Modeling and Extractive Properties of Quaternary Salt in a Two-Phase System

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Thermodynamic equilibrium parameters of seven kinds of 1:1 electrolytes of quaternary salts in an organic and aqueous phase, including an extraction constant for ion-pair and free-ion, distribution constant, and dissociation constant in an organic solvent/aqueous solution, were determined by a numerical iteration method. Temperature, the kinds of solvents and quaternary salts, and the concentration of quaternary salts were evaluated to understand the thermodynamic properties. The free energies of extraction constant, distribution constant, dissociation constant, and the transfer of dissociated ions and ion pairs for quaternary ions were obtained as well. The amount of coextracted water and thermodynamic parameters were correlated with the solvent property. The equation of hydrophile−lipophile balance for selecting proper quaternary salt was also developed.

Introduction

Phase-transfer catalysis (PTC) is an effective tool for synthesizing organic chemicals from two immiscible reactants (Dehmlow and Dehmlow, 1993; Starks et al., 1994). Quaternary salts are generally used as phase-transfer catalysts. The reactivity in phase-transfer catalysis is controlled by (1) the reaction rate in the organic phase, (2) the mass-transfer steps between the organic and aqueous phases, and (3) the distribution equilibrium of the quaternary salts between two phases. The distribution of quaternary salts between two phases directly affects the entire system reactivity (Wu, 1994; Wu and Jou, 1995; Wu and Lai, 1995). The extraction behavior and distribution coefficients of quaternary salts in various media have also been investigated (Agarwal and Diamond, 1963; Asai et al., 1991; Cerna et al., 1993; Dehmlow and Vehre, 1987, 1989; Gibson and Weatherburn 1972a, b; Irving and Damodaran, 1971a, b; Wu et al., 1998a, b).

On the basis of experimental data and earlier literature (Dehmlow and Dehmlow, 1993; Starks et al., 1994; Wu, 1996), a generalized approach describing a liquid−liquid phase-transfer catalyzed (LLPTC) reaction system uses a pseudo-first-order reaction. The rate expression is written as

$$-\frac{d\left[\overline{RX}\right]}{dt} = k_{\mathrm{app}}\left[\overline{RX}\right] \tag{1}$$

The fixed value k_{app} is called the apparent first-order reaction-rate constant. The overbar, $\overline{}$, denotes the species in the organic phase.

Previous works (Wu, 1996; Wu and Meng, 1997) indicated that the pseudo-steady-state LLPTC model could describe the complicated nature of LLPTC reaction. The rate equation from the report of Wu (1996) is expressed as

$$\frac{d\left[\overline{RX}\right]}{dt} = \frac{k\left[\overline{RX}\right]Q_I/\overline{V}}{\dfrac{\alpha m_{QY}+1}{\alpha m_{QY}} + \left(\dfrac{Da_{QY}}{\alpha m_{QY}} + Da_{QX}\right) + \left(1-\alpha m_{QX}\right)\left(\dfrac{Da_{QY}+1}{\alpha m_{QY}}\beta + \alpha\gamma\right)} \tag{2}$$

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where

$$Da_{QY} = \left(\frac{k\left[\overline{RX}\right]}{K_{QY}A/\overline{V}} \right) \qquad \text{and} \qquad Da_{QX}\left(= \frac{k\left[\overline{RX}\right]}{K_{QX}A/\overline{V}} \right)$$

are Damkohler numbers QY and QX, respectively; β ($= k_{-2}[MX]/k_2[MY]$) is the reaction ratio of aqueous reverse reaction to forward reaction; and γ ($= k/[\overline{RX}]/k_2[MY]$) is the reaction ratio of organic phase to aqueous forward reaction. Before evaluating Eq. 3, the parameters of kinetics, mass transfer, and thermodynamic equilibrium must be dealt with. The aim of this work is to evaluate the equilibrium and quaternary salt extraction in an organic solvent/aqueous solution. The studies on distribution equilibrium of quaternary salts make one clarify the true mechanism through which the reactant anion is transferred.

Brändström (1977) indicated that the distribution of quaternary salt between two (liquid–liquid) phases exists as complicated multiequilibrium constants, which depend on the structure of the anion, cation, and solvent, as well as on pH, ionic strength, and concentrations in the aqueous solution. Such equilibrium properties have not yet been evaluated completely. The relationship of quaternary salt and the extraction constant is an important consideration for PTC work.

It is interested in determining the crude free energies of phase transfer between organic and aqueous phases for quaternaries. Combined with free transfer energies, halide ions give free energies for the tetrabutylammonium and tetrabutylphosphonium ions, which are not well established. Do different salts give the same values? In this article, we report the free transfer energy of some anions from water to various kinds of solvents based on distribution data of quaternary salts, and evaluate the extraction behavior of quaternary onium salts to understand their performance in a phase-transfer-catalyzed reaction system.

Experimental Section

Materials

Tetra-*n*-butylammonium bromide (TBAB, Merck), tricaprylmethylammonium chloride (Aliquat 336, ACROS), tetra-*n*-butylammonium iodide (TBAI, RDH), tetra-*n*-butylammonium chloride (TBAC, RDH), tetra-*n*-butyl phosphonium bromide (TBPB, Aldrich), 2,4,6-tribromophenol (TCI), 4-bromophenol (Janssen), solvents (RDH), and other reagents are reagent-grade chemicals. Water is of deionized grade.

Synthesis of tetra-n-butylammonium 4-bromophenoxide (TBA-TBPO)

An aqueous solution (50 cm^3) of potassium hydroxide (0.03 mol) and 4-bromophenol (0.015 mol) was prepared and introduced into the reactor (three-necked flask, 250 cm^3), which was set at the desired temperature (50 ± 0.02°C) and agitated at 300 rpm. After those compounds dissolved completely, TBAB was added into the reactor. The reaction mixture was agitated for 3 h. The aqueous phase was extracted twice with dichloromethane. Most of dichloromethane in the oil phase was removed with an aspirator. The material was dried and submitted for analysis. The purity was greater than 98% based on the quaternary group, using the extractive-titration method (Sakai et al., 1977; Wu and Lin, 1994).

Synthesis of tetra-n-butylammonium 2,4,6-tribromophenoxide (TBA-TBPO)

An aqueous solution (50 cm^3) of potassium hydroxide (0.03 mol) and 2,4,6-tribromophenol (0.015 mol) was prepared and introduced into the reactor (three-necked flask, 250 cm^3), which was set at the desired temperature (25 ± 0.02°C) and agitated at 300 rpm. After those compounds dissolved completely, TBAB was added to the reactor. The reaction mixture was agitated for 3 h. The material was filtered and washed seven times with water. The obtained white solid was dried and submitted for analysis. The purity was greater than 99% based on the quaternary group, using the extractive-titration method.

Equilibrium procedure

Quaternary onium salt was prepared and mixed with an equal volume (25 cm^3) of organic solvent and water in a flask (125 cm^3). The flask was immersed in a thermostatic constant-temperature water-bath shaker. The shaking was carried out for an extended period (at least 1 h) to allow the reagents to uniformly distribute between the two phases. In the final equilibrium state, the samples were withdrawn from the aqueous and organic phases, respectively, and analyzed. The mass balance accuracy was within 5%. The concentrations of quaternary salts were determined by the extractive-titration method using sodium tetraphenylborate as the titrant and tetrabromophenol phthalein ethyl ester potassium salt as the indicator (Sakai et al., 1977; Wu and Lin, 1994). The water content in the organic phase was measured by a potential meter (Karl Fischer Titration). The water-content difference in the organic phase ($\Delta[\overline{H_2O}]$) equals the difference between the measured water content in the solvent and that in the solution at the same temperature.

