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Extraction Equilibria of Hydrochloric Acid by Trioctylamine in Low-Polar Organic Solvents

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Two-phase emf titrations have been performed for the extraction of hydrochloric acid from aqueous solution containing 1 M NaCl (M=mol dm^{-3}) by trioctylamine (TOA) dissolved in cyclohexane, toluene, benzene, chlorobenzene, nitrobenzene, cyclohexane-benzene mixtures, and benzene-nitrobenzene mixtures. It has been found that the extraction is accompanied with the formation of monomeric trioctylammonium chloride and its successive aggregation from dimer to micell (n-mer) in organic phase: $\overline{\mathrm{TOA}}+\mathrm{H}^++\mathrm{Cl}^-=\overline{\mathrm{TOAHCl}}$, K_d; $(\overline{\mathrm{TOAHCl}})_{i-1}+\overline{\mathrm{TOAHCl}}=(\overline{\mathrm{TOAHCl}})_i$, $\overline{K}_i(i=2,3,\cdots,n)$, where the concentration quotients of successive aggregation, $\overline{K}_i$, satisfy the relation $2\,\overline{K}_2=3\,\overline{K}_3/2=\cdots=n\,\overline{K}_n/(n-1)$. The quotients K_d and $\overline{K}_2$ vary with the total volume fraction of TOA in organic phase, $\overline{\psi}^\circ_\mathrm{R}$, according to equations, $\ln K_\mathrm{d}=\ln K^\circ_\mathrm{d}+g\,\overline{\psi}^\circ_\mathrm{R}$ and $\ln \overline{K}_2=\ln \overline{K}^\circ_2+h\,\overline{\psi}^\circ_\mathrm{R}$. Diluent effect on the equilibrium constants K°_d and $\overline{K}^\circ_2$ are discussed in detail based on the theory of regular solution.

Long-chain tertiary amines have been well-known as useful extractants of metal ions in acidic aqueous solutions, but detailed extraction mechanisms are not completely elucidated. It has been frequently assumed that the extraction of acid by the amines in water-insoluble organic solvents is accompanied with the formation of salts which exist as an ion pair in organic phase

$$\overline{\mathrm{R_3N}} + \mathrm{H^+} + \mathrm{X^-} = \overline{\mathrm{R_3NH^+X^-}}, \qquad (1)$$

and that the extraction of metal ions is substantially the anion exchange in the salts as follows:

$$\mathrm{M}^{n+} + m\mathrm{X}^- = \mathrm{MX}_m^{(m-n)-}, \qquad (2)$$

$$(m-n)\overline{\mathrm{R_3NH^+X^-}} + \mathrm{MX}^{(m-n)-} = \overline{(\mathrm{R_3NH^+})_{m-n}\mathrm{MX}^{(m-n)-}} + (m-n)\mathrm{X}^-, \qquad (3)$$

where a superscript bar on symbols denotes the organic phase. However, several investigations on the extraction equilibrium of acids,[3–12] light scattering,[13] freezing point lowering[14] and vapor pressure lowering[15–19] of organic solutions of long-chain alkylammonium salts have shown that the salts have a strong tendency for electrostatic molecular aggregation into dimer, trimer and higher aggregates in nonpolar organic solvents. Therefore, in order to elucidate the extraction mechanism of metal ions, it is necessary to obtain detailed information on the aggregation equilibrium of the salts in organic solvents.

The most reliable information was given by Högfeldt et al.[3–8] who determined precisely the quantitative relationship between the total concentration of acids extracted by tridodecylamine in organic phase and the hydrogen ion concentration in aqueous phase with a constant ionic strength by using the two-phase emf titration method. They analyzed the extraction data by considering all the possible reactions represented by

$$p\overline{\mathrm{R_3N}} + q\mathrm{H^+} + q\mathrm{X^-} = \overline{(\mathrm{R_3N})_p(\mathrm{HX})_q}, \qquad (4)$$
$$(p,q = 1,2,\cdots)$$

and by assuming the ideal behavior of each species in organic phase, and concluded the presence of aggregates $(\mathrm{R_3NHX})_p$. The data were best described by assuming the formation of such low aggregates as dimer and trimer, and a high aggregate containing as many as 10—90 monomers, where the aggregation number depends on the nature of amine salts and diluents. For example, tridodecylammonium nitrate forms dimer, trimer and decamer in *o*-xylene,[3] while tridodecylammonium perchlorate forms dimer, octamer and 90-mer in *o*-xylene.[8]

Kertes and Markovits[17] studied the aggregation of tridodecylammonium chloride, bromide, nitrate, perchlorate and hydrogensulfate in benzene, carbon tetrachloride and cyclohexane by vapor-pressure lowering, and showed that the salts formed dimer and two higher aggregates, which depend on the kinds of salts and organic solvents, and that the aggregation constants of the dimer in benzene increased in the order, chloride<bromide<nitrate<perchlorate<hydrogensulfate. The values of dimerization constant of the bromide and nitrate in benzene were found to be in fairly good agreement with those in *o*-xylene, which were obtained by the two-phase emf titration method. This agreement implies that coextracted water does not play a decisive part in determining the extent of aggregation.

Diamond and co-workers[10–12] obtained the following conclusion from the investigation of extraction equilibrium of perchloric acid and hydrohalogenic acids with tridodecylamine. Both the dielectric constant and chemical property of diluents greatly affect the extent of extraction of acids and the degree of aggregation of the resulting salts. In general, the higher the dielectric constant and the stronger the chemical interaction of diluents with one or both of the ions of the salt, the better the extraction and the smaller the degree of aggregation. By examining Diamond's data[12] for the equilibrium constants (K_1) in the extraction of $\mathrm{HReO_4}$ by tridodecylamine in various diluents, Freiser[20] found that there was little correlation between log K_1 and the dielectric constant of organic solvents, but a good linear relation existed between log K_1 and the solubility parameter of organic solvents. He pointed out that the postulation of specific chemical interaction between diluents and the salts might be superfluous and that the diluent effect on the equilibrium constants might be better explained on the theory of regular solution.

Kertes[21)] showed that the values of solubility parameter of long-chain primary, secondary and tertiary alkylamines calculated from their solubilities in nonpolar organic solvents, based on the regular solution theory, agreed fairly well with those determined from their heats of vaporization. This agreement was taken as reasonable evidence of the validity of the theory for such binary solutions. Further, he[22)] evaluated the values of solubility parameter of primary, secondary and tertiary amine hydrochlorides from their solubilities in low-polar organic solvents, and showed that the solubility parameters decreased markedly from the primary to the tertiary amine salts, and that the values of activity coefficient of these salts in the organic solvents, which were calculated by using the values of solubility parameters, increased sharply in the order of the tertiary to the primary amine salts at a given concentration. The difference in the concentration dependence of the activity coefficients was explained in terms of electrostatic molecular association of these salts. However, this explanation can not be accepted, because it was implicitly assumed in the evaluation of the solubility parameters that these salts are still monomeric in saturated solutions. Nevertheless, the calculated results shown in this investigation seem to indicate that the regular solution theory is also valid for these salt solutions, but the evaluated solubility parameters are the apparent solubility parameters, which are given by a function of the solubility parameters and concentrations of the monomeric salt and its aggregates in saturated solution.

In the present investigation, the extraction equilibria of hydrochloric acid from an aqueous solution containing 1 M NaCl by TOA in cyclohexane, toluene, benzene, chlorobenzene, and nitrobenzene were measured by using the two-phase emf titration method. The experimental results are analyzed by considering the aggregation equilibria from dimer to micelle in organic phase. The analyzed results are discussed in detail based on the regular solution theory.

Experimental

Reagents. Trioctylamine (Tokyo Chemical Industry Co., Ltd.) was distilled three times under reduced pressure, and the fraction in the range of 190—192 °C at 4×10^2 Pa was used. The other chemicals were of analytical grade and used without further purification. Laboratory distilled water was used.

Solutions. Stock solutions containing 8% (v/v) TOA were prepared by weighing appropriate amounts of TOA and diluting with cyclohexane, toluene, benzene, chlorobenzene, and nitrobenzene in measuring flasks at 25±1 °C. Less concentrated TOA solutions were prepared by dilution of the stock solutions. An aqueous solution containing 0.1 M HCl and 1.00 M NaCl was used as a titrant.

Procedure and Analysis. The extraction equilibria of HCl by TOA solutions were measured by the two-phase emf titration method[3)] with a Corning digital 112 pH meter and a glass electrode GS-135 (Toa Electronics Co., Ltd.). An appropriate amount of 1.00 M NaCl aqueous solution (usually 50 cm^3) was pippetted into a titration vessel kept in a thermostat at 25±0.1 °C, and carbon dioxide dissolved in the solution was removed by stirring with a magnetic stirrer under an atmosphere of nitrogen introduced through 1.0 M NaCl solution. After the reading of the pH meter settled, a suitable amount of TOA solutions (10—40 cm^3) was pippetted and then appropriate amounts of 0.1 M HCl titrant were added through a buret. The extraction equilibria were reached by rapid stirring (500 rpm) of the organic and aqueous solutions. The equilibration time was 1—2 h for the first point and a few minutes for the last point. The hydrogen ion concentrations in the aqueous phase, [H$^+$], were evaluated from the electrode potential E measured by the pH meter according to the equation

$$E = E_0 + j[\mathrm{H^+}] + 59.16\log[\mathrm{H^+}], \tag{5}$$

where E_0 and j are constants. The values of E_0 and j were determined from the titration in the absence of organic solution. The total concentration of HCl extracted into organic phase, $[\overline{\mathrm{HCl}}]_T$, was calculated by

$$[\overline{\mathrm{HCl}}]_T = C(V/\overline{V}) - h(v+V)/\overline{V}, \tag{6}$$

where C and h are the concentrations of HCl and H$^+$ in the titrant and aqueous phase, respectively, and v, V, and $\overline{V}$ denote the volumes of the titrant, 1.00 M NaCl aqueous solution, and TOA organic solutions, respectively. The concentrations of TOA in organic solutions were determined by measuring the concentrations of HCl in organic solutions at the extraction equilibrium with 1.0 M HCl aqueous solution. The measurement was carried out by back-titration with a standard base.

