

EXTRACTION EQUILIBRIUM OF HYDROCHLORIC ACID WITH TRI-*n*-OCTYLAMINE

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Extraction equilibrium of hydrochloric acid in aqueous solution with tri-*n*-octylamine in toluene, water content accompanying the acid extraction and average aggregation number of the species formed in the organic solution were measured under various conditions. Formation constants of several species formed were estimated, and the species estimated by these experimental results were confirmed by the infrared spectra of the organic solution. It was found that the acid, A, reacts with the amine, B, to form three species of $(AB)_n$ ($n = 1, 2$ and 3) in the organic solution. The formation constants of these species were estimated.

Introduction

Long-chain alkyl amines are used as extractants of metal ions from acidic aqueous solution. Knowledge of the chemistry of acid extraction by the amine is necessary as a basis for designing metal extraction processes. Many investigators have indicated that some oligomer or polymer of ion-paired species is formed by the reaction between the amine and the acid, judging by measurements of the extraction equilibrium of acids,^{5,8)} vapor pressure lowering^{3,7,13)} or IR spectra.^{1,4,6)} The aggregation number and its equilibrium constant are known to be affected by the dielectric constant and chemical properties of the diluent,^{2,8,12)} and the volume fraction of amine.⁸⁾ In the extraction of hydrochloric acid by quaternary ammonium chloride, the water content in the organic solution was reported to play an important role in the extraction mechanism.⁹⁾

In the present study, the extraction equilibrium of hydrochloric acid with tri-*n*-octyl amine in toluene solution is measured under various conditions, and the aggregation number of the species formed in the organic solution is estimated by ebullioscopy or by vapor-phase osmometry. The species formed and their formation constants are then, estimated.

IR spectra of the organic solution and water content in the organic solution were measured for various equilibrium conditions. Utilizing these experimental results, the chemical species formed are estimated.

1. Experimental

1.1 Reagents

Tri-*n*-octyl amine (TOA) supplied by Koei Chemical Co. was used as the extractant without further purification. The purity of the amine was over 99.8%. Toluene and hydrochloric acid were GR reagents.

1.2 Experimental procedure

Equal volumes of aqueous hydrochloric acid and toluene solution of TOA were shaken in a flask and allowed to attain equilibrium in a water bath thermostated at 30.0°C. The solutions were separated and analyzed for acid concentration by titration with an aqueous solution of sodium hydroxide for the aqueous solution and with a butanol-methanol solution of potassium hydroxide for the organic solution, using phenolphthalein as indicator.

The average aggregation number of the species formed in the organic solution was measured by vapor-phase osmometry on a HITACHI-PARKIN ELMER 115 and by ebullioscopy.

Infrared spectra of the species in the organic solution were observed. The effect of the concentration of acid on the absorbance of IR spectra was examined to confirm the species estimated. Finally, water content in the organic solution was determined by Karl-Fisher titration.

2. Experimental Results

The equilibrium concentration of the acid in the organic solution, $C_{A,org}$, is plotted in Fig. 1 against the equilibrium concentration of the acid in the aqueous solution, $C_{A,aq}$, for various amine concentrations, C_{BO} .

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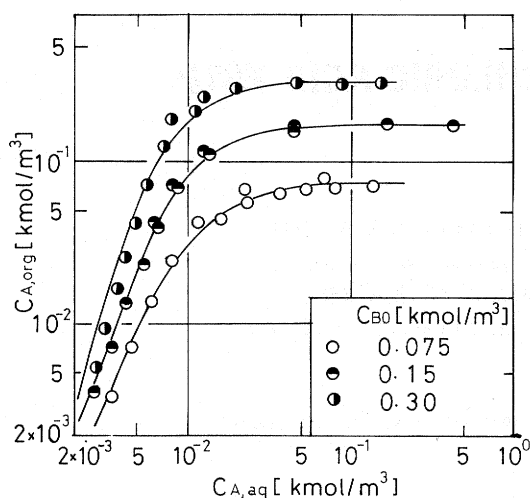


Fig. 1. Relation between acid concentration in organic solution, $C_{A,org}$, and in aqueous solution, $C_{A,aq}$.