Mathematical Modeling

The distribution coefficient of quaternary cation, D_Q, was obtained by measuring the concentrations of the quaternary cation (Q) in the organic and aqueous phases, respectively. The distribution coefficient is highly dependent on the nature and concentration of the quaternary salts

$$D_Q = \frac{\overline{[Q]_{\text{obs}}}}{[Q]_{\text{obs}}} \tag{3}$$

At equilibrium, apparent extraction coefficients, E_{QX}, were calculated from the distribution of the quaternary salts between water and various solvents (Brändström, 1977)

$$E_{QX} = \frac{\left[\overline{QX}\right]}{[Q^+][X^-]} = \frac{\overline{[Q]}_{\text{obs}}}{[Q]^2_{\text{obs}}} \tag{4}$$

The true extraction constants of quaternary salts QX, corresponding to their infinitely dilute solutions in a two-phase system, were calculated using the following equation

$$E^T_{QX} = \frac{a_{\overline{QX}}}{a_{Q^+}a_{X^-}} = \frac{\overline{[QX]}}{[Q^+][X^-]\gamma^2_{\pm}} \tag{5}$$

where a and $\gamma_{\pm}^{2}$ are the activity and the mean ionic activity coefficient of quaternary salts, respectively.

The distribution constant of quaternary salt at equilibrium between two phases is

$$m=\frac{\overline{[Q^{+}X^{-}]}}{[Q^{+}X^{-}]} \tag{6}$$

The dissolved $Q^{+}X^{-}$ in the aqueous and organic phases may dissociate to

$$Q^{+}X^{-} \rightleftharpoons Q^{+}+X^{-} \tag{7}$$

$$\overline{Q^{+}X^{-}} \rightleftharpoons \overline{Q^{+}}+\overline{X^{-}} \tag{8}$$

Thus, the dissociation constants K_{da} and K_{da} of QX in the aqueous and organic phases are written as

$$K_{da}=\frac{[Q^{+}][X^{-}]\gamma_{\pm}^{2}}{[Q^{+}+X^{-}]} \tag{9}$$

$$K_{do}=\frac{\overline{[Q^{+}]}\,\overline{[X^{-}]}\bar{\gamma}_{\pm}^{2}}{\overline{[Q^{+}X^{-}]}} \tag{10}$$

Ion-Pair Type for Quaternary Salt in the Organic Phase (Wu et al., 1998a). The mass balances of quaternary cation Q^{+} in both phases can be displayed as

$$\overline{[Q]}_{\text{obs}}=\overline{[Q^{+}X^{-}]} \tag{11}$$

$$[Q]_{\text{obs}}=[Q^{+}X^{-}]+[Q^{+}] \tag{12}$$

From Eqs. 5, 6, 9, 11, and 12 we can obtain

$$\frac{[Q]_{\text{obs}}}{\sqrt{\overline{[Q]}_{\text{obs}}}}=\frac{\sqrt{\overline{[Q]}_{\text{obs}}}}{m}+\frac{1}{\gamma_{\pm}}\sqrt{\frac{K_{d}}{m}} \tag{13}$$

or

$$\frac{[Q]_{\text{obs}}}{\sqrt{\overline{[Q]}}_{\text{obs}}}=\frac{\sqrt{\overline{[Q]}_{\text{obs}}}}{m}+\frac{1}{\gamma_{\pm}\sqrt{E_{QX}^{T}}} \tag{14}$$

Equation 14 is identical to that derived by Asai et al. (1991) based on the ideal solution (that is, $\gamma_{\pm}=1$).

The true extraction constants on various quaternary salts can be calculated by (1) extrapolating the dependence of log E_{QX}^{T} on the ionic strength of the aqueous phase to its zero value, using the second-order polynomial approach; (2) taking the intercept of $[Q]_{\text{obs}}/\sqrt{\overline{[Q]}_{\text{obs}}}$ vs. $\sqrt{\overline{[Q]}_{\text{obs}}}$ in Figure 3 by a least-squares regression. The distribution constants m of quaternary salt between both phases and dissociation constants, K_{da}, of quaternary salts in the aqueous phase are obtained from Eq. 13.

Aggregation States for Quaternary Salt in the Organic Phase. Brändström (1982) reported that the ionic aggregation states of quaternary salt existing in the organic phase were of various types, that is, dissociated ions $(Q^{+}+X^{-})$, ion pairs $(Q^{+}X^{-})$, and quadruples $((Q^{+}X^{-})_{2})$. Hence, the total concentration of quaternary salt in an organic phase can be written as

$$\overline{C}_{Q}=\overline{[Q^{+}]}+\overline{[QX]}+2\overline{[Q_{2}X_{2}]}+\cdots \tag{15}$$

Since the organic system is in the electrical neutrality,

$$\overline{[Q^{+}]}=\overline{[X^{-}]} \tag{16}$$

Equation 15 can be transformed into

$$\overline{C}_{Q}=E_{Q^{+}}^{T\,1/2}\frac{\gamma_{\pm}}{\overline{\gamma}_{\pm}}([Q^{+}][X^{-}])^{1/2}+E_{QX}^{T}\gamma_{\pm}^{2}([Q^{+}][X^{-}])$$
$$+2E_{Q_{2}X_{2}}^{T}{}^{2}\gamma_{\pm}^{4}([Q^{+}][X^{-}])^{2}+\cdots \tag{17}$$

where $E_{Q^{+}}^{T}$, E_{QX}^{T}, and $E_{Q_{2}X_{2}}^{T}$ are the concentration quotients represented as

$$E_{Q^{+}}^{T}=\frac{\overline{[Q^{+}]}\,\overline{[X^{-}]\gamma_{\pm}^{2}}}{[Q^{+}][X^{-}]\gamma_{\pm}^{2}} \tag{18}$$

$$E_{QX}^{T}=\frac{\overline{[QX]}}{[Q^{+}][X^{-}]\gamma_{\pm}^{2}} \tag{19}$$

$$E_{Q_{2}X_{2}}^{T}=\frac{\overline{[Q_{2}X_{2}]}}{[Q^{+}][X^{-}]\gamma_{\pm}^{2}} \tag{20}$$

When no excess anions exist in the system, the relationship of quaternary cation and anion in the aqueous phase is given by

$$[Q^{+}]=[X^{-}] \tag{21}$$

Hence, Eq. 18 can be rewritten as

$$\overline{C}_{Q}=E_{Q^{+}}^{T\,1/2}\frac{\gamma_{\pm}}{\bar{\gamma}_{\pm}}[Q^{+}]+E_{QX}^{T}\gamma_{\pm}^{2}[Q^{+}]^{2}$$
$$+2E_{Q_{2}X_{2}}^{T}{}^{2}\gamma_{\pm}^{4}[Q^{+}]^{4}+\cdots \tag{22}$$

The values of $E_{Q^{+}}^{T}$, E_{QX}^{T}, and $E_{Q_{2}X_{2}}^{T}$ were calculated by obtaining the intercept of

$$\frac{\overline{C}_{Q}}{[Q^{+}]}\text{ vs. }[Q^{+}],\qquad \frac{\overline{C}_{Q}-E_{Q^{+}}^{T\,1/2}[Q^{+}]}{[Q^{+}]^{2}}\text{ vs. }[Q^{+}]^{2},\text{ and}$$

$$\frac{\overline{C}_{Q}-E_{Q^{+}}^{T\,1/2}[Q^{+}]-E_{QX}^{T}[Q^{+}]^{2}}{[Q^{+}]^{4}}\text{ vs. }[Q^{+}]^{2}$$

respectively, in Figure 5 using a least-square regression. Corrections for the activity coefficient in the organic phase were made using the Marshall−Grunwald expression (Marshall and Grunwald, 1953).

