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Extraction of Hydrochloric Acid by Tri-*n*-octylamine in Benzene

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The equilibria involved in the extraction of HCl by tri-*n*-octylamine (TOA) in benzene have been investigated as a function of the HCl and TOA concentrations. Two distinctly different extractions were observed for two different acidity ranges. From the extraction in the low acidity range (<0.001 M HCl), it has been found that two complexes of TOA·HCl and $(\text{TOA}\cdot\text{HCl})_2$ are formed in the organic phase and that the equilibrium constants for the two reactions,

$$\text{TOA(org)} + \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)} = \text{TOA}\cdot\text{HCl(org)}$$

and

$$2\text{TOA(org)} + 2\text{H}^+\text{(aq)} + 2\text{Cl}^-\text{(aq)} = (\text{TOA}\cdot\text{HCl})_2\text{(org)},$$

are $K_{11} = (1.51 \pm 0.02) \times 10^4$ and $K_{22} = (2.92 \pm 0.07) \times 10^9$ respectively. For higher concentrations of $\text{HCl} > 3$ M, it seems probable that two major complexes of $(\text{TOA}\cdot\text{HCl})_2\text{HCl}$ and $(\text{TOA}\cdot\text{HCl})_3(\text{HCl})_2$ besides the monomer and the dimer, and three minor complexes of $(\text{TOA}\cdot\text{HCl})_2(\text{HCl})_2$, $(\text{TOA}\cdot\text{HCl})_3\text{HCl}$, and $(\text{TOA}\cdot\text{HCl})_3(\text{HCl})_3$ are formed in the organic phase.

Since Smith and Page[1] extracted various weak and strong acids with a chloroform solution of methyl-di-octylamine, the extraction of various metal ions from acid solutions by high-molecular-weight amines has been studied and used for various separation processes and analytical techniques. Several reviews[2-4] of this kind of work have been published. On the other hand, although many studies on the extraction mechanism have been reported, in all of these studies except a few,[5-6] the amine salts have been assumed to be monomeric and the possibility of the aggregation of amine salts has been neglected or disregarded.

Since Allen[7] tried to explain the insensitivity of the activity of TOA and di-decylamine sulfates and bisulfates to change in their concentrations by assuming them to form large colloidal aggregates, systematic investigations of the aggregation of several amine salts in the organic phase have been carried out using the methods of light scattering,[8] freezing-point lowering,[9-10] vapor-pressure lowering,[11-12] and two-phase e.m.f. titration.[13] Although it has been found that the amine salts tend to aggregate in an inert solvent with a low dielectric constant, there are still many contradictions in the quantitative treatment of the extraction equilibria.

The main purpose of the work reported here has been to evolve a quantitative description of the extraction equilibria and to find the composition of aggregates of the amine salt in the organic phase. In the present paper, a study of the extraction of HCl from an aqueous solution by TOA in benzene will be reported.

Experimental

Reagents. TOA (supplied by the Kao Saop Co., Tokyo) was purified by vacuum distillation (10 mmHg, and 190—200°C). The other chemicals used were of an analytical grade and were used without further purification. Laboratory-distilled water was used.

Solutions. The TOA solutions were prepared volu-

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[1] E. L. Smith and J. E. Page, *J. Soc. Chem. Ind. (London)*, **67**, 48 (1948).

[2] C. F. Coleman, K. B. Brown, J. G. Moore and K. A. Allen, Paper, No. 510, 2nd United Nations Intern. Conference on the Peaceful Uses of Atomic Energy (1958).

[3] F. L. Moore, NAS-NS-3101 (1960).

[4] Y. Macus, *Chem. Revs.*, **63**, 139 (1963).

[5] P. J. Lloyd and E. A. Mason, *J. Phys. Chem.*, **68**, 3120 (1964).

[6] L. Kuca, E. Högfeldt and L. G. Sillen, "Solvent Extraction Chemistry," ed. by D. Dyrseen, J. O. Liljenzin and J. Rydberg, North-Holland Publishing Co., Amsterdam (1967), p. 454; D. Dyrssen and M. De Jesus Tavares, *ibid.*, p. 467.