The value of $C_{A,org}$ depends on C_{B0} and increases with $C_{A,aq}$, approaching the respective value of C_{B0} . The value of Z defined by $(C_{A,org}/C_{B0})$ is plotted against $C_{A,aq}$ in Fig. 2. The value of Z increases with $C_{A,aq}$ and approaches unity for all amine feed concentrations. The value of $\log(1/Z-1)$ is plotted against $\log C_{A,aq}$ for various values of C_{B0} in Fig. 3. The value depends on C_{B0} at high $C_{A,aq}$, but becomes independent of C_{B0} at low $C_{A,aq}$.

The total concentrations of unreacted amine and ammonium salts formed in the organic solutions equilibrated with pure water or 1.0 kmol/m^3 hydrochloric acid solution were measured. At high concentrations, it is impossible to measure the concentration of their species in the organic solution by vapor-phase osmometry. In this range, the concentration was measured by ebullioscopy. Under this experimental condition, the elevation of the boiling point of the amine solution equilibrated with pure water varied linearly with the concentration of amine. The ebullioscopic constant estimated by the slope of the straight line was nearly equal to that calculated by Trouton's approximation equation.¹¹⁾ The average aggregation number, \bar{n} , is calculated by (C_{B0}/C_{Pt}) , where C_{B0} is the amine concentration in the organic solution equilibrated with pure water and C_{Pt} is total concentration of the species formed in the organic solution equilibrated with 1.0 kmol/m^3 hydrochloric acid. The average aggregation number, \bar{n} , is plotted against C_{B0} in Fig. 4. The value of \bar{n} increases from unity to a value greater than 2.0 with increasing C_{B0} .

The infrared spectra of the organic solution were measured. Several specific absorption signals were observed at 2200–2700 cm^{-1} as broad peaks at 3450 and 3705 cm^{-1} . The maximum absorbance for these spectra is plotted against $C_{A,aq}$ in Fig. 5. The absorbance increases and approaches values depen-

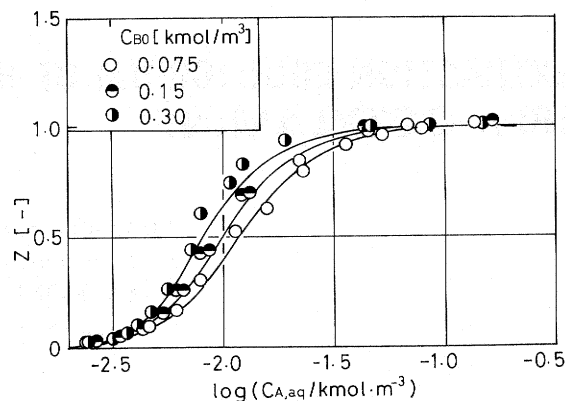


Fig. 2. Relation between extraction, Z , and acid concentration in aqueous solution, $C_{A,aq}$.

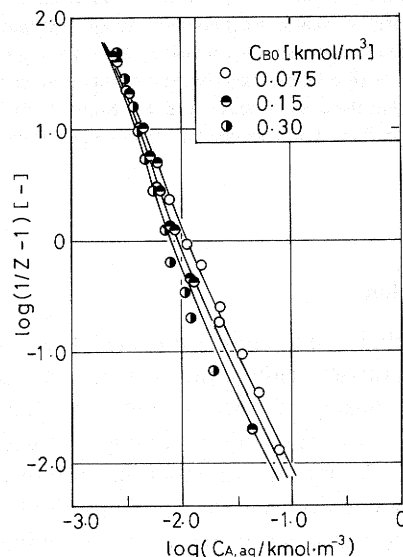


Fig. 3. Relation between $\log(1/Z-1)$ and $\log(C_{A,aq})$ at constant C_{B0} .

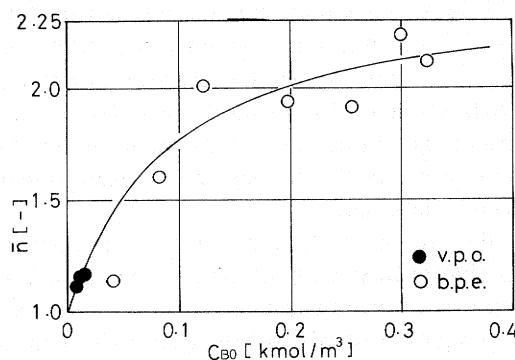


Fig. 4. Relation between average aggregation constant, \bar{n} , and C_{B0} .

dent on each band with increasing $C_{A,aq}$.