Quaternary salts in an organic phase must be determined experimentally to know whether the salts are dissociated or associated, and to what degree. How many molecules of co-extracted water are carried by each quaternary salt? Hence, the equation for distribution of tetralkylammonium halide into an organic phase can be written as (Kenjo and Diamond, 1972, 1974)

$$Q^+ + X^- + j\mathrm{H_2O} \rightleftharpoons \overline{Q^+} + \overline{X^- \cdot j\mathrm{H_2O}} \tag{23}$$

$$Q^+ + X^- + j\mathrm{H_2O} \rightleftharpoons \overline{Q^+ \cdots X^- \cdot j\mathrm{H_2O}} \tag{24}$$

Depending upon whether the species in the organic phase is dissociated as free ions (Eq. 23) or associated as ion pairs (Eq. 24), the corresponding equilibrium constants can be written as

$$E^T_{Q^+,\mathrm{H_2O}} = \frac{\overline{[Q^+]}\ \overline{[X^- \cdot j\mathrm{H_2O}]\gamma_\pm^2}}{[Q^+][X^-][\mathrm{H_2O}]^j\gamma_\pm^2} \tag{25}$$

$$E^T_{QX,\mathrm{H_2O}} = \frac{\overline{[QX \cdot j\mathrm{H_2O}]}}{[Q^+][X^-][\mathrm{H_2O}]^j\gamma_\pm^2} \tag{26}$$

The j-value can be calculated by dividing $\Delta\overline{(\mathrm{H_2O})}$ by the amount of quaternary salts in the organic phase. The water content difference in the organic phase ($\Delta\overline{(\mathrm{H_2O})}$) equals the difference between the measured water content in the solvent and that in the solution at the same temperature.

Results and Discussion

The functional groups of the quaternary salts are known to generally influence the dissolution of the catalyst in the organic phase. Furthermore, the anion phase transfer also influences the reaction rate in a phase-transfer-catalyzed two-phase reaction. Therefore, proper selection of quaternary salts is crucial in promoting the reaction rate. The use of quaternary salts in the phase-transfer-catalyzed reaction was investigated in this study. The abbreviations of quaternary salts are defined in the Experimental section.

Distribution coefficient D_Q between two phases

The distribution coefficient of quaternary salt between both phases not only provides information between the phases to facilitate the modeling of two-phase-transfer catalysis systems, but it can also give a criterion to evaluate the suitability of the catalyst. Figure 1 depicts the distribution coefficient, D_Q, of the quaternary cation in the initial amount of quaternary salts in various quaternary salts and solvents. The order of magnitude of D_Q for quaternary salts is Aliquat 336 > TBA-TBPO > TBAI > TBPB > TBAB > TBAC. The sequence of D_Q for solvents is $\mathrm{CHCl_3} > \mathrm{CH_2Cl_2} >$ 1,2-$\mathrm{C_2H_2Cl_2} > \mathrm{C_6H_5Cl}$. The orders of influencing the extraction capability of the quaternary salts are $\mathrm{Br_3C_6H_2O^-} > \mathrm{I^-} >$

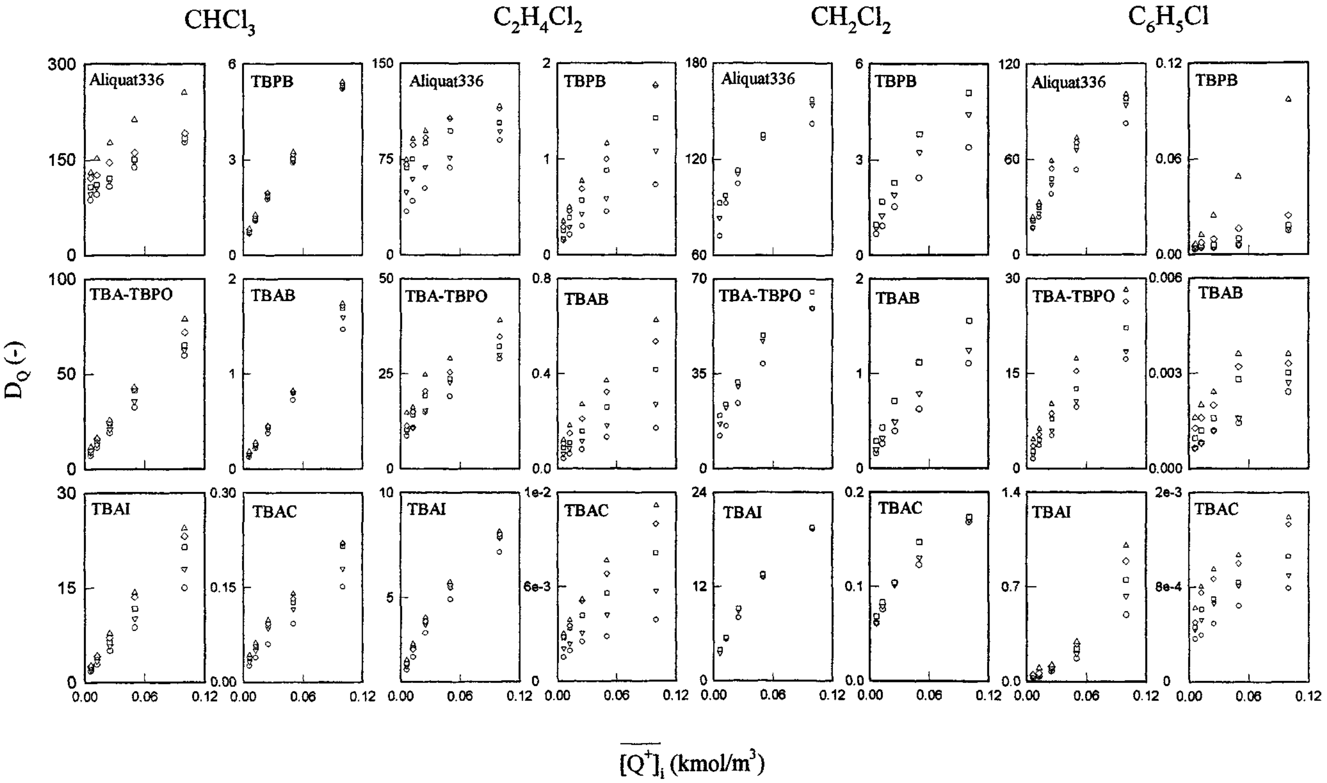

Figure 1. Distribution coefficients vs. initial concentration of quaternary salts for various kinds of solvent and temperature: (○) 10°C; (▽) 20°C; (□) 30°C; (◇) 40°C; (△) 50°C.

$Br^- > Cl^-$ and $P^+ > N^+$ for the anion and central cation, respectively. Reasons for these behaviors have been discussed in earlier work (Agarwal and Diamond, 1963; Brändström, 1977; Gibson and Weatherburn, 1972a; Wu et al., 1998a,b). The D_Q-value increased when the temperature increased (Figure 1).

Hydration number of quaternary salts in the organic phase

Figure 2 shows the water content ($\Delta\overline{[H_2O]}$) of the equilibrium concentration of quaternary salts in the organic phase ($\overline{[Q^+]}_{eq}$) in various kinds of quaternary salts and solvents. The order of magnitude of $\Delta\overline{[H_2O]}$ for quaternary salts is mostly Aliquat 336 > TBA-TBPO > TBAI > TBPB > TBAB > TBAC. The sequence of $\Delta\overline{[H_2O]}$ for solvents is mostly 1,2-$C_2H_4Cl_2$ > CH_2Cl_2 > $CHCl_3$ > C_6H_5Cl. This coextracted water sequence is identical to the water solubility in the organic phase of 1,2-$C_2H_4Cl_2$ (1.3) > CH_2Cl_2 (0.81) > $CHCl_3$ (0.08) > C_6H_5Cl (0.05) at 20°C. The orders of influencing the extraction capability of H_2O are $Cl^- > Br_3C_6H_2O^- > Br^- > I^-$ and $N^+ > P^+$ for the anion and central cation, respectively. The water content trend in the organic phase varied with increasing temperature (Figure 2). Landini et al. (1982) indicted that the solvating capability between quaternary salt and water could reduce the quaternary salt's reactivity in the organic phase in a phase-transfer-catalyzed reaction. This result was confirmed by previous work (Agarwal and Diamond, 1963; Wu and Jou, 1995). Hence, the study of the liquid–liquid phase-transfer catalyzed reaction is significant, and evaluation of the number of molecules of the coextracted water is carried out by each quaternary salt. The $\Delta\overline{[H_2O]}$ value increased when the charge-to-volume ratio of the anion increased. The $\Delta\overline{[H_2O]}$ value increased as the polarity of solvent increased, and decreased as the lipophility of the quaternary salt increased. These tendencies correspond to those reported by Landini et al. (1978, 1989). Kenjo and Diamond (1974) reported that the average water contents in a nitrobenzene/water system at 23°C were 3.3, 1.8, and 1 (mol/mol quaternary salt) for Cl^-, Br^-, and I^-. Starks and Owens (1973) suggested that the hydration numbers of $C_{16}H_{33}Bu_3\,P^+X^-$ are 0.4, 4, and 5 for NO_3^-, Cl^-, and CN^-, respectively. Figure 2 reveals that the average water content in the organic phase ($\Delta\overline{[H_2O]}$) was about 1 to 3 moles per mole of quaternary salt, except for TBAC. Because the hydration numbers for different anions were different when the quaternary salt was TBA^+ ($(n\text{-}C_4H_9)_4N^+$), the results demonstrate that the water of hydration is primarily associated with the anion, rather than the quaternary cation.