Results

Since it has been found that the ionic dissociation of trialkylammonium salts is practically negligible in low dielectric organic solvents,[3,11)] the extraction mechanism of HCl by TOA in low-polar organic solvents can be written by

$$\overline{\mathrm{TOA}} + \mathrm{H^+} + \mathrm{Cl^-} = \overline{\mathrm{TOAHCl}}, \tag{7}$$

$$i\,\overline{\mathrm{TOAHCl}} = \overline{(\mathrm{TOAHCl})_i}, \tag{8}$$

$$(i = 2, 3, \cdots)$$

where TOAHCl represents TOAH$^+$Cl$^-$. The equilibrium constants of Eqs. 7 and 8 are given by

$$^{\circ}K_\mathrm{d} = \frac{[\overline{\mathrm{RHCl}}]}{[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}]}\cdot\frac{\overline{y}_1}{\overline{y}_\mathrm{R}\,y_\mathrm{H^+}y_\mathrm{Cl}}, \tag{7'}$$

$$\overline{\beta}_i^{\circ} = \frac{[\overline{(\mathrm{RHCl})_i}]}{[\overline{\mathrm{RHCl}}]^i}\cdot\frac{\overline{y}_i}{\overline{y}_1{}^i}, \tag{8'}$$

where R denotes TOA, a bracket the molarity, and y the molar activity coefficient. $\bar{y}_1$ and $\bar{y}_i$ represent the molar activity coefficients of RHCl and $(\mathrm{RHCl})_i$ in organic phase, respectively. Since the ionic strength in aqueous phase is kept constant (1.00 M NaCl) in this study, it is convenient to introduce another equilibrium constant defined by

$$K_\mathrm{d}^\circ = {}^\circ K_\mathrm{d}(y_{\mathrm{H}^+}y_{\mathrm{Cl}^-}) = \frac{[\overline{\mathrm{RHCl}}]}{[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]}\cdot\frac{\bar{y}_1}{\bar{y}_\mathrm{R}}. \qquad (7'')$$

On the other hand, $[\overline{\mathrm{R}}]_T$ and $[\overline{\mathrm{HCl}}]_T$, the total concentrations of TOA and HCl in organic phase, respectively are given by

$$[\overline{\mathrm{R}}]_T = [\overline{\mathrm{R}}] + \sum_{i=1} i[\overline{(\mathrm{RHCl})_i}], \qquad (9)$$

$$[\overline{\mathrm{HCl}}]_T = \sum_{i=1} i[\overline{(\mathrm{RHCl})_i}], \qquad (10)$$

where the values of free TOA concentration in organic phase, $[\overline{\mathrm{R}}]$, can be easily evaluated from those of $[\overline{\mathrm{R}}]_T$ and $[\overline{\mathrm{HCl}}]_T$. From Eqs. 9, 10, 7″, and 8′, the average number of HCl combined with TOA, Z, is given by

$$\mathrm{Z} = \frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}]_T} = \frac{K_\mathrm{d}[\mathrm{H}^+][\mathrm{Cl}^-] + \sum_{i=2} i\bar{\beta}_i K_\mathrm{d}^i[\overline{\mathrm{R}}]^{i-1}[\mathrm{H}^+]^i[\mathrm{Cl}^-]^i}{1 + K_\mathrm{d}[\mathrm{H}^+][\mathrm{Cl}^-] + + \sum_{i=1}\sum_{i=2} i\bar{\beta}_i K_\mathrm{d}^i[\overline{\mathrm{R}}]^{i-1}[\mathrm{H}^+]^i[\mathrm{Cl}^-]^i}, \qquad (11)$$

where K_d and $\bar{\beta}_i$ are the equilibrium concentration quotients defined by

$$K_\mathrm{d} = K_\mathrm{d}^\circ(\bar{y}_\mathrm{R}/\bar{y}_1) = [\overline{\mathrm{RHCl}}]/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-], \qquad (12)$$

$$\bar{\beta}_i = \bar{\beta}_i^\circ(\bar{y}_1^i/\bar{y}_i) = [\overline{(\mathrm{RHCl})_i}]/[\overline{\mathrm{RHCl}}]^i. \qquad (13)$$

Figure 1 shows the plots of Z vs. $\log[\mathrm{H}^+][\mathrm{Cl}^-]$ in the extraction with toluene as a diluent. The plots give sigmoidal curves depending on $[\overline{\mathrm{R}}]_T$. Plots similar to the plots in Fig. 1 were obtained with respect to cyclohexane, benzene, and chlorobenzene, while the plots with nitrobenzene gave a curve which is nearly independent of $[\overline{\mathrm{R}}]_T$. These facts suggest that trioctylammonium chloride is practically monomeric in nitrobenzene, but aggregates in the other solvents. In order to obtain further detailed information on the aggregation equilibria, it is convenient to analyze the experimental data by using Eq. 14 derived from Eqs. 10, 12, and 13.

$$\frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]} = K_\mathrm{d} + \sum_{i=2} i\bar{\beta}_i K_\mathrm{d}^i\{[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]\}^{i-1}. \qquad (14)$$

As is seen in Fig. 2, the plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ give the curves whose intercepts and curvatures depend on $[\overline{\mathrm{R}}]_T$. This indicates that the values of K_d and $\bar{\beta}_i$ (i=2,3,$\cdots$,n) change with $[\overline{\mathrm{R}}]_T$, i.e. the ratios of actitvity coefficient, $\bar{y}_\mathrm{R}/\bar{y}_1$ and $\bar{y}_1^i/\bar{y}_i$, depend on $[\overline{\mathrm{R}}]_T$. We tried to determine the values of K_d and $\bar{\beta}_i$ at constant $[\overline{\mathrm{R}}]_T$ by the least-squares method,

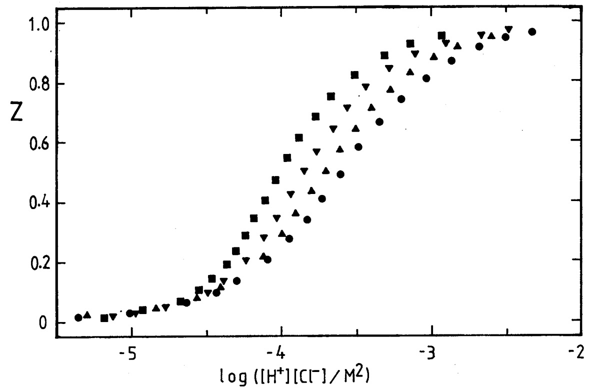

Fig. 1. Plots of Z vs. $\log[\mathrm{H}^+][\mathrm{Cl}^-]$ in the extraction of HCl by TOA in toluene. ●: 0.0231 M TOA, ▲: 0.0462 M TOA, ▼: 0.0923 M TOA, ■: 0.1843 M TOA.

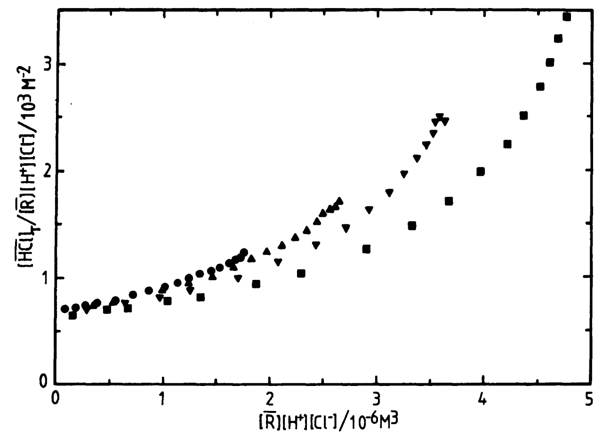

Fig. 2. Plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ in the extraction of HCl by TOA in benzene. ●: 0.0230 M TOA, ▲: 0.0461 M TOA, ▼: 0.0922 M TOA, ■: 0.1843 M TOA.

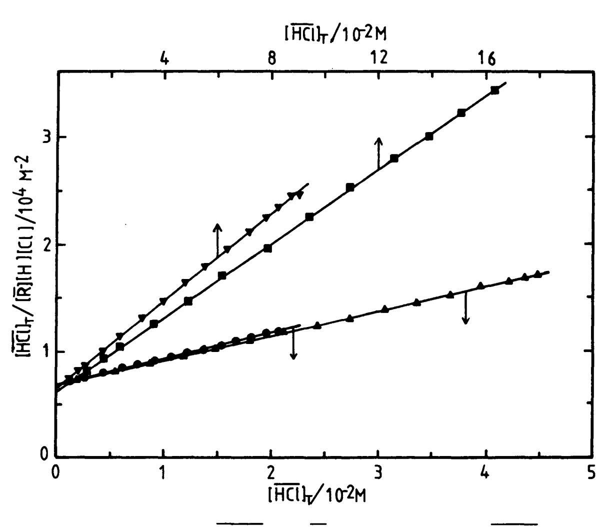

Fig. 3. Plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{HCl}}]_T$ in the extraction of HCl by TOA in benzene. ●: 0.0230 M TOA, ▲: 0.0461 M TOA, ▼: 0.0922 M TOA, ■: 0.1843 M TOA.