[7] K. A. Allen, *J. Phys. Chem.*, **60**, 239 (1956).

[8] K. A. Allen, *ibid.*, **62**, 1119 (1958).

[9] V. V. Formin, P. A. Zagorets and A. F. Morgunov, *Zhur. Neorgan Khim.*, **4**, 700 (1959).

[10] V. Vdovenko, B. J. Galikin and A. A. Chaikhorskii, *Radiokhmiya*, **3**, 448 (1961).

[11] C. D. Strehlow, M. S. Thesis, Dept. of Chem., Massachusetts Institute of Technology (1964).

[12] A. S. Kertes, *J. Inorg. Nucl. Chem.*, **27**, 209 (1965).

[13] E. Högfeldt, "Ion Exchange," ed. by J. A. Marinsky, Marcel Dekker, New York (1966), p. 153.

metrically from TOA and benzene. Aqueous solutions of hydrochloric acid were prepared by the dilution of 12 M HCl. The ionic strengths of HCl solutions with low concentrations (<TOA concentration) were adjusted with 1 M NaCl in order to keep the mean activity coefficient of HCl in the aqueous phase constant, while no such adjustments were made to solutions with high HCl concentrations (>1 M).

Procedure and Analysis. The TOA solutions were shaken in the extraction tubes with equal volumes of HCl aqueous solutions for 15 min. After centrifuging, suitable aliquots of the aqueous phase and of the organic phase were pipetted out for the determination of HCl concentrations. For the extraction of HCl from a solution of a low acidity, the activities of hydrogen ions in the aqueous phase were measured with a pH meter (Radiometer PHM4c, Copenhagen), the concentrations of HCl extracted into the organic phase were determined from the difference in the HCl concentrations of the aqueous phase before and after the equilibrium. For the extraction of HCl from highly-acidic solutions, the concentrations of HCl in the aqueous phase and in the organic phase were determined titrimetrically by the use of a standard base in an 80% ethanol aqueous solution with a mixed indicator of thymol blue and phenolphthalein. Corrections for the excess HCl extracted by benzene itself were made for the extractions with concentrations higher than 8 M HCl.

The concentrations of TOA solutions were determined titrimetrically by measuring the concentration of HCl which was extracted by shaking with a 1 M HCl aqueous solution. All the experiments were performed in a room with the temperature controlled at 25±1°C.

Results and Discussion

It is convenient to present our results in two parts, since two distinctly different extractions were

TABLE 1. EQUILIBRIUM DATA FOR THE EXTRACTION OF HCl BY TOA IN BENZENE AT 25±1°C AND 1M NaCl (AQ.) IONIC MEDIUM

0.0264 M*		0.0529 M*		0.1064 M*		0.2128 M*	
$-\log(H^+)$	Z	$-\log(H^+)$	Z	$-\log(H^+)$	Z	$-\log(H^+)$	Z
4.936	0.110	4.957	0.110	5.000	0.110	5.063	0.110
4.602	0.221	4.648	0.221	4.688	0.220	4.782	0.220
4.379	0.330	4.425	0.331	4.493	0.330	4.601	0.331
4.197	0.440	4.250	0.441	4.325	0.440	4.440	0.441
4.022	0.549	4.079	0.551	4.158	0.550	4.277	0.551
3.843	0.656	3.900	0.660	3.979	0.660	4.098	0.661
3.633	0.760	3.689	0.768	3.767	0.769	3.885	0.771
3.372	0.859	3.415	0.873	3.480	0.876	3.585	0.880
3.028	0.930	2.942	0.955	2.872	0.967	2.830	0.979
2.717	0.967	2.500	0.989	2.226	0.991	1.948	0.998

* Total concentration of TOA in benzene.

