentration of Q as

$$\lim_{q_M \rightarrow 0} \left(-\frac{\partial q_W}{\partial q_M} \right)_Q = 3 - W_1 \quad (16)$$

This slope is obtained from Fig. 8 to be nearly 2 and then $W_1 = 1$. The solid and broken lines represent the results calculated from Eqs. (6), (8), (9) and (15) by assuming $W_2 = 0$ and 1, respectively. The calculated values for $W_2 = 0$ approximately agree with the observed ones.

From the experiments of distribution equilibrium of mercury(II) from 0.1 mol/dm³ hydrochloric acid solution, it was determined similarly that one molecule of $(\text{RH})_2\text{HgCl}_4$ combines with one molecule of water. Therefore, it is inferred that the extracted

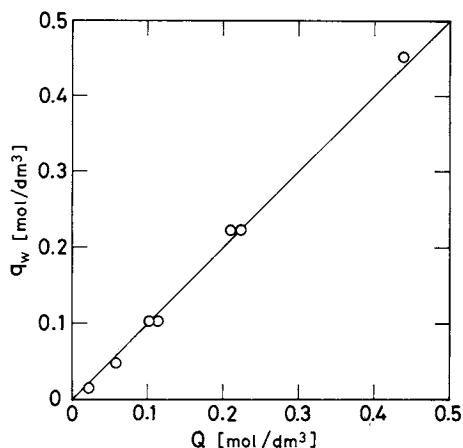


Fig. 7. Water content combined with amine-hydrochloric acid salt.

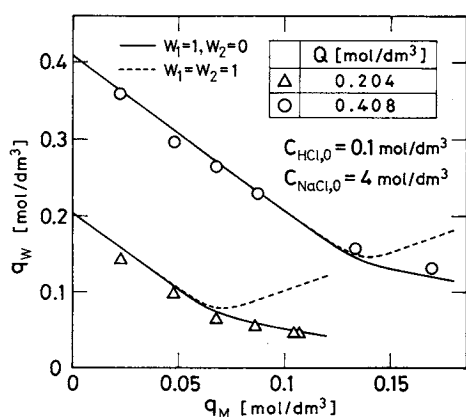
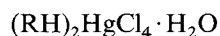
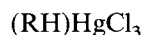
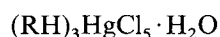


Fig. 8. Combined water content in organic phase in extraction equilibrium of mercury(II).

mercury(II) complexes exist in the following forms in the organic phase.



Conclusion

The extraction equilibria of mercury(II) from acidic chloride solutions by TOA-hydrochloric acid salt in xylene were studied.

The distribution coefficient decreases with an increase of chloride ion concentration, but mercury(II) is extracted efficiently from the aqueous solution containing 4 mol/dm³ of chloride ion.

In extraction from the aqueous solution containing high chloride ion concentration, the equilibrium relation was expressed by Eq. (11) and the $K_{e,3,4}$ and $K_{e,1,3}$ values of the formation constant were obtained as 4.6×10^9 dm³/mol and 1.0×10^5 , respectively.

Equation (12) with the $K_{e,2,2}$ value of 1.0×10^{10} (dm³/mol)² was approximately applied to the distribution equilibrium from 0.1 mol/dm³ hydrochloric acid solution in the range of q_H less than 3×10^{-3} mol/dm³. Furthermore, the water co-extracted into the organic phase together with mercury(II) was determined.

Nomenclature

C_{HCl}	= concentration of hydrochloric acid in the aqueous phase	[mol/dm ³]
C_M	= concentration of mercury(II) in the aqueous phase	[mol/dm ³]
C_{NaCl}	= concentration of sodium chloride in the aqueous phase	[mol/dm ³]
$f_n([\text{Cl}^-])$	= function of $[\text{Cl}^-]$ defined by Eq. (7)	[(mol/dm ³) ²⁻ⁿ]
j	= association number for amine	[—]
K_A	= dimerization constant of amine salt defined by Eq. (3)	[dm ³ /mol]
K_D	= distribution coefficient of mercury(II)	[—]
$K_{e,j,n}$	= formation constant for Eq. (4)	[(dm ³ /mol) ^{j-n+2}]
Q	= total concentration of amine in the organic phase	[mol/dm ³]
q_H	= monomer concentration of amine-hydrochloric acid salt in the organic phase	[mol/dm ³]
q_M	= concentration of mercury(II) in the organic phase	[mol/dm ³]
q_w	= concentration of combined water in the organic phase	[mol/dm ³]
W_1, W_2	= number of combined water	[—]
β_n	= stability constant defined by Eq. (1) ($n=1-4$)	[(dm ³ /mol) ⁿ]
[]	= concentration	[mol/dm ³]
overbar	= organic phase	

<Subscript>

0 = initial

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