Table 1. Values of Intercept A and Slope B in the Plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{HCl}}]_T$

Diluent (S)	δ_S[a)] $\mathrm{cal_{th}}^{1/2}\,\mathrm{cm}^{-3/2}$	$[\overline{\mathrm{R}}]_T$ M $(100\,\bar{\psi}_R^\circ)$	A M^{-2}	B M^{-3}	B/2A M^{-1}
Cyclohexane	8.20	0.0231 (1.0)	$(2.01\pm0.12)\times10$	$(7.43\pm0.14)\times10^3$	185±15
		0.0462 (2.0)	$(2.37\pm0.12)\times10$	$(6.90\pm0.05)\times10^3$	146± 9
		0.0924 (4.0)	$(2.83\pm0.24)\times10$	$(7.27\pm0.06)\times10^3$	128±12
Toluene	8.91	0.0231 (1.0)	$(2.67\pm0.02)\times10^3$	$(1.06\pm0.01)\times10^5$	19.8±0.3
		0.0462 (2.0)	$(2.68\pm0.02)\times10^3$	$(1.03\pm0.01)\times10^5$	19.2±0.3
		0.0923 (4.0)	$(2.64\pm0.05)\times10^3$	$(9.53\pm0.09)\times10^4$	18.0±0.5
		0.1846 (8.0)	$(2.63\pm0.04)\times10^3$	$(8.23\pm0.03)\times10^4$	15.6±0.3
Benzene	9.16	0.0230 (1.0)	$(6.84\pm0.03)\times10^3$	$(2.45\pm0.03)\times10^5$	17.9±0.3
		0.0461 (2.0)	$(6.74\pm0.05)\times10^3$	$(2.29\pm0.02)\times10^5$	17.0±0.3
		0.0922 (4.0)	$(6.55\pm0.15)\times10^3$	$(2.04\pm0.03)\times10^5$	15.6±0.6
		0.1860 (8.0)	$(6.28\pm0.06)\times10^3$	$(1.71\pm0.01)\times10^5$	13.6±0.2
Chlorobenzene	9.68	0.0233 (1.0)	$(4.75\pm0.02)\times10^4$	$(4.58\pm0.18)\times10^5$	4.82±0.21
		0.0465 (2.0)	$(4.43\pm0.04)\times10^4$	$(4.30\pm0.18)\times10^5$	4.85±0.25
		0.0930 (4.0)	$(4.17\pm0.03)\times10^4$	$(4.08\pm0.05)\times10^5$	4.89±0.10
		0.1860 (8.0)	$(3.65\pm0.04)\times10^4$	$(3.58\pm0.04)\times10^5$	4.90±0.11
Nitrobenzene	10.78	0.0230 (1.0)	$(2.71\pm0.01)\times10^6$	$(6.95\pm0.16)\times10^6$	1.28±0.04
		0.0460 (2.0)	$(2.59\pm0.02)\times10^6$	$(7.11\pm0.20)\times10^6$	1.37±0.05
		0.0919 (4.0)	$(2.39\pm0.03)\times10^6$	$(6.66\pm0.20)\times10^6$	1.39±0.06
		0.1838 (8.0)	$(1.91\pm0.02)\times10^6$	$(6.90\pm0.12)\times10^6$	1.81±0.05

a) The values were determined from the values of heat of vaporization and density listed in Ref. 24. $1\,\mathrm{cal_{th}}=4.184\,\mathrm{J}$.

Table 2. Values of Intercept A and Slope B in the Plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{HCl}}]_T$[a)]

Diluent	Volume% of benzene	A M^{-2}	B M^{-3}	B/2A M^{-1}
Cyclohexane-benzene mixtures	0	$(2.01\pm0.12)\times10$	$(7.43\pm0.14)\times10^3$	185±15
	12.5	$(5.61\pm0.13)\times10$	$(1.35\pm0.01)\times104$	120± 4
	24.0	$(1.37\pm0.02)\times10^2$	$(2.13\pm0.02)\times10^4$	77.4±1.9
	49.0	$(5.75\pm0.06)\times10^2$	$(5.22\pm0.06)\times10^4$	45.4±1.0
	74.0	$(2.02\pm0.03)\times10^3$	$(1.17\pm0.02)\times10^5$	29.0±0.9
	99.0	$(6.84\pm0.03)\times10^3$	$(2.45\pm0.03)\times10^5$	17.9±0.3
Benzene-nitrobenzene mixtures	99.0	$(6.84\pm0.03)\times10^3$	$(2.45\pm0.03)\times10^5$	17.9±0.3
	87.5	$(4.00\pm0.05)\times10^4$	$(4.19\pm0.33)\times10^5$	5.24±0.96
	75.0	$(1.21\pm0.01)\times10^5$	$(7.31\pm0.33)\times10^5$	3.02±0.16
	50.0	$(4.85\pm0.04)\times10^5$	$(1.71\pm0.27)\times10^6$	1.76±0.29
	25.0	$(1.26\pm0.01)\times10^6$	$(4.14\pm0.54)\times10^6$	1.64±0.23
	0	$(2.71\pm0.01)\times10^6$	$(6.95\pm0.47)\times10^6$	1.28±0.09

a) $[\overline{\mathrm{R}}]_T=0.0230\,\mathrm{M}$ $(\bar{\psi}_R^\circ=0.01)$.

varying n from 2 to 5 in Eq. 14. The calculation yielded fairly good results at $n=3$ for the extraction equilibria with the following solutions: 1, 2, 4, and 8% (v/v) TOA-nitrobenzene, 1, 2, 4, and 8% (v/v) TOA-chlorobenzene, 1 and 2% (v/v) TOA-benzene, 1 and 2% (v/v) TOA-toluene, and 1% (v/v) TOA-benzene-nitrobenzene. On the other hand, the calculation for the extraction equilibria with 4 and 8% (v/v) TOA-benzene, 4 and 8% (v/v) TOA-toluene, 1, 2, and 4% (v/v) TOA-cyclohexane and 1% (v/v) TOA-cyclohexane-benzene showed that the calculated values of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ at $n=5$ had still a systematic error for the experimental values. These results suggest that the existence of high aggregates of aggregation number>5 can not be neglected in these extraction equilibria or the values of $\bar{y}_R/\bar{y}_1$ and $\bar{y}_1^{i}/\bar{y}_i$ change with varying $[\overline{\mathrm{HCl}}]_T$.

As is seen in Fig. 3, the plots of $[\overline{\mathrm{HCl}}]_T/[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]$ vs. $[\overline{\mathrm{HCl}}]_T$ give good straight lines in all the extraction equilibria studied. This indicates that a quantitative relationship in the extraction equilibria can be represented by

$$\frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}][\mathrm{H}^+][\mathrm{Cl}^-]} = A + B[\overline{\mathrm{HCl}}]_T, \tag{15}$$

where A and B are constants which are independent of $[\overline{\mathrm{HCl}}]_T$ at constant $[\overline{\mathrm{R}}]_T$. The values of A and B calculated by the least-squares method are given in Tables 1 and 2.

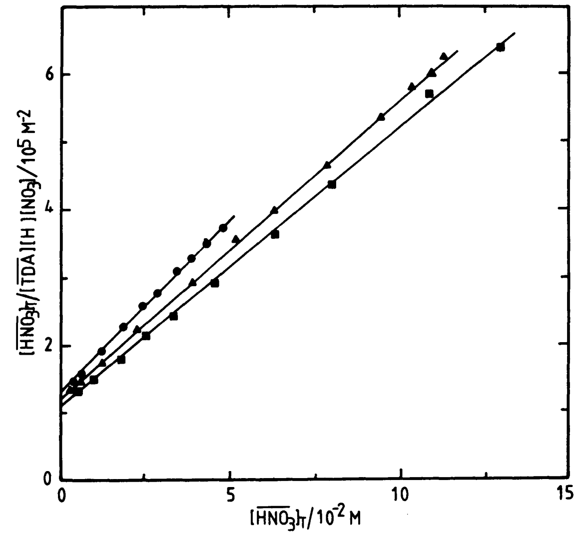

Fig. 4. Plots of $[\overline{\mathrm{HNO_3}}]_T/[\overline{\mathrm{TDA}}][\mathrm{H^+}][\mathrm{NO_3^-}]$ vs. $[\overline{\mathrm{HNO_3}}]_T$ in the extraction of HNO_3 by TDA in toluene from HNO_3+2.75 M $LiNO_3$ solution (data from Ref. 7). ●: 0.0502 M TDA, ▲: 0.1210 M TDA, ■: 0.2460 M TDA.