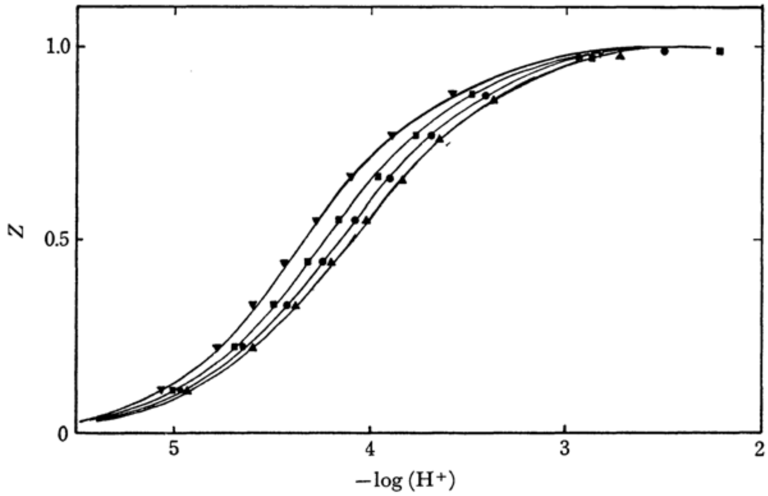

Fig. 1. Z plotted against $-\log(H^+)$ for the extraction of HCl by TOA in benzene from (H, 1 M Na)Cl aqueous solution.
▲ 0.0264 M TOA, ● 0.0529 M TOA, ■ 0.1064 M TOA, ▼ 0.2128 M TOA

observed the two different acidity ranges.

(I) Extraction of HCl the in Low-acidity Range. Since it has been found that the ionic dissociation of amine salts is practically negligible in the low dielectric diluents,[14] a general expression for the extraction of HCl by TOA in benzene can be written by:

$$l\overline{\mathrm{TOA}} + m\mathrm{H}^+ + m\mathrm{Cl}^- = \overline{(\mathrm{TOA})_l(\mathrm{HCl})_m} \qquad (1)$$

where the upperlined species are those in the organic phase.

The application of the law of mass action to Eq. (1) gives Eq. (2) on the assumption of ideal behavior in the organic phase:

$$\overline{[(\mathrm{TOA})_l(\mathrm{HCl})_m]} = K_{lm}[\overline{\mathrm{TOA}}]^l(\mathrm{H}^+)^m(\mathrm{Cl}^-)^m \qquad (2)$$

where brackets denote the concentration, and parentheses, the activity.

Since the ionic strength in the aqueous phase is adjusted with 1 M NaCl, Eq. (2) is replaced by:

$$\overline{[(\mathrm{TOA})_l(\mathrm{HCl})_m]} = K'_{lm}[\overline{\mathrm{TOA}}]^l(\mathrm{H}^+)^m \qquad (3)$$

where:

$$K'_{lm} = K_{lm}(\mathrm{Cl}^-)^m{}_{1\mathrm{M\ NaCl}} \qquad (4)$$

Using Eq. (3), the following equations can be obtained from the material balance:

$$[\overline{\mathrm{TOA}}]_\mathrm{T} = [\overline{\mathrm{TOA}}] + \sum\sum lK'_{lm}[\overline{\mathrm{TOA}}]^l(\mathrm{H}^+)^m \qquad (5)$$

$$[\overline{\mathrm{HCl}}]_\mathrm{T} = \sum\sum mK'_{lm}[\overline{\mathrm{TOA}}]^l(\mathrm{H}^+)^m \qquad (6)$$

where $[\overline{\mathrm{TOA}}]_\mathrm{T}$ is the total concentration of TOA and where $[\overline{\mathrm{HCl}}]_\mathrm{T}$ represents that of HCl in the organic phase. Using Eq. (5) and Eq. (6) we can introduce the average number of HCl combined with TOA, Z:

$$Z = \frac{[\overline{\mathrm{HCl}}]_\mathrm{T}}{[\overline{\mathrm{TOA}}]_\mathrm{T}} = \frac{\sum\sum mK'_{lm}[\overline{\mathrm{TOA}}]^{l-1}(\mathrm{H}^+)^m}{1 + \sum\sum lK'_{lm}[\overline{\mathrm{TOA}}]^{l-1}(\mathrm{H}^+)^m} \qquad (7)$$

The results of Z and $\log(\mathrm{H}^+)$ for TOA concentrations ranging from 1.25% to 10% by volume are given in Table 1. Plots of Z *vs.* $\log(\mathrm{H}^+)$ are shown in Fig. 1. As may be seen by comparing it with Eq. (7), the disagreement between the plots of Z *vs.* $\log(\mathrm{H}^+)$ for different TOA concentrations indicates that the complexes of $l>1$ are formed.