Determination of extraction constant for ion pair and dissociated ion

If $\gamma_\pm = 1$ is employed in Eq. 13 in method (A) to describe this equilibrium system, the results are presented in Figure 3. The physical parameters will be obtained from the slope or intercept of a straight line. The slope of Eq. 13 equals to the

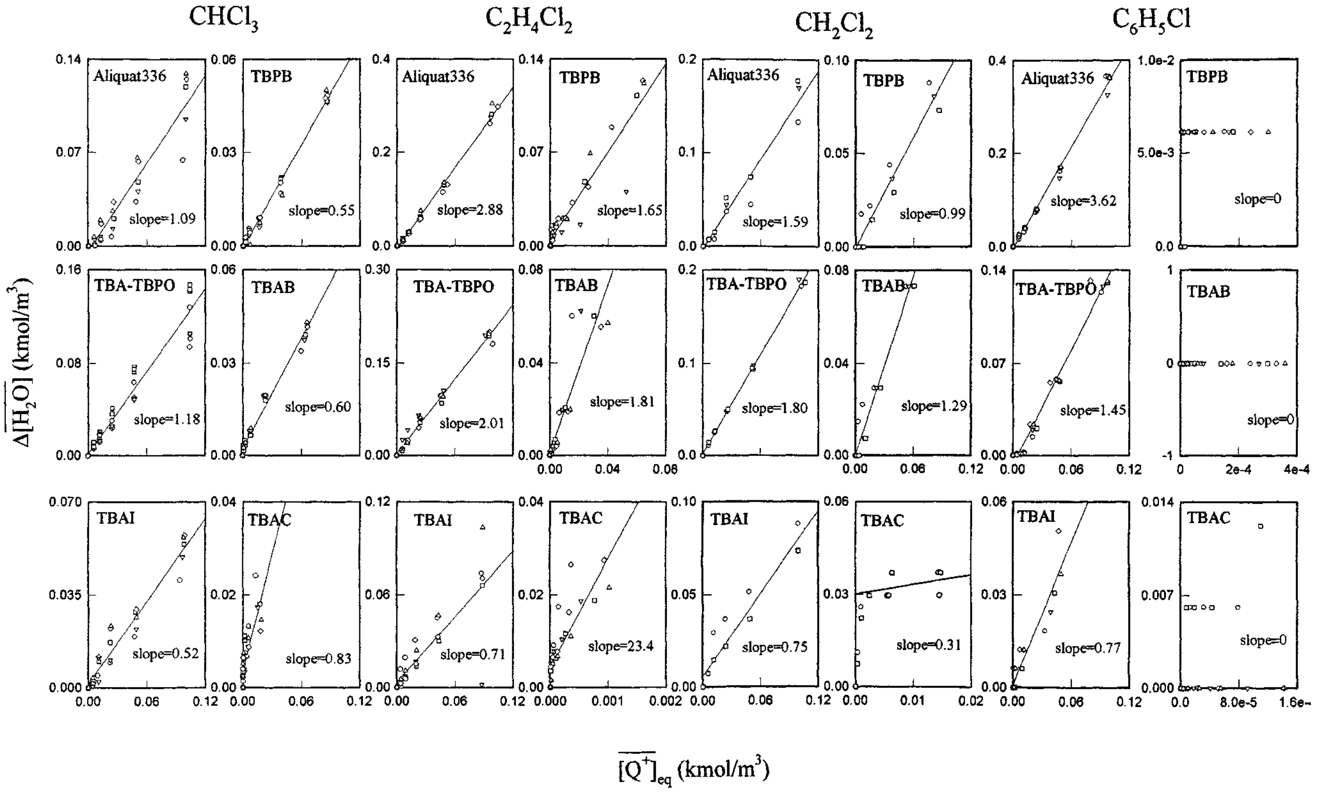

Figure 2. Water content in organic phase vs. equilibrium concentration of quaternary for various kinds of solvents and temperature: (○) 10°C; (▽) 20°C; (□) 30°C; (◇) 40°C; (△) 50°C.

reciprocal of the distribution constant, m, and must be positive. However, the slopes for Aliquat 336 and TBA-TBPO at various solvents in Figure 3 are not all positive. Hence, the mean activity coefficient, $\gamma_\pm$, in the aqueous solution does not equal 1. Our previous work (Wu et al., 1998a) developed a numerical method to calculate the distribution constant, m, of quaternary salt between the phases and the dissociation constant of the quaternary salt in the aqueous phase, from apparent extraction constant by using Eq. 13. Because method (A) assumes that the quaternary salt in the organic phase is only one type (ion pairs), we constructed a new model to describe the extraction system by method (B) (Eqs. 15–22), which considers the ionic aggregation states of the quaternary salt existing in the organic phase are various types. Inoue and Tochiyama (1980) reported the methyltrioctylammonium chloride distribution between water (or 0.1 kmol/m^3 aqueous NaCl solution) and the other nine kinds of solvents. They presented a special case of $[QX]=0$, $\gamma_\pm=1$, and $\overline{\gamma_\pm}=1$ in Eqs. 15–22. Thus, the slope of the log-log plot for the organic-phase salt activity vs. the aqueous-phase value yields the degree of association (Eq. 17). A half-slope means complete dissociation, a line of slope 1 means pure ion pairs, and a slope greater than two means aggregation beyond the ion pair. According to the results of Inoue and Tochiyama (1980) and Figure 4, the slope varied with different kinds of solvents and quaternary salts ranging from 1 to 3, even greater than 4. This result demonstrates that quaternary salts existing in the organic phase are various types. According to Eq. 22, the values $E^T_{Q^+}$, E^T_{QX}, and $E^T_{Q_2X_2}$ were determined by extrapolating the dependence $E^T_{Q^+}$, E^T_{QX}, and $E^T_{Q_2X_2}$ on the ionic strength of the aqueous phase at zero value, that is, by obtaining the interception of the plot of

$$\frac{\bar{C}_Q}{[Q^+]} \text{ vs. } [Q^+], \qquad \frac{\bar{C}_Q - E^{T\,1/2}_{Q^+}[Q^+]}{[Q^+]^2} \text{ vs. } [Q^+]^2,$$

$$\frac{\bar{C}_Q - E^{T\,1/2}_{Q^+}[Q^+] - E^T_{QX}[Q^+]^2}{[Q^+]^4} \text{ vs. } [Q^+]^2,$$

respectively, using a least-square regression (such as TBA-TBPO in Figure 5). All regression factors were larger than 0.97. The calculated results are shown in Figure 6, which displays the values $E^T_{Q^+}$, E^T_{QX}, and $E^T_{Q_2X_2}$ for temperature and various kinds of quaternary salts and solvents. The sequence $E^T_{Q^+}$ and E^T_{QX} for a solvent corresponds to the polarity of that solvent. Most values $E^T_{Q^+}$ and E^T_{QX} were increased with increasing temperature. The values $E^T_{Q^+}$ and E^T_{QX} were dramatically increased with increasing lipophilicity of quaternary salts. The sequence $E^T_{Q^+}$ for quaternary salts is around Aliquat 336 > TBA-TBPO > TBAI > TBPB ≈ TBAB > TBAC. The sequence E^T_{QX} for quaternary salts is Aliquat 336 > TBA-TBPO > TBAI > TBPB > TBAB > TBAC. Most $E^T_{Q_2X_2}$ values are equal to zero, except for Aliquat 336 in CH_2Cl_2. This finding demonstrates that the quaternary salts existing in the organic phase are free ions and ion-pair types, not nearly the aggregative type. The dimerization constant is equal to zero. This result was different from Brändström (1977), which indicated that TBAC existed slightly in an aggregative type.