Discussion

Equation 15 or a similar equation has not been presented in the literature so far and Eq. 15 can not be derived unconditionally from Eq. 14. Accordingly, we examined whether Eq. 15 is compatible with the experimental results on the extraction of acids by tridodecylamine (TDA) reported by Högfeldt and coworkers.[7,8] Figure 4 shows that Eq. 15 is also applicable to these experimental results. Hence, we sought the conditions to derive Eq. 15 from Eq. 14. Equation 14 can be rewritten as follows:

$$\frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}]} = K_\mathrm{d} + \sum_{i=2} i\Big(\prod_{j=2}^{i}\overline{K}_j\Big)K_\mathrm{d}^i\{[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}]\}^{i-1}, \tag{16}$$

$$\overline{K}_j = \overline{\beta}_i/\overline{\beta}_{i-1} = \overline{K}_j^\circ(\bar{y}_{j-1}\bar{y}_1/\bar{y}_j), \tag{17}$$

where $\overline{K}_j$ and $\overline{K}_j^\circ$ are the equilibrium concentration quotient and equilibrium constant, respectively, in the successive aggregation expressed by

$$\overline{(\mathrm{TOAHCl})}_{j-1} + \overline{\mathrm{TOAHCl}} = \overline{(\mathrm{TOAHCl})}_j. \tag{18}$$

In the case where the following condition is satisfied,

$$2\overline{K}_2 = \frac{3}{2}\overline{K}_3 = \cdots\cdots = \frac{n}{n-1}\overline{K}_n, \tag{19}$$

Eq. 16 can be transformed to

$$\frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}]} = K_\mathrm{d}\{1 + \sum_{i=2}^{n}(2\overline{K}_2K_\mathrm{d}[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}])^{i-1}\}. \tag{20}$$

When n is a large number, i.e. there is a series of aggregates from dimer to micell (n-mer), the following condition

$$2\overline{K}_2K_\mathrm{d}[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}] < 1, \tag{21}$$

leads to Eq. 22.

$$\frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{R}}][\mathrm{H^+}][\mathrm{Cl^-}]} = K_\mathrm{d} + 2\overline{K}_2K_\mathrm{d}[\overline{\mathrm{HCl}}]_T, \tag{22}$$

A comparison of Eqs. 15 and 22 yields K_d=A and $2\overline{K}_2K_\mathrm{d}$=B. Although there is still a question about the validity of an assumption of Eq. 19, we will advance a detailed discussion on K_d and $\overline{K}_2$ determined by Eq. 22, and the physical meaning of Eq. 19 will be mentioned later.

As is seen in Table 1, the values of K_d (=A) and $\overline{K}_2$ (=B/2A) are well correlated with those of total volume fraction of TOA ($\overline{\psi}_\mathrm{R}^\circ$) and solubility parameter of diluents (δ_S). This result suggests that the change of K_d and $\overline{K}_2$ with varying $\overline{\psi}_\mathrm{R}^\circ$ and diluents may be explained on the basis of the regular solution theory. According to the theory, the activity of components j, $\dot{a}_j$, in which a pure liquid is chosen as the reference state, in the solution constituted of m components is given by[23]

$$\ln \dot{a}_j = \frac{v_j}{RT}\{\sum_{i=1}^{m}(\delta_j - \delta_i)\psi_i\}^2 + \ln\psi_j + \sum_{i=1}^{m}\Big(1 - \frac{v_j}{v_i}\Big)\psi_i, \tag{23}$$

where δ_i, v_i, and ψ_i are the solubility parameter, molar volume and volume fraction of component i, respectively. When a total solute concentration is not so high, a molar activity coefficient of solute j, $\dot{y}_j$ (=$\dot{a}_j/c_j$: c_j, molar concentration), may be evaluated approximately by the following equation,

$$\ln \dot{y}_j = \frac{v_j}{RT}(\delta_j - \delta_\mathrm{S})^2(1 - 2\psi_\mathrm{sol}^\circ) + \ln\frac{v_j}{1000} + \Big(1 - \frac{v_j}{v_\mathrm{S}}\Big)(1 - \psi_\mathrm{sol}^\circ), \tag{24}$$

where ψ°_sol is the total solute volume fraction, and δ_S and v_S are the solubility parameter and molar volume of solvents S, respectively. Since the molar activity coefficient of solute j, y_j, in which the infinitely dilute solution is chosen as the reference state, is given by

$$y_j = \dot{y}_j/\dot{y}_j(\psi_\mathrm{sol}^\circ \rightarrow 0, \psi_\mathrm{S} \rightarrow 1), \tag{25}$$

the following equation can be obtained by subtitution of Eq. 24 into Eq. 25.

$$\ln y_j = -\{2v_j(\delta_j - \delta_\mathrm{S})^2/RT + (1 - v_j/v_\mathrm{S})\}\psi_\mathrm{sol}^\circ, \tag{26}$$

Application of Eq. 26 to $\bar{y}_\mathrm{R}$ and $\bar{y}_1$ in Eq. 12 leads to

$$\ln K_\mathrm{d} = \ln K_\mathrm{d}^\circ + g\overline{\psi}_\mathrm{R}^\circ, \tag{27}$$

$$g = (2/RT)\{v_1(\delta_1 - \delta_\mathrm{S})^2 - v_\mathrm{R}(\delta_\mathrm{R} - \delta_\mathrm{S})^2\} + (v_\mathrm{R} - v_1)/v_\mathrm{S}, \tag{28}$$

where $\overline{\psi}_\mathrm{R}^\circ$ is the total volume fraction of TOA in organic phase, and δ_1 and v_1 denote the solubility parameter and molar volume of TOAHCl, respectively. As is seen from Fig. 5, the plots of ln K_d vs. $\overline{\psi}_\mathrm{R}^\circ$, where the values of A (=K_d) in Table 1 were used, give good straight lines as expected from Eq. 27. The values of ln K_d° and g calculated by the least-squares method are shown in Table 3. The values of g decrease with increasing the solubility parameter of diluents, and satisfy the relation $\partial g/\partial\delta_\mathrm{S} < 0$ which is derived from Eq. 28 by considering that δ_R=7.6 $\mathrm{cal_{th}^{1/2}}$ $\mathrm{cm^{-3/2}}$,[21]

Table 3. Values of $\ln K_d^\circ$, g, $\ln \bar{K}_2^\circ$, and h

Diluent (S)	S $\mathrm{cal}^{1/2}\mathrm{cm}^{-3/2}$	$\ln K_d^\circ$	g	$\ln \bar{K}_2^\circ$	h
Cyclohexane	8.20	2.90	11.4	5.11	−6.4
Toluene	8.91	7.83	−0.3	3.02	−3.3
Benzene	9.16	8.84	−1.2	2.91	−3.8
Chlorobenzene	9.68	10.79	−3.6	1.58	0.2
Nitrobenzene	10.78	14.78	−5.0	0.19	4.8

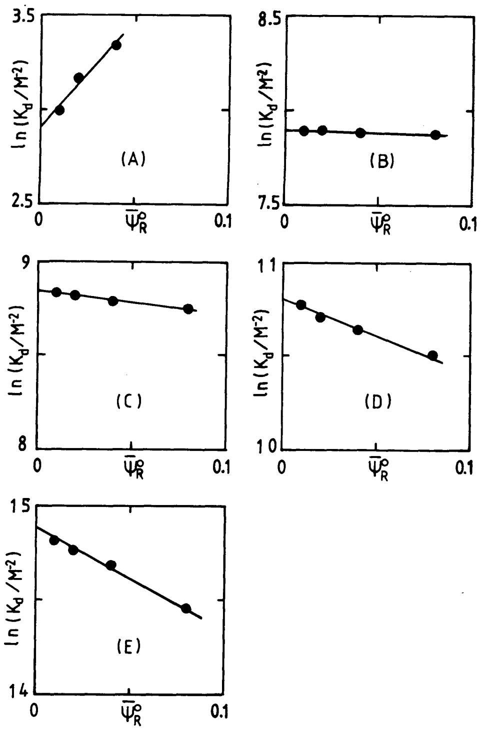

Fig. 5. Plots of $\ln K_d$ vs. $\bar{\psi}_R^\circ$ in the extraction of HCl by TOA in various organic solvents. (A): cyclohexane, (B): toluene, (C): benzene, (D): chlorobenzene, (E): nitrobenzene.

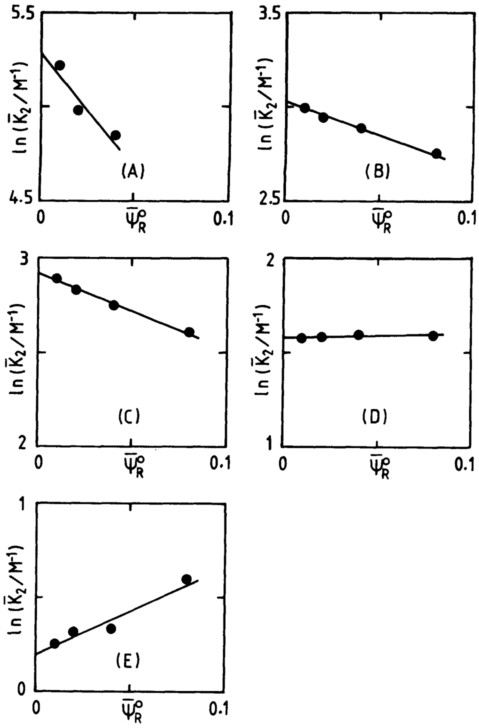

Fig. 6. Plots of $\ln \bar{K}_2$ vs. $\bar{\psi}_R^\circ$ for the aggregation of TOAHCl in various organic solvents. (A): cyclohexane, (B): toluene, (C): benzene, (D): chlorobenzene, (E): nitrobenzene.