The concentrations of free amine, $[\overline{\mathrm{TOA}}]$, which can not be determined directly, are obtained as follows. Considering the correlation between Eq. (5) and Eq. (6), the following partial differential equation can be obtained:

$$\left(\frac{\partial \ln b}{\partial \ln a}\right)_B = -\left(\frac{\partial A}{\partial B}\right)_a = -\left\{Z + \left(\frac{\partial Z}{\partial \ln B}\right)_a\right\} \qquad (8)$$

where $a=(\mathrm{H}^+)$, $b=[\overline{\mathrm{TOA}}]$, $A=[\overline{\mathrm{HCl}}]_\mathrm{T}$, and $B=[\overline{\mathrm{TOA}}]_\mathrm{T}$.

The integration of Eq. (8) at the B constant gives:

$$\log(b/B) = -\left[\int\left\{Z + \left(\frac{\partial Z}{\partial \ln B}\right)_a\right\}\mathrm{d}\log a\right]_B \qquad (9)$$

The values of b determined from graphical integration in Eq. (9), using the values of a, B, and Z in Table 1, were found to be identical with $(B-A)$ regardless of B, as is shown in Fig. 2. This finding leads to the conclusion that the value of $\sum\sum(l-m)K'_{lm}b^la^m$ is equal to zero, *i.e.*, $l=m$.

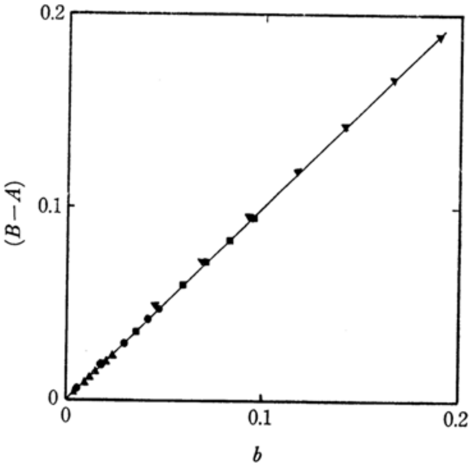

Fig. 2. The comparison between $(B-A)$ and b determined from graphical integration in Eq. (9) using the data in Table 1 where $A=[\overline{\mathrm{HCl}}]_\mathrm{T}$, $B=[\overline{\mathrm{TOA}}]_\mathrm{T}$ and $b=[\overline{\mathrm{TOA}}]$.
▲ 0.0264 M TOA, ● 0.0529 M TOA,
■ 0.1064 M TOA, ▼ 0.2128 M TOA

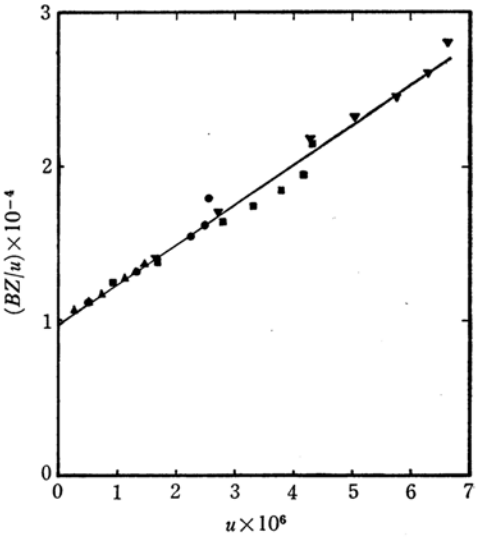

Fig. 3. BZ/u plotted against u for the extraction of HCl by TOA in benzene where $BZ=[\overline{\mathrm{HCl}}]$ and $u=[\overline{\mathrm{TOA}}](\mathrm{H}^+)$.
▲ 0.0264 M TOA, ● 0.0529 M TOA,
■ 0.1064 M TOA, ▼ 0.2128 M TOA

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[14] C. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