Water concentration in the organic solution, $C_{w,org}$, is plotted against acid concentration in the organic solution, $C_{A,org}$, in Fig. 6. Values of $C_{w,org}$ are clustered on the straight line having a slope of 1.0, and only the amount of water equivalent to the concentration of the acid in the organic solution is dissolved in the

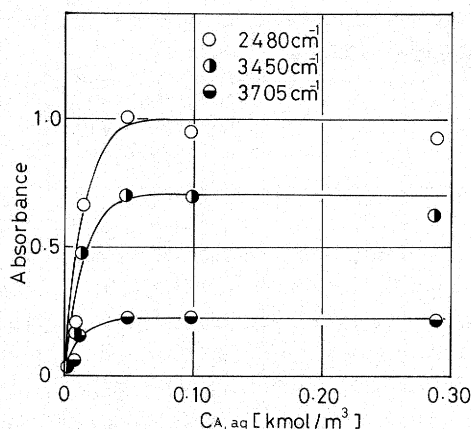


Fig. 5. Relation between absorbances and equilibrium concentration of acid, $C_{A,aq}$, at 2480 cm^{-1} , 3450 cm^{-1} and 3705 cm^{-1}

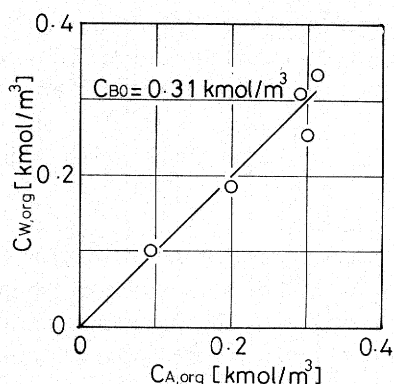


Fig. 6. Relation between water concentration, $C_{w,org}$, and acid concentration, $C_{A,org}$, in organic solution

organic solution in this concentration range.

3. Discussion

Hydrochloric acid itself scarcely dissolves in the organic diluent. It dissolves in the organic solution only as the ammonium chloride salts formed by the reactions with the amine. From the result in Fig. 6, the acid is found to be extracted with an equal amount of water in the organic solution. That is, water in the organic solution is assumed to exist as complexes hydrogen bonded equimolarly with the acid or/and the amine. As the ratio of water bonded to the acid or/and the amine is constant at 1.0 under the experimental conditions, the amount of water is not considered in the analysis of the formation constant of the complexes. The acid, A, reacts first with the amine, B, to form species AB in the organic solution. The species AB may react successively with A at the interface and with B or itself in the organic solution to form A_nB , AB_n or $(AB)_n$ ($n=2, 3, \dots, N$) by the following reactions:

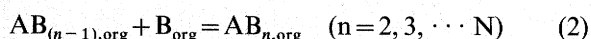
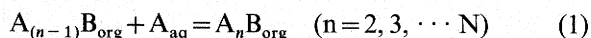
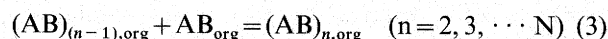


Table 1. Function Z and $\log(1/Z-1)$ where species A_nB , AB_n or A_nB_n is formed by the reactions of Eqs. (1), (2) or (3)