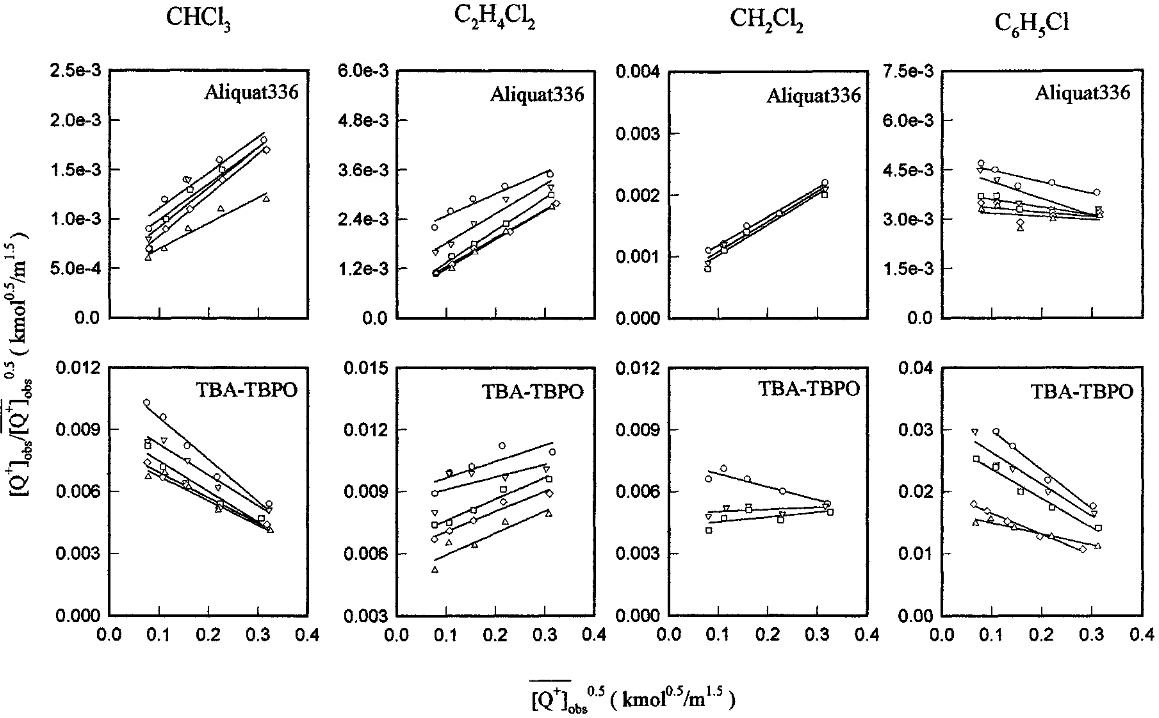

Figure 3. $[Q^+]_{obs}/\sqrt{[Q^+]_{obs}}$ vs. $\sqrt{[Q^+]_{obs}}$ of Aliquat 336 and TBA-TBPO for various solvents: (○) 10°C; (▽) 20°C; (□) 30°C; (◇) 40°C; (△) 50°C.

Dissociation of quaternary salts in the organic and aqueous phases

By using Eqs. 15–22, the values of $E_{Q^+}^T$, E_{QX}^T, and $E_{Q_2X_2}^T$ (Figure 6), the initial value of distribution constant m calculated from method (A), and the mean activity coefficient in the organic phase were made using the Marshall and Grunwald expression, and the values m, K_{da}, K_{do}, and $\gamma_\pm$ were calculated by a numerical iteration method. The calculated results are shown in Figure 7. Beronius and Brändström (1976) even clarified the identical value K_{do} at $[QX] = 0$ within the limits of experimental error by two methods: Eq. 22 and the conductance measurement. From Figure 7, most K_{da} values were located in the range between 1 and 10, while K_{do} values were located in the range between 10^{-1} and 10^{-5}. The dissociation ability of quaternary salt in the aqueous phase is larger than the organic phase. In view of the past reports, the dissociation constant in an organic or aqueous phase is listed in Table 1. According to Table 1, the experimental results are reasonable.

Figure 8 shows the cation-to-ion pair ratios (such as $[Q^+]/[QX]$) of quaternary salts in aqueous and organic phases. The initial concentration of quaternary salt is 0.0125 and 0.1 kmol/m^3 in various kinds of solvents. The quaternary salts QX can be completely dissociated to free ions (Q^+ and X^-) in aqueous phase ($\because [Q^+]/[QX] > 100$), and partially dissociated in the organic phase when the concentration of the quaternary salt is 0.0125 kmol/m^3. The quaternary salts QX can be partially dissociated to free ions in the aqueous and organic phases when the concentration of quaternary salt is 0.1 kmol/m^3. The dissociation degree of quaternary salt for 0.0125 kmol/m^3 is larger than that for 0.1 kmol/m^3. Aliquat 336 and TBA-TBPO have a higher degree of dissociation among the seven quaternary salts. Although the cation-to-ion pair ratios were calculated by method (B) (Eqs. 15–22), and some data varied because of experimental error, the following incremental rules of the dissociation degree of the quaternary salts were obtained: (1) increasing charge-to-volume ratio of central cation or counteranion (such as $P^+ > N^+$ or $I > Br^- > Cl^-$); (2) increasing the electro-releasing groups on the quaternary cation (e.g., Aliquat 336 > TBAC); and (3) increasing the electro-withdrawing groups on the quaternary anion (such as TBA-BPO > TBA-BPO > TBAC). Electron-releasing (or electron-withdrawing) groups apparently make the transition state more stable on the quaternary cation (or anion), while the ion-pair type of quaternary salts transferring through the interface between two phases is a transition state. However, the ionizing ability of four solvents solvating cations and anions was unobvious. This result corresponds to the result of Bockries and Reddy (1980) that the association constant decreased when the effective ion radius of the ion pair was increased.

Relationship between extraction constant and hydrophile-lipophile balance

Quaternary ammonium ions are used as the phase-transfer catalyst because they are least likely to interfere in chemical reactions. According to the experimental results of Brändström (1977), Herriott and Picker (1975), and Landini et al. (1978), the organophilic quaternary cations served as more effective phase-transfer catalysts than quaternary cations with small alkyl chains. Thus, the incremental number of C atoms surrounding the central atom (such as N) of a quaternary salt will increase its lipophilicity, raising the extraction constant. However, they did not give the relationship