Accordingly, Eq. (6) can be rewritten as:

$$A = BZ = \sum lK'_{ll}\, u^l \qquad (10)$$

where $u=ab$ and where $b=(B-A)$. The values of K'_{ll} may be easily determined with the values of BZ and u. The plots of BZ/u vs. u give a straight line, as is shown in Fig. 3. This relationship corresponds to the coexistence of two reactions:

$$\overline{\mathrm{TOA}} + \mathrm{H}^+ + \mathrm{Cl}^- = \overline{\mathrm{TOA\cdot HCl}} \qquad (11)$$

$$2\overline{\mathrm{TOA}} + 2\mathrm{H}^+ + 2\mathrm{Cl}^- = (\overline{\mathrm{TOA\cdot HCl}})_2 \qquad (12)$$

The values of the equilibrium constants of these reactions have been calculated using the computer program LETAGROP[15] on the data presented in Table 1; the values of $K'_{11}=(9.90\pm0.11)\times10^3$ and $K'_{22}=(1.26\pm0.03)\times10^9$ have also been obtained. By substituting these values into Eq. (4), the values of:

$$K_{11} = (1.51 \pm 0.02) \times 10^4$$

$$K_{22} = (2.92 \pm 0.07) \times 10^9$$

were determined, in which the mean activity coefficient of a 1 M NaCl aqueous solution[16] was used as the activity coefficient of the chloride ion.

The value of $K_{11}=(1.51\pm0.02)\times10^4$ is in good agreement with the corresponding equilibrium constants of $(1.4\pm0.4)\times10^4$ and $(1.3\pm0.3)\times10^4$ when these is no ionic medium and a 2 M LiCl

TABLE 2. EQUILIBRIUM DATA FOR THE EXTRACTION OF HCl BY TOA IN BENZENE AT 25±1°C

0.0527 M*			0.1050 M*			0.2014 M*		
[HCl]	(HCl)	$(Z-1)$	[HCl]	(HCl)	$(Z-1)$	[HCl]	(HCl)	$(Z-1)$
0.97 M	0.64	0.000	1.89 M	3.72	0.000	0.72 M	0.24	0.000
1.98	4.24	0.000	2.82	1.45×10	0.000	1.75	2.97	0.000
2.96	1.79×10	0.002	3.29	2.84	0.005	2.75	1.32×10	0.005
3.89	6.36	0.021	3.79	5.63	0.030	3.78	5.55	0.037
4.87	2.15×10^2	0.070	4.27	1.02×10^2	0.054	4.69	1.72×10^2	0.103
5.90	6.96	0.176	4.75	1.85	0.090	5.49	4.47	0.206
6.82	2.06×10^3	0.336	5.61	5.04	0.186	6.31	1.18×10^3	0.339
7.86	6.81	0.518	6.53	1.46×10^3	0.334	6.67	1.71	0.410
8.72	1.65×10^4	0.650	7.53	4.75	0.492	7.30	3.64	0.495
			7.79	6.31	0.543	7.69	5.68	0.552
			8.60	1.47×10^4	0.655	8.25	1.04×10^4	0.629

* Total concentration of TOA in benzene.

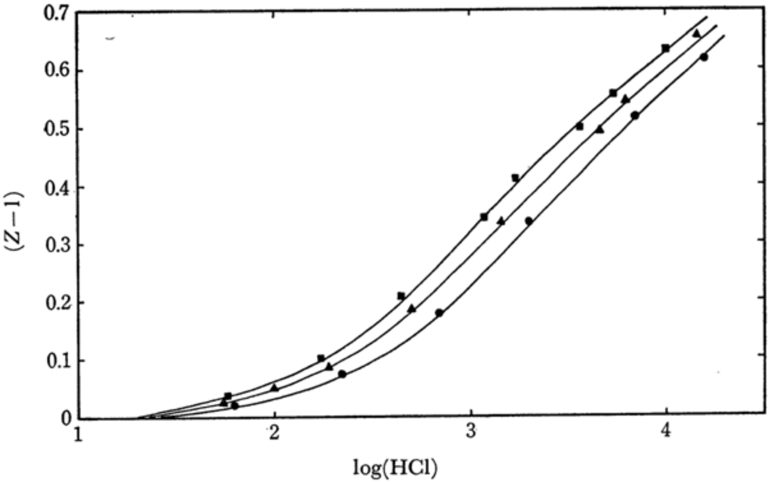

Fig. 4. $(Z-1)$ plotted against log(HCl) for the extraction of HCl by TOA in benzene. ● 0.0527 M TOA, ▲ 0.1050 M TOA, ■ 0.2014 M TOA

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[15] L. G. Sillén and N. Ingri, *Arkiv Kemi*, **23**, 97 (1964).