species	equations
A_nB	$Z = \left[\sum_{n=1}^N nK'_{n1} C_{A,aq}^{2n} \right] / \left[1 + \sum_{n=1}^N \{K'_{n1} C_{A,aq}^{2n}\} \right] \quad (7)$
	$K'_{n1} = \prod_{i=1}^n \{K_{i1}\} \quad (8)$
AB_n	$Z = \left[\sum_{n=1}^N \{K'_{1n} C_{A,aq}^2 C_{B,n}^{2n}\} \right] / \left[C_B + \sum_{n=1}^N \{nK'_{1n} C_{A,aq}^2 C_{B,n}^{2n}\} \right] \quad (9)$
	$C_{A,aq} \rightarrow 0;$
	$\log(1/Z-1) = -\log(K'_{11} C_{A,aq}^2) - \log \left\{ 1 + \sum_{n=1}^N (K'_{1n} C_{B0}^{n-1}) \right\} \quad (10)$
	$K'_{1n} = \prod_{i=1}^n (K_{i1}) \quad (11)$
A_nB_n	$Z = \left[\sum_{n=1}^N \{nK'_{nn} C_{A,aq}^{2n} C_{B,n}^{2n}\} \right] / \left[C_B + \sum_{n=1}^N \{nK'_{nn} C_{A,aq}^{2n} C_{B,n}^{2n}\} \right] \quad (12)$
	$C_{A,aq} \rightarrow 0;$
	$\log(1/Z-1) = -\log(K'_{11} C_{A,aq}^2) \quad (13)$
	$K'_{nn} = (K_{11})^n \prod_{i=1}^n (K_{ii}) \quad (14)$



Since hydrochloric acid, A, is dissociated completely in the aqueous solution, the equilibrium constants for the reactions above are written as follows;

$$K_{n1} = C_{A_nB,org} / \{C_{A_{n-1}B,org} \cdot C_{A,aq}^2\} \quad (4)$$

$$K_{1n} = C_{AB_n,org} / \{C_{AB_{n-1},org} \cdot C_{B,org}\} \quad (5)$$

$$K_{nn} = C_{(AB)_n,org} / \{C_{(AB)_{n-1},org} \cdot C_{AB,org}\} \quad (6)$$

As shown in previous papers,^{5,10} Z and $\log(1/Z-1)$ for the reactions above are derived as functions of C_{B0} , $C_{A,aq}$ and the equilibrium constants as shown in Table 1.

Where A_nB ($n > 1$) species are formed in the system, the value of Z is represented by Eq. (7) and increases to a value larger than unity with increasing C_{B0} . In Fig. 2, the value of Z depends on C_{B0} and is always smaller than unity. Then, it is concluded that A_nB ($n > 1$) species are not formed. Where AB_n ($n > 1$) species are formed, the value of $\log(1/Z-1)$ at limiting small value of $C_{A,aq}$ is represented by Eq. (10) and depends on C_{B0} . Furthermore, the value of Z given by Eq. (9) increases and approaches a value of $(1/n)$ ($n > 1$) with increasing $C_{A,aq}$ regardless of C_{B0} . In Fig. 2, the value of Z increases and approaches unity with increasing $C_{A,aq}$. These results suggest that AB_n ($n > 1$) species do not form in the system. Where AB successively reacts with $(AB)_{(n-1)}$ species to form $(AB)_n$ species according to Eq. (3), Z and $\log(1/Z-1)$ are given as Eqs. (12) and (13) in Table 1. From Eq. (12), the value of Z is expected to increase with increasing $C_{A,aq}$, the values of $\log(1/Z-1)$ approach

the line expressed by Eq. (13).^{5,10)} In Fig. 2, the value of Z depends on C_{B0} , and increases with $C_{A,aq}$ to approach 1.0. In Fig. 3, as $C_{A,aq}$ decreases, the value of $\log(1/Z-1)$ for various values of C_{B0} approach a single curve and coincide with each other regardless of C_{B0} . From these results, only $(AB)_n$ ($n > 1$) species is likely to form in the system. In this case, the average aggregation number for the species formed, \bar{n} , is expressed by the following equation:

$$\bar{n} = C_{B0}/C_{Pt} = [C_{(AB)} + \sum_{n=2}^N (nK_{nn}C_{(AB)n-1}C_{(AB)})] / [C_{(AB)} + \sum_{n=2}^N (K_{nn}C_{(AB)n-1}C_{(AB)})] \quad (15)$$