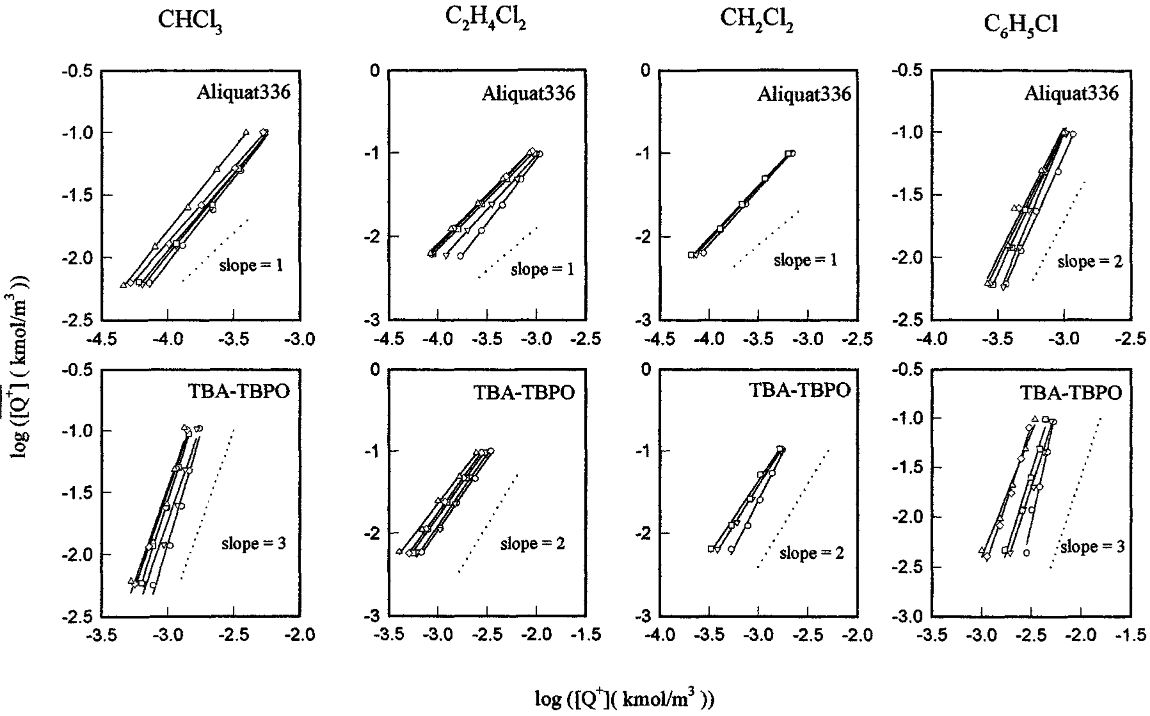

Figure 4. Log-log plot of extraction of Aliquat 336 and TBA-TBPO for various solvents method (A) and $\gamma_\pm = 1$: (○) 10°C; (▽) 20°C; (□) 30°C; (◇) 40°C; (△) 50°C.

between the extraction constant and the structure of quaternary salts. In view of the literature, three relationships of quaternary cation have been reported: (1) Gustavii (1967) observed a linear relationship between log E_{QX} and n, the number of C atoms in an ammonium ion. He extracted pictrates into methylene chloride using primary amines, symmetrical secondary and tertiary amines, and symmetrical quaternary ammonium salts. The relationships for quaternary ammonium salts is log $E_{Q\ \mathrm{picrate}} = -2.0 + 0.54n$. (2) A quantitative parameter for characterizing accessibility was suggested (Starks et al., 1994) based on the strong dependence of electrostatic interaction on the distance of closest approach between cation and anion (which is determined by steric factors). This parameter, termed q, is simply the sum of the reciprocals of the length of the linear alkyl chains attached to the central nitrogen of the quaternary cation. $q = 1/C\#_1 + 1/C\#_2 + 1/C\#_3 + 1/C\#_4$ where C# is the number of carbon atoms in each of the four alkyl chains in the quaternary cation. (3) Fukunaga et al. (1980) had presented a correlation function based on the hydrophile–lipophile balance (HLB) ideas to assess the efficiency of quaternary salts in the benzene–water system in terms of Hildebrand parameters

$$D(\delta_{QX}) = \frac{(\delta_{QX} - \delta)^2}{(\delta_{QX} - \bar{\delta})^2}$$

However, the two former relationships (parts (1) and (2)) were focused to access the distribution of quaternary cations. The equilibrium property cannot reveal when the total carbon number for various quaternary salts is the same (Figure 9). In part (3), the Hildebrand parameter cannot easily be obtained

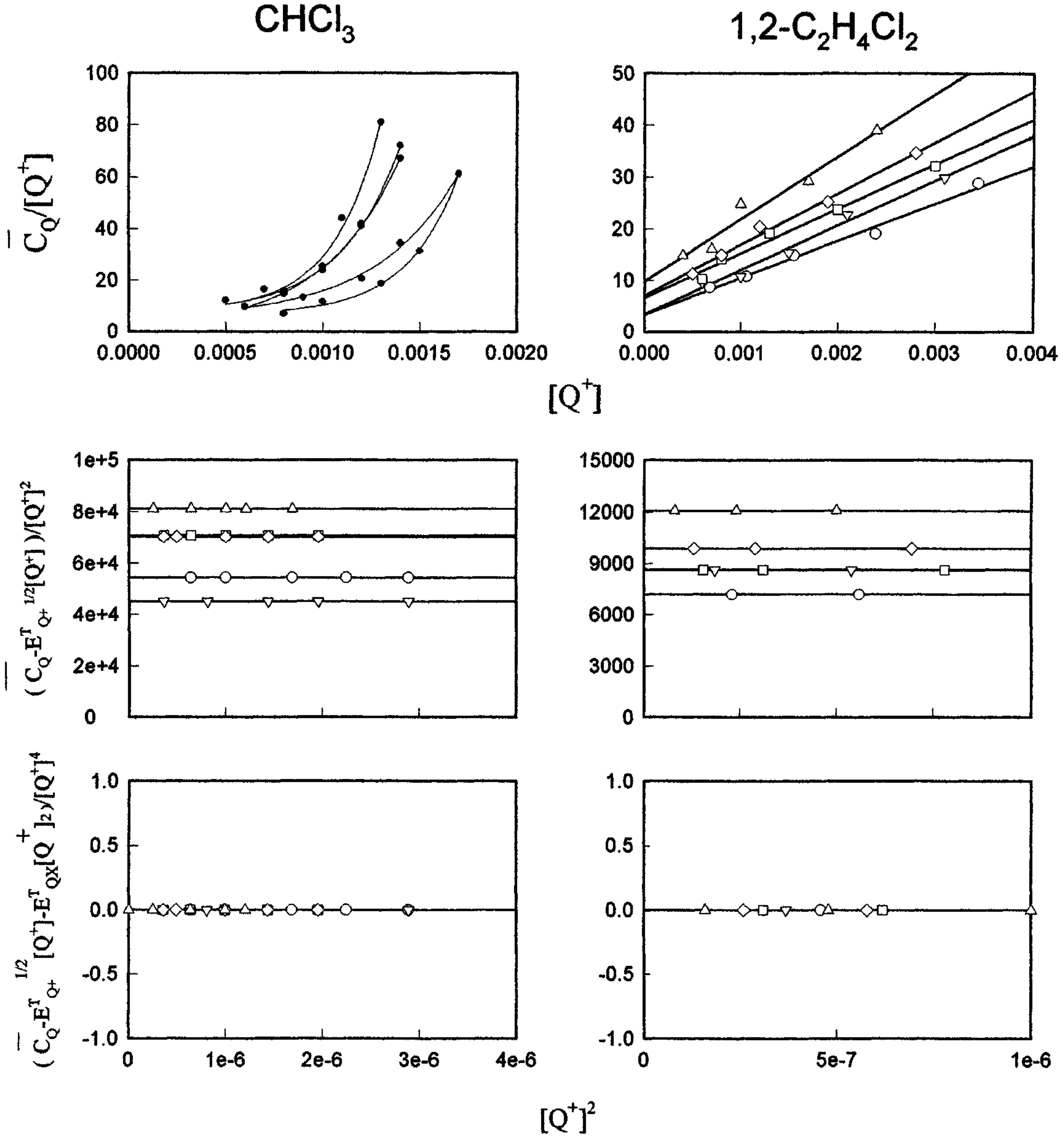

Figure 5. $\bar{C}_Q/[Q^+]$ vs. $[Q^+]$, $(\bar{C}_Q - E^{T1/2}_{Q^+}[Q^+])/[Q^+]^2$ vs. $[Q^+]^2$ and $(\bar{C}_Q - E^{T1/2}_{Q^+}[Q^+] - E^T_{QX}[Q^+]^2)/[Q^+]^4$ vs. $[Q^+]^2$: (○) 10°C; (▽) 20°C; (□) 30°C; (◇) 40°C; (△) 50°C.