[16] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions, 2nd ed., Butterworths, London (1959), p. 497.

aqueous solution at 25°C respectively, as reported by Newman and Klotz.[17]

The equilibrium constant, $\bar{\beta}_2$, of the dimer formation expressed by the equation:

$$2\overline{\text{TOA}\cdot\text{HCl}} = \overline{(\text{TOA}\cdot\text{HCl})_2} \qquad (13)$$

was calculated from $\bar{\beta}_2=K_{22}/K^2_{11}$; the value of $\bar{\beta}_2=12.9\pm0.5$ was obtained. This value is in close agreement with that of $\log\bar{\beta}_2=1.1$ (at 25°C) for tri-laurylamine (TLA) chloride in benzene obtained from the measurement of the vapor-pressure lowering by Markovits and Kertes,[18] but it is different from that of $\bar{\beta}_2=53$(at 25°C) for TLA chloride in benzene obtained by Scibona *et al.*,[19] using the same method.

(II) Extraction of HCl in the High-acidity Range. As may be seen in the extraction of HCl in the low acidity range, Z values approch unity at $(\text{H}^+)\simeq0.001$ regardless of the TOA concentration, and the relationship of $Z=1$ seems to be satisfied until 3 M HCl. When the concentration of HCl is, however, above 3 M, the Z values increase with the HCl and TOA concentrations; this means that more acid was extracted into amine than corresponds to the 1 : 1 composition. The results are listed in Table 2. The activities of HCl in Table 2 were calculated using the mean activity coefficient.[20] The plots of $(Z-1)$ *vs.* log(HCl) are shown in Fig. 4.

Since the free amine concentrations at high HCl concentrations are supposed to be negligible in view of the values of $K_{11}=(1.51\pm0.02)\times10^4$ and $K_{22}=(2.92\pm0.07)\times10^9$, the expression for the extraction of HCl can be written as:

$$l\overline{\text{TOA}\cdot\text{HCl}} + n\text{HCl} = \overline{(\text{TOA}\cdot\text{HCl})_l(\text{HCl})_n} \qquad (14)$$

Hence, the following equations can be derived from the material balance:

Table 3. The values of $\overline{[\text{TOA}\cdot\text{HCl}]}$ determined by graphical integration in Eq. (19) using the data in Table 2

(HCl)	0.0527 M*		0.1050 M*		0.2014 M*	
	$(Z-1)$	$\overline{[\text{TOA}\cdot\text{HCl}]}$	$(Z-1)$	$\overline{[\text{TOA}\cdot\text{HCl}]}$	$(Z-1)$	$\overline{[\text{TOA}\cdot\text{HCl}]}$
1.0×10^{2}	0.035	0.0289 M	0.052	0.0455 M	0.070	0.0674 M
2.0	0.067	0.0274	0.095	0.0425	0.120	0.0621
3.0	0.095	0.0260	0.130	0.0400	0.160	0.0575
5.0	0.138	0.0238	0.180	0.0358	0.220	0.0510
7.0	0.173	0.0221	0.223	0.0328	0.268	0.0458
1.0×10^{3}	0.215	0.0201	0.272	0.0291	0.319	0.0404
2.0	0.328	0.0158	0.375	0.0222	0.420	0.0297
3.0	0.390	0.0130	0.435	0.0180	0.475	0.0239
5.0	0.476	0.0101	0.508	0.0137	0.545	0.0179
7.0	0.526	0.0084	0.556	0.0112	0.585	0.0144
1.0×10^{4}	0.575	0.0067	0.605	0.0089	0.628	0.0114