As shown in Fig. 4, average aggregation number, \bar{n} , increases from unity to a value greater than 2 with an increase in C_{B0} . The maximum value of n in Eq. (15), N , is expected to be greater than 2. Then the experimental results in Figs. 2, 3 and 4 were analyzed for three respective species, AB, $(AB)_2$ and $(AB)_3$, which are formed in the organic solution. That is, Eqs. (12) and (15) with $N=3$ were used in the analysis. In this case, the concentration of the acid may be taken as the activity of the acid in the aqueous solution. In this concentration range, the activity coefficient of the acid is approximated to be 1.0 to simplify the calculation. The straight line having a slope of 2 obtained at very small $C_{A,aq}$ in Fig. 3 is represented by Eq. (13). Using the value of $C_{A,aq}$ at $\log(1/Z-1)=0$ on the straight line, the constant K_{11} is calculated from Eq. (13) and is shown in Table 2. The constants K_{22} and K_{33} are determined so that the standard deviation of the experimental results and that calculated by Eqs. (12) and (15) become minimum. The estimated equilibrium constants are shown in Table 2. The solid lines in Figs. 1, 2, 3 and 4 are the results calculated by Eqs. (12) and (15). The solid lines in these figures agree well with the experimental results. Therefore, the observed results of the extraction equilibrium of hydrochloric acid and the aggregation number of the ammonium chloride salt in the organic solution are interpreted by the reaction model in which three species of $(AB)_n$ ($n=1, 2$ and 3) are formed in the organic solution.

As shown in Fig. 5, the absorbance at 2480 cm^{-1} increases with $C_{A,aq}$ in the range smaller than 0.06 kmol/m^3 , and it tends to reach a constant value. The value of $C_{A,aq}$ at which the absorbance becomes constant is almost equal to that at which the value of Z becomes unity, as shown in Fig. 2. The spectra obtained at $2200\text{--}2700\text{ cm}^{-1}$ were assigned as the stretching frequency for NH^+ bond by Keder *et al.*⁶⁾ The result indicates that $\text{R}_3\text{NH}^+\text{HCl}^-$ is formed in the solution by an ion-paired reaction between TOA and hydrochloric acid, and that the species increases

Table 2. Formation constants of species formed by the reaction of Eq. (3)

K_{11}	$3.7 \times 10^3 \text{ [(m}^3/\text{kmol)}^2]$
K_{22}	$3.2 \times 10^4 \text{ [m}^3/\text{kmol}]$
K_{33}	$2.3 \times 10^5 \text{ [m}^3/\text{kmol}]$

with $C_{A,aq}$ to attain the respective value of C_{B0} . In the present work, the absorbances were also observed at 3450 and 3705 cm^{-1} . These spectra were assigned as hydrogen bonded and free water in the organic solution, respectively by Jedinakova *et al.*⁴⁾ and Keder *et al.*⁶⁾ The absorbances of these spectra increase with $C_{A,aq}$ and in the amounts of the ion-paired species as shown in Fig. 5. That is, the water content increases with the amounts of ion-paired species in the organic solution. As shown in Fig. 6, $C_{w,org}$ increases linearly, maintaining a slope of 1.0 with increasing $C_{A,org}$. These results suggest that each mole of ammonium chloride salt contains one mole of water. The ammonium chloride salt is estimated to exist as $(\text{R}_3\text{NH}^+\text{Cl}^- \cdot \text{H}_2\text{O})_n$ ($n=1, 2$ and 3) in the organic solution.

Conclusion

The extraction equilibrium of hydrochloric acid with tri-*n*-octyl amine in toluene solution was measured along with the measurement of average aggregation number of the species formed in the organic solution. Furthermore, IR spectra of the species formed and water content in the organic solution at equilibrium were measured and the following results were obtained.

- 1) The amine in the organic solution reacts with hydrochloric acid in the aqueous solution to form ammonium chloride salt and its oligomers.
- 2) The species formed were confirmed by the data of IR spectra and water content in the organic solution, it was found that the complexes contain water: $(\text{R}_3\text{NHClH}_2\text{O})$ ($n=1, 2$ and 3).
- 3) The formation constants for these complexes were determined as shown in Table 2.

Nomenclature

C	= Concentration	$[\text{kmol/m}^3]$
K	= Equilibrium constant	$[\text{m}^3/\text{mol}]^n$
N	= Maximum value of n	[—]
\bar{n}	= Average aggregation number	[—]
Z	= Fraction of extraction defined by $(C_{A,org}/C_{B0})$	[—]
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A	= Acid	
aq	= Aqueous solution	
B	= Amine	
org	= Organic solution	
0	= Initial condition	

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