$\delta_1=10.6\ \mathrm{cal}_{\mathrm{th}}^{1/2}\ \mathrm{cm}^{-3/2}$ [22] and $(v_1-v_R)/v_R \ll 1$.

From Eqs. 17 and 26, the following equation can be obtained by neglecting the volume change in aggregation of TOAHCl,

$$\ln \bar{K}_2 = \ln \bar{K}_2^\circ + h\bar{\psi}_R^\circ, \tag{29}$$

$$h = (4v_1/RT)(\delta_2-\delta_1)(\delta_1+\delta_2-2\delta_S), \tag{30}$$

where δ_2 denotes the solubility parameter of $(\mathrm{TOAHCl})_2$. Figure 6 shows the plots of $\ln \bar{K}_2$ vs. $\bar{\psi}_R^\circ$, where the values of B/2A ($=\bar{K}_2$) in Table 1 were used. The plots also give fairly good straight lines as expected from Eq. 29. The calculated values of $\ln \bar{K}_2^\circ$ and h are shown in Table 3. The values of h increase with the solubility parameter of diluents, and also satisfy the relation $\partial h/\partial\delta_S > 0$ which is derived from Eq. 30 by assuming that $\delta_1 > \delta_2$.

In order to evaluate the diluent effect on K_d°, it is convenient to introduce another equilibrium constant $K_d^\circ(1)$, where the liquid of TOA and the hypothetical liquid of TOAHCl are chosen as the reference states. The relation between K_d° and $K_d^\circ(1)$ is given by

$$K_d^\circ = K_d^\circ(1)\frac{\bar{y}_R(\bar{\psi}_R\to 0, \bar{\psi}_S\to 1)}{\bar{y}_1(\bar{\psi}_R\to 0, \bar{\psi}_S\to 1)}. \tag{31}$$

Application of Eq. 24 to $\bar{y}_R$ and $\bar{y}_1$ in Eq. 31 leads to

$$\ln K_d^\circ = A_0 + A_1\delta_S + A_2\delta_S^2, \tag{32}$$

$$A_0 = \ln K_d^\circ(1) + (v_R\delta_R^2 - v_1\delta_1^2)/RT + (v_R - v_1)/v_S, \tag{33}$$

$$A_1 = 2(v_1\delta_1 - v_R\delta_R)/RT, \tag{34}$$

$$A_2 = (v_R - v_1)/RT, \tag{35}$$

As is seen in Fig. 7, the plot of $\ln K_d^\circ$ vs. δ_S gives a parabolic curve with upward curvature which satisfies the relations $A_1 > 0$ and $A_2 < 0$ derived from Eqs. 34 and 35 by considering $\delta_1 > \delta_R$ and $v_1 > v_R$. The values of A_0, A_1, and A_2 were determined by the least-squares method as 110.9±2.1, 21.0±0.3 $\mathrm{cal}_{\mathrm{th}}^{-1/2}\ \mathrm{cm}^{3/2}$ and −0.87 ±0.03 $\mathrm{cal}_{\mathrm{th}}^{-1}\ \mathrm{cm}^3$, respectively. Equation 35 gives 515

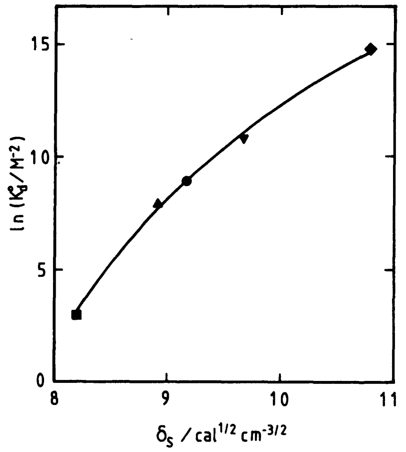

Fig. 7. Plot of ln K_d° vs. δ_s in the extraction of HCl by TOA in various organic solvents. □: Cyclohexane, ▲: toluene, ●: benzene, ▼: chlorobenzene, ◆: nitrobenzene.

±18 cm^3 mol^{-1} for $(v_1 - v_R)$ at RT=592 cal$_{th}$ mol^{-1}, but this value is too large for the difference in molar volume of TOA and TOAHCl. Therefore, this result shows that the regular solution theory can not give an exact explanation for the diluent effect of K_d°, but the above equations describe a semiquantitative relationship between ln K_d° and δ_S.

With respect to the diluent effect on the dimerization constant of TOAHCl, the following equations can be obtained in a similar manner to the derivation of Eq. 32 by neglecting the volume change in dimerization,

$$\ln \bar{K}_2^\circ = B_0 + B_1\delta_S, \tag{36}$$

$$B_0 = \ln K_2^\circ(1) + 2v_1(\delta_1^2 - \delta_2^2), \tag{37}$$

$$B_1 = 4v_1(\delta_2 - \delta_1), \tag{38}$$

where $\bar{K}_2^\circ(1)$ is the dimerization constant, and the hypothetical liquids of TOAHCl and (TOAHCl)$_2$ are chosen as the reference states. The plot of ln $\bar{K}_2^\circ$ vs. δ_S gives no straight line, but a parabolic curve with downward curvature as shown in Fig. 8. This fact indicates that ln $\bar{K}_2^\circ$ is expressed by

$$\ln \bar{K}_2^\circ = B_0 + B_1\delta_S + B_2\delta_S^2. \tag{39}$$

The values of B_0, B_1, and B_2 are 55.3±1.2, −9.35±0.18 cal$_{th}^{-1/2}$ cm$^{3/2}$, and 0.393±0.012 cal$_{th}^{-1}$ cm^3, respectively. The negative value of B_1 suggests that $\delta_1 > \delta_2$, and is consistent with the presumption that higher aggregates will have lower solubility parameters.

Next we deal with extraction equilibria in mixed solvents. According to Eq. 23, the molar activity coefficient of solute i, $\dot{y}_i$, in the mixed solvents (S1 and S2) containing amall amounts of solutes is given by

$$\begin{aligned}\ln \dot{y}_j = {} & (v_j/RT)(\delta_j - \delta_{S1})^2 + (\delta_j - \delta_{S2})(\delta_{S1} - \delta_{S2})\bar{\psi}_{S2} \\ & + (\delta_{S1} - \delta_{S2})^2\bar{\psi}_{S2}^2 + \ln(v_j/1000) + (1 - v_j/v_{S1}) \\ & + v_j(1/v_{S1} - 1/v_{S2})\bar{\psi}_{S2}.\end{aligned} \tag{40}$$

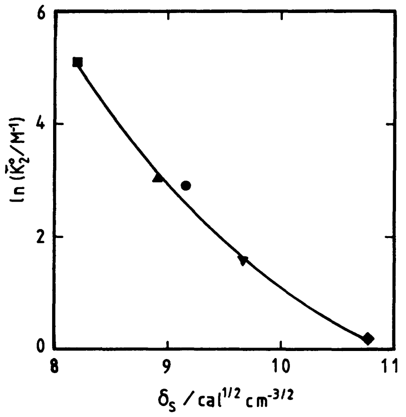

Fig. 8. Plot of ln $\bar{K}_2^\circ$ vs. δ_S for the aggregation of TOAHCl in various organic solvents. ■: Cyclohexane, ▲: toluene, ●: benzene, ▼: chlorobenzene, ◆: nitrobenzene.

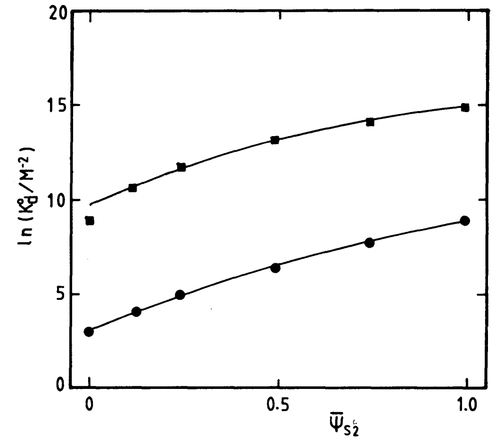

Fig. 9. Plots of ln K_d° vs. $\bar{\psi}_{S2}$ in the extraction of HCl by TOA in mixed solvents. ●: Cyclohexane(S1)–benzene(S2), ■: benzene(S1)–nitrobenzene(S2).