* Total concentration of TOA in benzene

Table 4. Equilibrium constants for the reaction, $l\overline{\text{TOA}\cdot\text{HCl}} + n\text{HCl} = \overline{(\text{TOA}\cdot\text{HCl})_l(\text{HCl})_n}$ ($t=25\pm1$°C)

Reaction	K_{ln}
$2\overline{\text{TOA}\cdot\text{HCl}}+\text{HCl}=\overline{(\text{TOA}\cdot\text{HCl})_2\text{HCl}}$	$K_{21}=1.7\times10^{-2}$
$2\overline{\text{TOA}\cdot\text{HCl}}+2\text{HCl}=\overline{(\text{TOA}\cdot\text{HCl})_2(\text{HCl})_2}$	$K_{22}=4\times10^{-7}$
$3\overline{\text{TOA}\cdot\text{HCl}}+\text{HCl}=\overline{(\text{TOA}\cdot\text{HCl})_3\text{HCl}}$	$K_{31}=1.1\times10^{-1}$
$3\overline{\text{TOA}\cdot\text{HCl}}+2\text{HCl}=\overline{(\text{TOA}\cdot\text{HCl})_3(\text{HCl})_2}$	$K_{32}=2.2\times10^{-4}$
$3\overline{\text{TOA}\cdot\text{HCl}}+3\text{HCl}=\overline{(\text{TOA}\cdot\text{HCl})_3(\text{HCl})_3}$	$K_{33}=5\times10^{-9}$

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17) L. Newman and P. Klotz, *J. Phys. Chem.*, **65**, 769 (1961).

18) G. Markovits and A. S. Kertes, "Solvent Extraction Chemistry," ed. by D. Dyrssen, J. O. Liljenzin and J. Rydberg, North-Holland Publishing Co., Amsterdam (1967), p. 390.

19) G. Scibona, S. Basol, P. R. Danesi and F. Orlandini, *J. Inorg. Nucl. Chem.*, **28**, 1441 (1966).

20) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London (1959), p. 504.

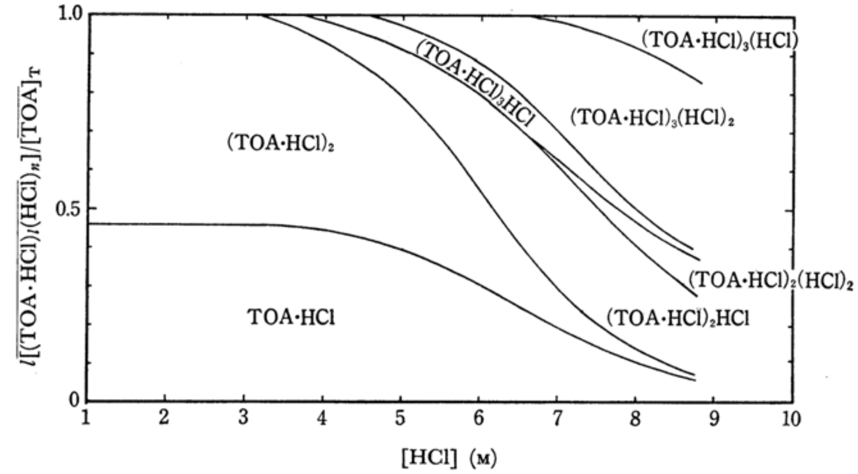

Fig. 5. $l[\overline{(\mathrm{TOA\cdot HCl})_l(\mathrm{HCl})_n}]/\overline{[\mathrm{TOA}]}_\mathrm{T}$ plotted against [HCl] at $\overline{[\mathrm{TOA}]}_\mathrm{T}=$ 0.1 M. The curves were determined from the material balance using $\bar{\beta}_2=$ 12.9 and the values of $\boldsymbol{K}_{ln}$ in Table 4.