for all quaternary salts. Hence, we took the results of parts (1)–(3) and the concept of hydrophile–lipophile balance for the surfactant that the dispersal efficiency of surfactant or emulsifier molecules is a function of the relative interactions of their polar, hydrophilic "heads" with the aqueous phase, and of their nonopolar, lipophilic "tails" with the hydrocarbon phase (Griffin, 1949, 1952). We developed the following new model

$$HLB = \left(q \cdot \frac{0.475}{(M_T - M_H)} + \frac{9.4}{M_{NX}} \right) \cdot M_{TBAB} \qquad (27)$$

in which 0.475 and 9.4 are the hydrophilic group numbers of CH_2 and N, respectively, defined by Davies (1957). The first

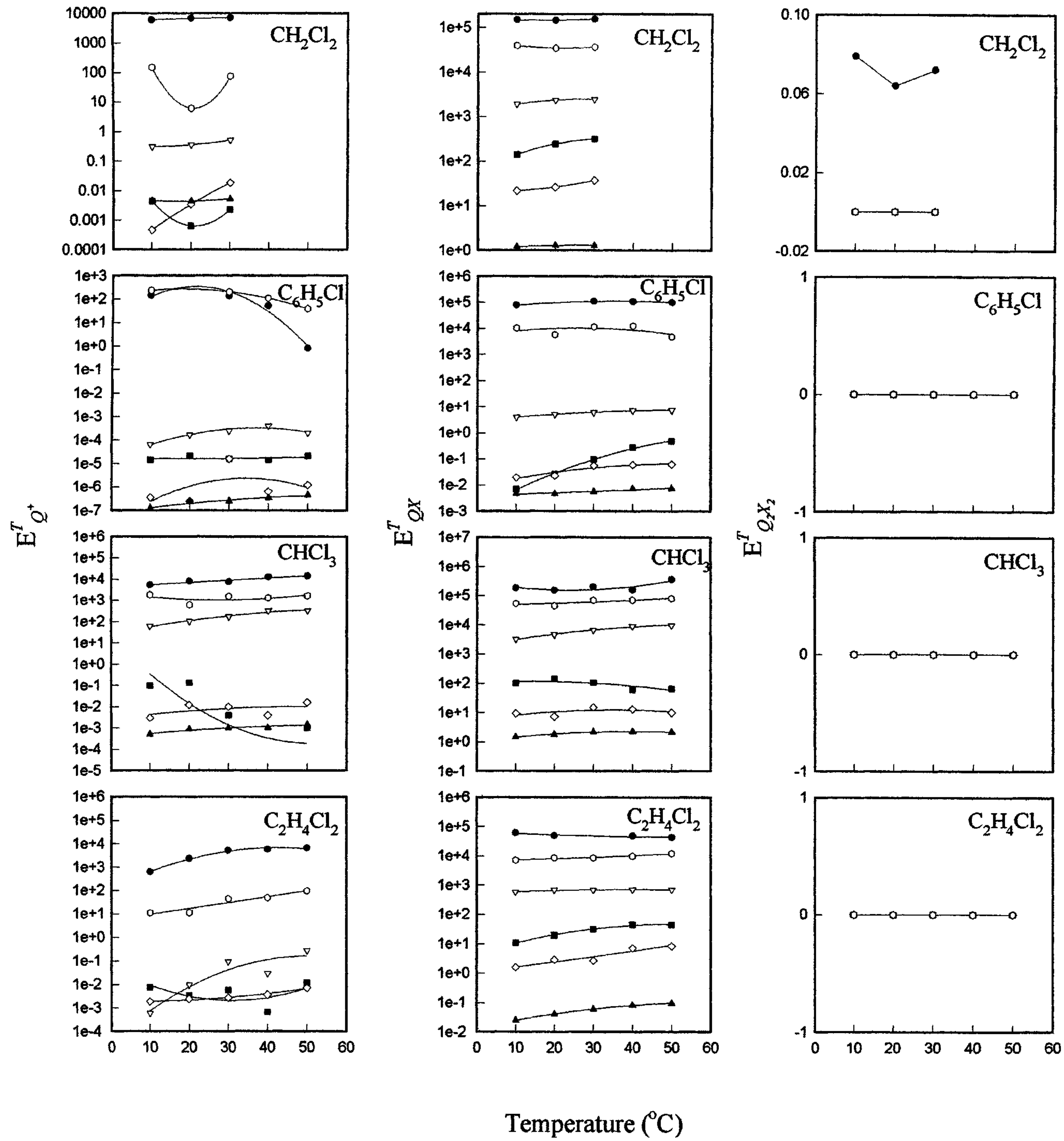

Figure 6. Temperature effect for $E^T_{Q^+}$, E^T_{QX} and $E^T_{Q_2X_2}$ for various kinds of solvents: (●) Aliquat 336; (○) TBA-TBPO; (■) TBPB; (▲) TBAC; (▽) TBAI; (◇) TBAB.

and second terms in the parentheses denote the hydrophilic ability of the lipophilic group and ionic group, respectively; q-value denotes the symmetrical degree of quaternary cation, and M_{TBAB} is the molecular weight of TBAB as a standard compound. From Figure 9, the thermodynamics parameters were obviously indicated by the HLB-value of the quaternary salts by using Eq. 27. Such an expression obviously suffers from using a single-parameter carbon number C# (or q-value), and some progress has been made with multicomponent parameters. According to the results in Figure 10, two