The extraction equilibrium constant of HCl by TOA in the mixed organic solvents, K_d°, is correlated to that in S1, K_d°(S1), by

$$K_d^\circ = K_d^\circ(\mathrm{S1})\,\frac{\bar{\dot{y}}_R(\bar{\psi}_R \to 0, \bar{\psi}_{S2})\,\bar{\dot{y}}_1(\bar{\psi}_R \to 0, \bar{\psi}_{S2} = 0)}{\bar{\dot{y}}_R(\bar{\psi}_R \to 0, \bar{\psi}_{S2} = 0)\,\bar{\dot{y}}_1(\bar{\psi}_R \to 0, \bar{\psi}_{S2})}$$

From Eqs. 40 and 41, the following equations can be derived by neglecting the sixth term in Eq. 40.

$$\ln K_d^\circ = C_0 + C_1\bar{\psi}_{S2} + C_2\bar{\psi}_{S2}^2, \tag{42}$$

$$C_0 = \ln K_d^\circ(\mathrm{S1}), \tag{43}$$

$$C_1 = 2\{v_1(\delta_1 - \delta_{S1}) - v_R(\delta_R - \delta_{S1})\}(\delta_{S2} - \delta_{S1})/RT, \tag{44}$$

$$C_2 = (v_R - v_1)(\delta_{S2} - \delta_{S1})^2/RT, \tag{45}$$

When $\delta_{S1} < \delta_{S2}$, it may be expected that $C_1 > 0$ and $C_2 < 0$. Figure 9 shows that the plots of ln K_d° vs. $\bar{\psi}_{S2}$ in the extraction with cyclohexane(S$_1$)-benzene(S$_2$) and benzene(S$_1$)-nitrobenzene(S$_2$) mixtures give the curves with upward curvatures which are in agreement with the expectation. The calculated values of C_0, C_1, and

Table 4. Values of C_0, C_1, and C_2

Diluent		$\ln K_d^\circ$(S1)	C_0	C_1	C_2
S1	S2				
Cyclohexane	Benzene	3.00	3.07±0.09 (3.22±0.09)[a]	7.71±0.09 (7.09±0.15)[a]	−1.96±0.11 (−1.47±0.08)[a]
Benzene	Nitrobenzene	8.83	9.14±0.35 (9.75±0.15)[a]	11.0±0.5 (8.5±0.2)[a]	−5.4±0.4 (−3.4±0.1)[a]

a) The values in parentheses were obtained from the calculation except for the value of $\ln K_d$ at $\bar{\psi}_{S2}=0$.

Table 5. Values of D_0, D_1, and D_2

Diluent		$\ln \bar{K}_2^\circ$(S1)	D_0	D_1	D_2
S1	S2				
Cyclohexane	Benzene	5.22	5.19±0.10 (5.10±0.12)[a]	−3.33±0.12 (−2.99±0.12)[a]	1.06±0.08 (0.79±0.08)[a]
Benzene	Nitrobenzene	2.89	2.58±0.53 (1.98±0.27)[a]	−6.2±0.5 (−3.7±0.5)[a]	4.0±1.4 (2.1±0.5)[a]

a) The values in parentheses were obtained from the calculation except for the value of $\ln \bar{K}_2^\circ$ at $\bar{\psi}_{S2}=0$.

C_2 are shown in Table 4. In the extraction with cyclohexane-benzene mixtures, the C_0 value is very close to that of ln K_d° (cyclohexane), but the agreement between C_0 and ln K_d° (benzene) is not so good in benzene-nitrobenzene mixtures. Since this difference appears to indicate that there is a specific interaction between TOAHCl and nitrobezene molecules, we carried out the calculation except for the data at $\bar{\psi}_{S2}=0$ in order to make more clear the difference, and the values are given in parentheses in Table 4. Recalculated values in cyclohexane-benzene do not change so much, but those in benzene-nitrobenzene change significantly. These facts strongly suggest that nitrobenzene molecules preferentially solvate to TOAHCl.

In a similar manner to derivation of Eq. 42, the following equations can be obtained for the dependence of $\bar{K}_2^\circ$ on the composition of mixed diluents by neglecting the volume change in the dimerization of TOAHCl,

$$\ln \bar{K}_2^\circ = D_0 + D_1\bar{\psi}_{S2}, \tag{46}$$

$$D_0 = \ln \bar{K}_2^\circ(\mathrm{S1}), \tag{47}$$

$$D_1 = 4v_1(\delta_1 - \delta_2)(\delta_{S1} - \delta_{S2})/RT, \tag{48}$$

where $\bar{K}_2^\circ$ (S1) denotes the dimerization constant in solvent S1. In the preceding discussion, since it was found that $\delta_1 > \delta_2$, it may be expected that $D_1 < 0$ when $\delta_{S1} < \delta_{S2}$, i.e. the plot of ln $\bar{K}_2^\circ$ vs. $\bar{\psi}_{S2}$ gives a straight line with a negative slope. However, the plots for mixed diluents do not yield straight lines as shown in Fig. 10. This indicates that the dependence of ln $\bar{K}_2^\circ$ on the composition of the mixed diluents may be represented as follows:

$$\ln \bar{K}_2^\circ = D_0 + D_1\bar{\psi}_{S2} + D_2\bar{\psi}_{S2}^2, \tag{49}$$

where D_1 and D_2 are constants. The calculated values of D_0, D_1, and D_2 are listed in Table 5. The values of D_0 in cyclohexane-benzene is very close to that of $\bar{K}_2^\circ$ (cyclohexane), but the difference between D_0 in benzene-nitrobenzene and $\bar{K}_2^\circ$ (benzene) is not little. The recalculated values except for the data at $\bar{\psi}_{S2}=0$ are given in parentheses in Table 5. The relationship between the values obtained from the two calculations are similar to that obtained for the values of C_0, C_1, and C_2 as shown in Table 4. The results in Table 5 also suggest that nitrobenzene molecules solvate to TOAHCl and contribute to weaken the aggregation.

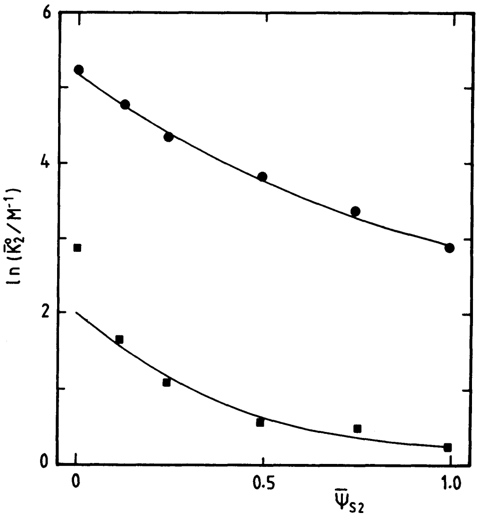

Fig. 10. Plots of ln $\bar{K}_2^\circ$ vs. $\bar{\psi}_{S2}$ for the aggregation of TOAHCl in mixed solvents. ●: Cyclohexane(S1)-benzene(S2), ■: benzene(S1)-nitrobenzene(S2).

From the above discussion, it was found that the experimental results in the present work can be explained fairly well on the assumption of Eqs. 19 and 23.

Estimation of the monomer concentration and mean aggregation number of trioctylammonium chloride in organic phase is carried out by using the total concentration and the dimerization quotient. Since Eq. 22 is rewritten as

$$[\overline{\mathrm{HCl}}]_T = [\overline{\mathrm{RHCl}}]\{1 + 2\overline{K}_2[\overline{\mathrm{HCl}}]_T\},$$

the monomer concentration, $[\overline{\mathrm{RHCl}}]$, is given by

$$[\overline{\mathrm{RHCl}}] = \frac{[\overline{\mathrm{HCl}}]_T}{1 + 2\overline{K}_2[\overline{\mathrm{HCl}}]_T}. \tag{50}$$

On the other hand, in order to estimate the mean aggregation number $<i>$ defined by

$$<i> = \frac{\sum\limits_{i=1} i[\overline{(\mathrm{RHCl})_i}]}{\sum\limits_{i=1}[\overline{(\mathrm{RHCl})_i}]} = \frac{[\overline{\mathrm{HCl}}]_T}{[\overline{\mathrm{RHCl}}] + \sum\limits_{i=2}\overline{\beta}_i[\overline{\mathrm{RHCl}}]^i}, \tag{51}$$

it is necessary to estimate the value of the denominator of Eq. 51. From Eqs. 17 and 19

$$\overline{\beta}_i = \frac{1}{i}(2\overline{K}_2)^{i-1}, \tag{52}$$

and

$$[\overline{\mathrm{RHCl}}] + \sum_{i=2}\overline{\beta}_i[\overline{\mathrm{HCl}}]^i = -\frac{1}{2\overline{K}_2}\ln(1 - 2\overline{K}_2[\overline{\mathrm{RHCl}}]). \tag{53}$$

Substitution of Eqs. 53 and 50 into Eq. 51 yields

$$<i> = \frac{2\overline{K}_2[\overline{\mathrm{HCl}}]_T}{\ln(1 + 2\overline{K}_2[\overline{\mathrm{HCl}}]_T)}. \tag{54}$$

Consequently, the values of $<i>$ can be easily calculated by using $[\overline{\mathrm{HCl}}]_T$ and $\overline{K}_2$. The calculated values of $<i>$ in several solutions are given in Fig. 11 as a function of $[\overline{\mathrm{HCl}}]_T$. Figure. 13 shows that the values of $<i>$ depend markedly on diluents and increase in the order nitrobenzene < chlorobenzene < benzene < toluene < cyclohexane, where $<i>$ values are determined to be 1.04, 1.17, 1.61, 1.70, and 7.82 at $[\overline{\mathrm{HCl}}]_T$=0.1 M in 8% (v/v) TOA solutions, respectively.