$$\overline{[\mathrm{TOA}]}_\mathrm{T} = \overline{[\mathrm{TOA\cdot HCl}]} + 2\bar{\beta}_2\overline{[\mathrm{TOA\cdot HCl}]}^2 + \sum\sum l\boldsymbol{K}_{ln}\overline{[\mathrm{TOA\cdot HCl}]}^l(\mathrm{HCl})^n \tag{15}$$

$$\overline{[\mathrm{HCl}]}_\mathrm{T} - \overline{[\mathrm{TOA}]}_\mathrm{T} = (\mathrm{Z}-1)\overline{[\mathrm{TOA}]}_\mathrm{T} = \sum\sum n\boldsymbol{K}_{ln}\overline{[\mathrm{TOA\cdot HCl}]}^l(\mathrm{HCl})^n \tag{16}$$

where $\boldsymbol{K}_{ln}$ is the equilibrium constant of Eq. (14) given by:

$$\boldsymbol{K}_{ln} = \frac{[\overline{(\mathrm{TOA\cdot HCl})_l(\mathrm{HCl})_n}]}{\overline{[\mathrm{TOA\cdot HCl}]}^l(\mathrm{HCl})^n} \tag{17}$$

The values of $\overline{[\mathrm{TOA{\cdot}HCl}]}$, which can not be measured directly, are determined as follows. From Eq. (15) and Eq. (16),

$$\left(\frac{\partial \ln b}{\partial \ln a}\right)_B = -\left\{(Z-1) + \left(\frac{\partial(Z-1)}{\partial \ln B}\right)_a\right\} \tag{18}$$

where $a=(\mathrm{HCl})$, $b=\overline{[\mathrm{TOA{\cdot}HCl}]}$, and $B=\overline{[\mathrm{TOA}]}_\mathrm{T}$.

By integration at the B constant, Eq. (18) becomes:

$$\log(b/b_0) = -\left[\int_{a=a_0}^{a}\left\{(Z-1) + \left(\frac{\partial(Z-1)}{\partial \ln B}\right)_a\right\}\mathrm{d}\log a\right]_B \tag{19}$$

where a_0 is the value of a at $Z=1$ and b_0, the value of b at $a=a_0$, which is given by:

$$b_0 = \frac{-1+\sqrt{1+8\bar{\beta}_2B}}{4\bar{\beta}_2}$$

The values of $b(a,Z-1)_B$ are shown in Table 3; they were determined by graphical integration in Eq. (19) using the data in Table 2. In order to evaluate the values of $\boldsymbol{K}_{ln}$, it is convenient to introduce a new parameter:

$$\boldsymbol{K}'_l = \sum_{n=1}\boldsymbol{K}_{ln}a^n \tag{20}$$

The substitution of Eq. (20) into Eq. (16) yields:

$$A_a = \sum_{l=1} l\boldsymbol{K}'_l b^l \tag{21}$$

where A_a represents the values of $(Z-1)B$ at the a constant.

The method of least squares was used to evaluate the values of $\boldsymbol{K}_{ln}$ fitted to the data in Table 3. Although several combinations of l and n have been tried, the data can be best fitted in with the presence of five species of (TOA·HCl)$_2$HCl, (TOA·HCl)$_2$(HCl)$_2$, (TOA·HCl)$_3$HCl, (TOA·HCl)$_3$(HCl)$_2$, and (TOA·HCl)$_3$(HCl)$_3$. The equilibrium constants for Eq. (14) are given in Table 4. The curves shown in Fig. 3 were determined from the material balance using the values of $\boldsymbol{K}_{ln}$ in Table 4.

As may be seen in Fig. 3, the calculated values of $(Z-1)$ are in good agreement with the experimental values. When the total concentration of TOA and the concentration of HCl in the aqueous phase are given, it should be possible to calculate the concentration of each complex in the organic phase. As an example of the calculation, a graph of $l[\overline{(\mathrm{TOA\cdot HCl})_l(\mathrm{HCl})_n}]/\overline{[\mathrm{TOA}]}_\mathrm{T}$ against [HCl] at $\overline{[\mathrm{TOA}]}_\mathrm{T}=0.1$ M is mapped in Fig. 5. From Fig. 5 it may be seen that, besides the monomer and the dimer, the two species of (TOA·HCl)$_2$HCl and (TOA·HCl)$_3$(HCl)$_2$ are the major complexes, while the other three species of (TOA·HCl)$_2$(HCl)$_2$, (TOA·HCl)$_3$HCl and (TOA·HCl)$_3$(HCl)$_3$ are the minor complexes.

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