Finally, we should consider the physical meaning of Eq. 19. The fact that the extraction equilibria are well explained on Eqs. 19 and 23 seems to indicate that the volume fraction is a more reasonable concentration scale than the molarity to describe the extraction equilibria. We introduce a new equilibrium concentration quotient for the successive aggregation, which is defined by

$$\overline{K}_i(\overline{\psi}) = \frac{\overline{\psi}}{\overline{\psi}_{i-1}\overline{\psi}_1}. \tag{55}$$

This quotient can be related to $\overline{K}_i$ by

$$\overline{K}_i(\overline{\psi}) = \frac{1000v_i}{v_{i-1}v_1}\overline{K}_i. \tag{56}$$

When the volume change in aggregation is negligible, i.e. $v_i = i\,v_1$, Eq. 56 shows that Eq. 19 is equivalent to

$$\overline{K}_2(\overline{\psi}) = \overline{K}_3(\overline{\psi}) = \cdots\cdots = \overline{K}_n(\overline{\psi}). \tag{57}$$

Equation 57 implies that the binding energy of the aggregate $(\mathrm{TOAHCl})_i$ increases in proportion to the aggregation number, i, and the molar entropy change of each aggregate is proportional to the logarithm of volume fraction of the aggregate. However, we can not answer a question that why the aggregates have such property with respect to the binding energy. In order to make clear the validity of Eq. 19 or Eq. 57, it is instructive to analyze the experimental data so far reported on the aggregation equilibria of trialkylammonium salts by using Eqs. 19 or 57.

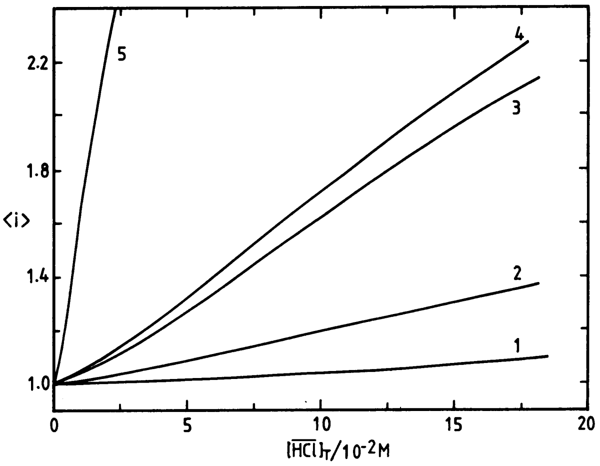

Fig. 11. Mean aggregation numbers of TOAHCl $<i>$ in various organic solvents at 25 °C as a function of $[\overline{\mathrm{HCl}}]_T$ at 8% (v/v) TOA. 1: Nitrobenzene, 2: chlorobenzene, 3: benzene, 4: toluene, 5: cyclohexane (4% (v/v) TOA).

As mentioned in the introduction, the most reliable information on the aggregation equilibria was given by the two investigations which were carried out by the two-phase emf titration[3-8] and osmotic measurement.[15-19] The data analysis for the former investigation was carried out based on the following equations assuming the ideal behavior of organic phase,

$$Z = U/W, \tag{58}$$

$$U = \sum_{i=1} ik_iu^i, \tag{59}$$

$$W = w + \sum_{i=1} ik_iu^i, \tag{60}$$

where $u = w\,[\mathrm{H}^+][\mathrm{X}^-]$, U and W denote the total molar concentrations of acid (HX) and amine, respectively, w is the molar concentration of free amine, and k_i is an equilibrium constant corresponding to $(K_d)^i\overline{\beta}_i$ in the present work. The data of the two-phase emf titration were best described with the formation of monomer, two low aggregates and one high aggregate of the salts in organic phase, i.e. Eqs. 59 and 60 were expressed by

$$U = k_1u + pk_pu^p + qk_qu^q + rk_ru^r, \tag{59'}$$

$$W = w + k_1u + pk_pu^p + qk_qu^q + rk_ru^r, \tag{60'}$$
$$(1 < p < q < r).$$

Values of the aggregation equilibrium constants β_p, β_q, and β_r, where $\beta_i = k_i/k_1^i$, were determined by calcu-

Table 6. Values of $\overline{K}_2$, $\overline{\beta}_i$, and β_i of Tridodecylammonium Salts in Organic Solvents at 25 °C

Salt	Concentration range of salt	Solvent	Measurement	$\log \overline{K}_2$ [a]	i	$\log \overline{\beta}_i$ [b]	$\log \beta_i$ [c]	Ref.
TDAHBr	0.03—0.3 M	*o*-Xylene	Two-phase	1.40—1.06	2	1.40—1.06	1.49±0.3	9
					3	2.93—2.25	3.13±0.3	
					30	47.94—38.12	46.04±1.3	
TDAHBr	0.01—0.1 M	Benzene	Osmotic	1.24	2	1.24	1.34	17
					3	2.61	2.76	
$TDAHNO_3$	0.02—0.25 M	Toluene	Two-phase	1.40—1.28	2	1.40—1.28	1.65±0.3	7
					3	2.93—2.69	3.15±0.3	
					50	81.89—75.82	80.10±2.1	
$TDAHNO_3$	0.01—0.1 M	Benzene	Osmotic	1.26	2	1.26	1.81	15
					3	2.65	2.59	
$TDAHClO_4$	0.04—0.15 M	*o*-Xylene	Two-phase	1.57—1.63	2	1.57—1.63	2.96±0.2	8
					8	12.21—12.64	16.21±0.7	
					90	164.82—170.22	208.09±8.10	
$TDAHClO_4$	0.01—0.1 M	Benzene	Osmotic	1.45	2	1.45	2.41	17
					8	11.38	14.00	
					16	25.11	29.78	

a) The values were determined by using the data in the reference. b) $\overline{\beta}_i=\prod_{j=2}^{i}\overline{K}_j=(1/i)(2\overline{K}_2)^{i-1}$. c) The values in the reference.

lating the values of k_1, k_p, k_q, and k_r, which give the minimum value of the error-square sum $\sum(Z_{\text{exp}}-Z_{\text{cal}})^2$. The values of β_p, β_q, and β_r of tridodecylammonium bromide perchlorate in *o*-xylene, and tridodecylammonium nitrate in toluene are given in Table 6 together with those of the dimerization concentration quotient $\overline{K}_2$, which were evaluated by assuming the validity of Eq. 19. Values of the aggregation equilibrium concentration quotients $\overline{\beta}_p$, $\overline{\beta}_q$, and $\overline{\beta}_r$, which were evaluated by using the equation $\overline{\beta}_i=(1/i)(2\overline{K}_2)^{i-1}$, corresponding to those of β_p, β_q, and β_r, respectively, are given in Table 6.

In the osmotic measurements, the concentration dependence of osmotic coefficient Φ of the solution containing trialkylammonium salt was analyzed by

$$\Phi = Y/W, \tag{61}$$

$$W = w_1 + \sum_{i=2} i\beta w_1{}^i, \tag{62}$$

$$Y = w_1 + \sum_{i=2} \beta w_1{}^i, \tag{63}$$

where W and w_1 denote the total molar concentration of the salts and the molar concentration of monomer. Kertes and Markovits[17] assumed the formation of three aggregates, which follows the equations

$$W = w_1 + p\beta_p w_1{}^p + q\beta_q w_1{}^q + r\beta_r w_1{}^r, \tag{62'}$$

$$Y = w_1 + \beta_p w_1{}^p + \beta_q w_1{}^q + \beta_r w_1{}^r, \tag{63'}$$

and evaluated the values of β_p, β_q, and β_r, which give the lowest value of the error-square sum $\sum(W_{\text{exp}}-W_{\text{cal}})^2+\sum(Y_{\text{exp}}-Y_{\text{cal}})^2$. The values of β_q, β_q, and β_r of tridodecylammonium bromide, nitrate and perchlorate in benzene are also shown in Table 6. In the above report, it was implicitly assumed that the change in activity of solvents resulted from only the change in effective concentration of the solute on the formation of aggregates, but it is found from the present work that this assumption is only applicable to very dilute solutions. Therefore, it is necessary to take into account the change in activity of solvents with varying the total salt concentration and the distribution of aggregates for evaluation of accurate values of aggregation equilibrium concentration quotient from the values of osmotic coefficient. According to Eq. 23, the activity of solvent, $\dot{a}_S$, in the solution containing monomer to n-mer of trialkylammonium salt is given by

$$\ln \dot{a}_S = \frac{v_S}{RT}\left\{\sum_{i=1}^{n}(\delta_S-\delta_i)\psi_i\right\}^2 + \ln \psi_S + \sum_{i=1}^{n}\left(1-\frac{v_S}{v_i}\right)\psi_i. \tag{64}$$

Equation 64 can be rewritten as

$$-\ln \dot{a}_S = \sum_{i=1}^{n}\frac{v_S}{v_i}\psi_i + \left(\frac{1}{2}-\sigma\right)\psi_T^2 + \frac{1}{3}\psi_T^3 + \cdots, \tag{64'}$$

$$\psi_T = \sum_{i=1}^{n}\psi_i, \tag{65}$$

$$\sigma = (v_S/RT)(<\delta> - \delta_S)^2, \tag{66}$$

$$<\delta> = \sum_{i=1}^{n}\delta_i\psi_i \Big/ \sum_{i=1}^{n}\psi_i. \tag{67}$$

Under the condition $\psi_T \ll 1$, Eq. 64′ reduces to

$$-\ln \dot{a}_S = \frac{v_S}{RT}\sum_{i=1}^{n}w_i + \left(\frac{1}{2}-\sigma\right)\left(\frac{v_S}{1000}\right)^2 W^2, \tag{68}$$

where W and w_i are the total molar concentration of the salt and the molar concentration of its i-mer, respectively. Application of Eq. 19 to the successive

Table 7. Values of $\overline{K}_2$ and ρ of Tridodecylammonium Salts in Organic Solvents[a)]

Salt	Solvent (S)	δ_S	t	$\overline{K}_2$	ρ
		$\mathrm{cal_{th}}^{1/2}\mathrm{cm}^{-3/2}$	°C	M^{-1}	M^{-1}
TDAHCl	Benzene	9.16	25	11.5	1.84
TDAHCl	Benzene	9.16	37	14.8	2.79
TDAHCl	CCl_4	8.6	25	23.1	1.27
TDAHBr	Benzene	9.16	25	17.4	1.58
TDAHBr	Benzene	9.16	37	17.4	2.48
TDAHBr	Cyclohexane	8.20	25	86.2	1.58
TDAHBr	Cyclohexane	8.20	37	72.8	1.77
TDAHBr	Cyclohexane	8.20	50	62.1	1.91
TDAHBr	CCl_4	8.6	25	40.6	0.0
$TDAHNO_3$	Benzene	9.16	25	18.3	1.91
$TDAHNO_3$	Cyclohexane	8.20	25	84.8	1.37
$TDAHNO_3$	CCl_4	8.6	25	44	1.31
$TDAHClO_4$	Benzene	9.16	25	28.4	0.15
$TDAHClO_4$	Cyclohexane	8.20	25	162	0.65
$TDAHClO_4$	Cyclohexane	8.20	37	117	0.62
$TDAGClO_4$	Cyclohexane	8.20	50	109	0.57
$TDAH_2SO_4$	Benzene	9.16	25	60	1.82
$TDAH_2SO_4$	CCl_4	8.6	25	134	0.98

a) The values of $\overline{K}_2$ and ρ were determined by using the data in Ref. 17.

aggregation concentration quotient $\overline{K}_i$, which is defined by $\overline{K}_i = w_i/w_1 w_{i-1}$, leads to Eq. 69 under the condition $2\overline{K}_2 w_1 < 1$.

$$-\ln \dot{a}_S = \frac{v_S}{1000}\frac{1}{2\overline{K}_2}\ln(1+2\overline{K}_2 W) + (\frac{1}{2}-\sigma)(\frac{v_1}{1000})^2 W^2, \tag{69}$$

Substitution of the relation $-\ln \dot{a}_S = (v_S/1000)\, W$[17)] into Eq. 69 yields

$$W\Phi = (1/2\overline{K}_2)\ln(1+2\overline{K}_2 W) + \rho W^2, \tag{70}$$

$$\rho = (1/2-\rho)(v_1^2/1000 v_S). \tag{71}$$

Accordingly, the values of $\overline{K}_2$ and ρ can be determined from Φ and W by the least-squares method. The values of $\overline{K}_2$ and ρ for tridodecylammonium chloride, bromide, nitrate, perchlorate and hydrogensulfate in benzene, carbon tetrachloride and cyclohexane are given in Table 7, where the data of Kertes and Markovits[17)] were used. Regardless of the salts, Table 7 shows that the temperature dependences of $\overline{K}_2$ and ρ are as follows: 1) The values of $\overline{K}_2$ in benzene are approximately independent of temperature ($(\partial\overline{K}_2/\partial T)\simeq 0$). 2) The values of $\overline{K}_2$ in cyclohexane decrease with the increase of temperature ($(\partial\overline{K}_2/\partial T)<0$). 3) The values of ρ in benzene increase with temperature ($(\partial\rho/\partial T)>0$). 4) The values of ρ in cyclohexane are nearly independent of temperature ($(\partial\rho/\partial T)\simeq 0$).

The reason why such temperature dependences are obtained is explained mathematically as follows. Equation 67 is rewritten as

$$<\delta> = \frac{1}{2\overline{K}_2 W}\sum_{i=1}^{n}\delta_i\{\frac{2\overline{K}_2 W}{1+2\overline{K}_2 W}\}^i. \tag{72}$$

When $\delta_1<\delta_2<\cdots<\delta_n$, i.e. higher aggregates have lower solubility parameters, Eq. 72 leads to $(\partial<\delta>/\partial\overline{K}_2)<0$. Therefore, it is obvious from the relation $(\partial<\delta>/\partial T) = (\partial<\delta>/\partial\overline{K}_2)(\partial\overline{K}_2/\partial T)$ that $(\partial<\delta>/\partial T)\simeq 0$ at $(\partial\overline{K}_2/\partial T)\simeq 0$ and $(\partial<\delta>/\partial T)>0$ at $(\partial\overline{K}_2/\partial T)<0$. On the other hand, Eq. 73 is derived from Eqs. 71 and 66,

$$\frac{\partial\rho}{\partial T} = \frac{v_1^2(<\delta>-\delta_S)}{1000RT^2}\{(<\delta>-\delta_S) - 2T(\partial<\delta>/\partial T)\}, \tag{73}$$

and this leads to the following relations: $(\partial\rho/\partial T)>0$ at $(\partial<\delta>/\partial T)\simeq 0$ or $(\partial\overline{K}_2/\partial T)\simeq 0$ and $(\partial\rho/\partial T)\simeq 0$ at $(\partial<\delta>/\partial T)\simeq(<\delta>-\delta_S)/2T>0$. The former relation is consistent with the temperature dependences of $\overline{K}_2$ and ρ in benzene, and the latter corresponds to those of $\overline{K}_2$ and ρ in cyclohexane. Accordingly, it is obvious that the values of $\overline{K}_2$ and ρ evaluated based on Eq. 19 have no self-contradiction. This presents suggestive evidence that Eq. 19 is valid, or at least not an unreasonable relationship for the aggregation equilibria of long-chain trialkylammonium salts in low-polar organic solvents.

In order to compare the values of aggregation equilibrium constants (concentration quotients) of tridodecylammonium salts (TDAHX), some values of $\overline{K}_2$ obtained by our analysis are shown in Table 6. As is seen in Table 6, the values of $\overline{\beta}_2$, $\overline{\beta}_3$, and $\overline{\beta}_r$ for TDAHBr and $TDAHNO_3$ having relatively small values of $\overline{K}_2$ are in fairly good agreement with those of β_2, β_3, and β_r, respectively, except for the value of β_2 for $TDAHNO_3$ in benzene obtained by extrapolation from the osmometric data.[15)] The values of $\overline{\beta}_2$, $\overline{\beta}_8$, and $\overline{\beta}_r$ for $TDAHClO_4$ with relatively large values of $\overline{K}_2$ are considerably small compared with those of β_2, β_8, and β_r, respectively. The reason for these results can be explained as follows. Since the bromide and nitrate in o-xylene, toluene, and benzene have relatively small values of $\overline{\beta}_i$ ($i=2,3,\cdots$), the concentrations of intermediate and high aggregates may be negligibly small compared with those of such low aggregates as dimer and trimer in the wide range of total concentration of the salts. On the other hand, in *o*-xylene and benzene solutions of the perchlorate with relatively large values of $\overline{\beta}_i$ (i=2,3,$\cdots$), the concentrations of intermediate aggregates may not be neglected compared with those of low aggregates even at the low total concentration of the salt. Accordingly, it seems that the values of β_2, β_8, and β_r for $TDAHClO_4$, which were determined based on Eqs. 59′ and 60′ or Eqs. 62′ and 63′, are not the true values, but the mean values of formation constants of low, intermediate and high aggregates, respectively, i.e. the calculated values of β_2, β_8, and β_r correspond to those of β'_2, β'_8, and β'_r, respectively, which are represented by

$$\beta'_2 = \sum_{i=2}^{s} \beta_i w_1^i / w_1^2, \qquad (74)$$

$$\beta'_8 = \sum_{i=s+1}^{t} \beta_i w_1^i / w_1^8, \qquad (75)$$

$$\beta'_r = \sum_{i=t+1} \beta_i w_1^i / w_1^r, \qquad (76)$$

$$(2 < s < 8 < t < r).$$

From Eqs. 74, 75, and 76, it is estimated that when the values of β_i equal to those of $\overline{\beta}_i$, the values of β'_i become larger than those of $\overline{\beta}_i$ and the ratios of $\beta'_i/\overline{\beta}_i$ increase with the increase of $\overline{\beta}_i$. These relations agreed with those between the calculated values of β_i and $\overline{\beta}_i$ shown in Table 6. This agreement may be taken as additional evidence that Eq. 19 or Eq. 57 is valid not only for the aggregation equilibrium of trioctylammonium chloride, but also for the aggregation equilibria of other long-chain trialkylammonium salts, and the assumption of the formation of at most three aggregates, which was introduced by Högfeldt et al.[3-8] and by Kertes and Markovits,[17] seems to be too simplified, particularly for tridodecylammonium perchlorate in *o*-xylene and benzene.

From the above-mentioned discussion, the following conclusion can be drawn. The extraction of hydrochloric acid by trioctylamine in low-polar organic solvents is accompanied with the formation of trioctylammonium chloride which exists as an ion-pair and of electrostatic molecular aggregates from dimer to micelle. The concentration quotients for the successive aggregation equilibria satisfy Eqs. 19 or 57. Equation 19 is valid also for the aggregation equilibria of other long-chain trialkylammonium salts in the organic solvents. The total solute concentration dependence on the quotients for the extraction equilibrium of hydrochloric acid by trioctylamine and for the successive aggregation of trioctylammonium chloride can be explained reasonably by the theory of regular solution. The diluent effect on the extraction equilibrium constant and on the successive aggregation constant can be also explained reasonably by the theory.

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