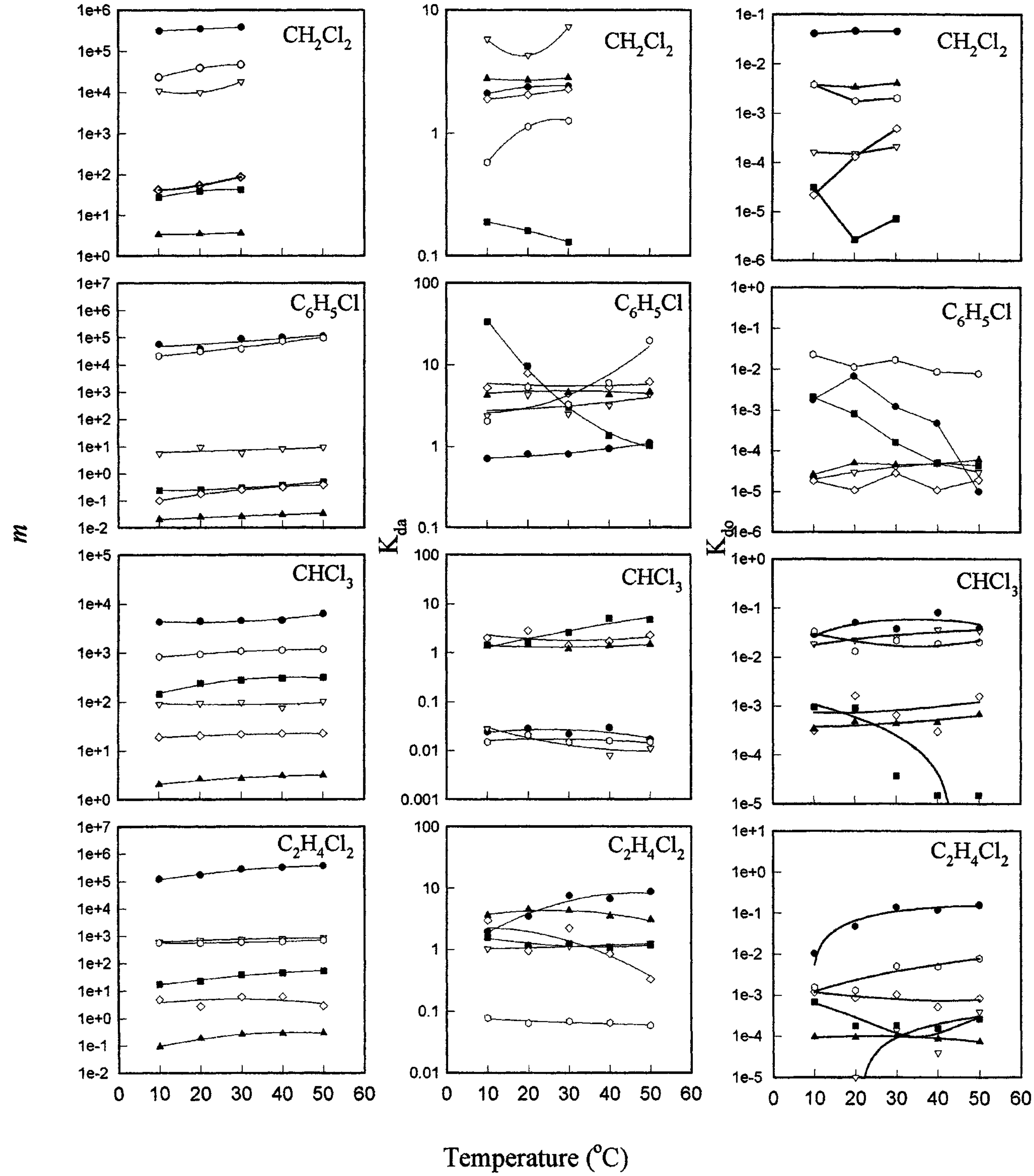

Figure 7. Temperature effect for m, K_{da}, and K_{do} for various kinds of solvents: (●) Aliquat 336; (○) TBA-TBPO; (■) TBPB; (▲) TBAC; (▽) TBAI; (◇) TBAB.

Table 1. Dissocation Constants in the Organic and Aqueous Phases

QX	$\log(k_{da})$	$\log(k_{da})$	Conditions	Reference
Et_4NI	$-6 \sim 0$		18 kinds of solvents	Abraham (1971)
R_4NX	$-3 \sim -5$		1,2-dichloroethane and 1.1-dichloromethane	Abraham and de Namor (1976)
R_4NBr		~ -1	10 wt % isopropanol/water mixture	Ansari and Islam (1988)
R_4NX	$-4 \sim -5$		CH_2Cl_2/water	Brändström (1982)
R_4Npicrate	$-3 \sim -4$		CH_2Cl_2/water	Beronius and Brändström (1976)
TBAX	$-1 \sim -5$	$0 \sim 1$	Organic solvent/water	This study

relationships can be expressed as

$$\text{Log } E_{QX} = a + b \cdot \text{HLB} \qquad \text{for cation} \qquad (28)$$

$$\text{Log } E_{QX} = c + d \cdot \text{HLB} + e \cdot \text{HLB}^2 + f \cdot \text{HLB}^3 \cdots \qquad \text{for anion} \qquad (29)$$

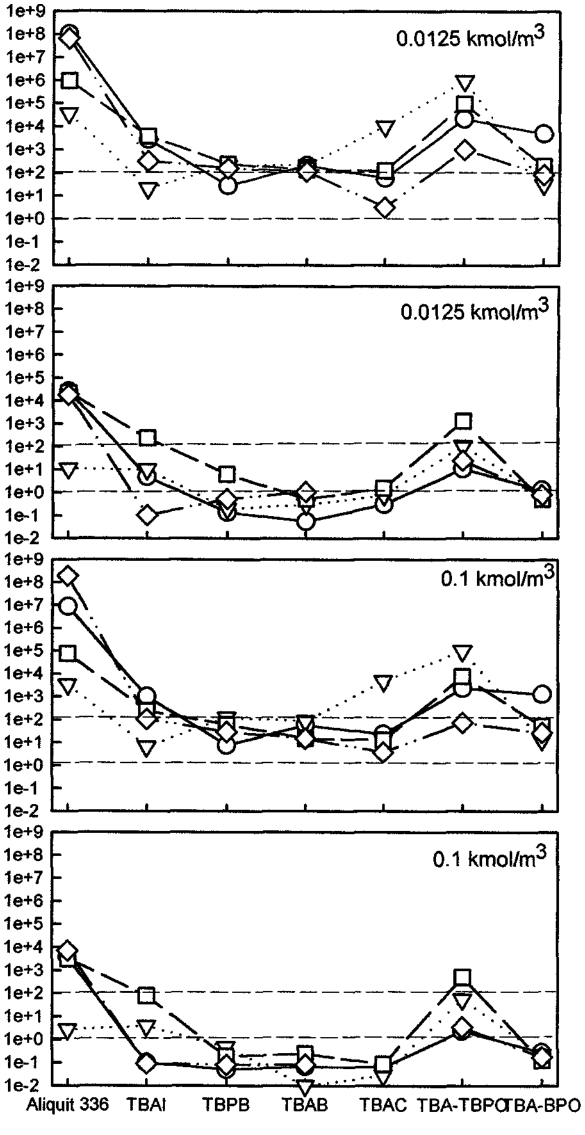

Figure 8. Ratio of free ions to ion-pair for various kinds of quaternary salts and temperature: (○) 10°C; (□) 20°C; (△) 30°C; (▽) 40°C; (◇) 50°C.

A linear relationship was observed for ammonium cations when the counteranion is identical (Eq. 28). The *a*-value strongly depends on the character of the cation. The *a* and *b* values for ammonium bromide ($RNEt_3Br$) are around 350 and −10.5 (that is, Log E_{QX} = 350−10.5·HLB). An average decrease in log E_{QX} is about 10.52 ± 2 units per HLB value for various counteranions. The nonlinear relationship (Eq. 29) observed for $(C_4H_9)_4NX$ can be displayed as

$$\text{Log } E_{QX} = 7.27 - 0.25 \cdot \text{HLB} + 2.1 \times 10^{-3} \cdot \text{HLB}^2 - 5.4 \times 10^{-6} \cdot \text{HLB}^3 \qquad (30)$$

By using Eqs. 28 and 29, the extraction constant E_{QX} can be predicted for various quaternary salts. However, if the

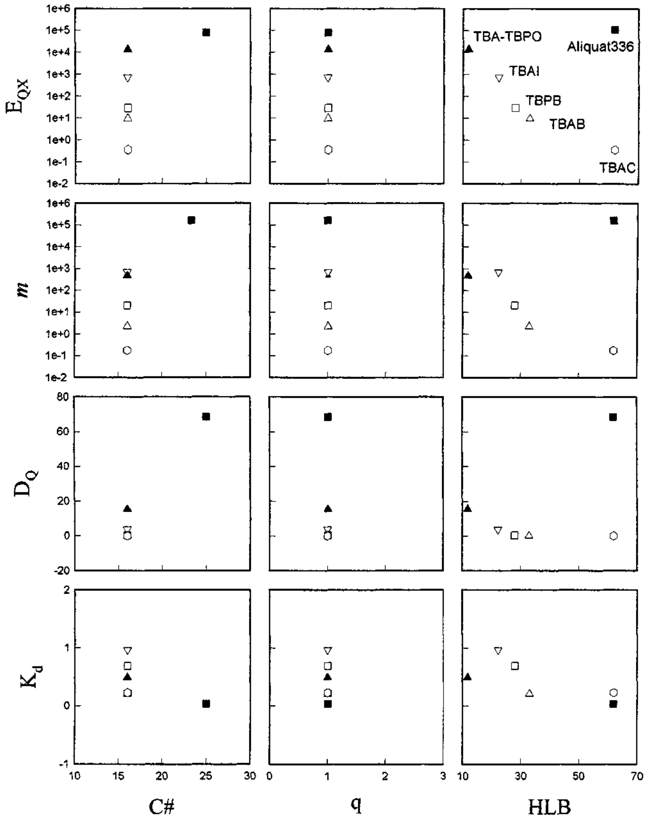

Figure 9. E_{QX}, m, D_Q and K_{da} vs. $C\#$, q and HLB for various kinds of quaternary salts: (■) Aliquat 336, (▲) TBA-TBPO, (□) TBPB, (○) TBAC, (▽) TBAI, (△) TBAB.

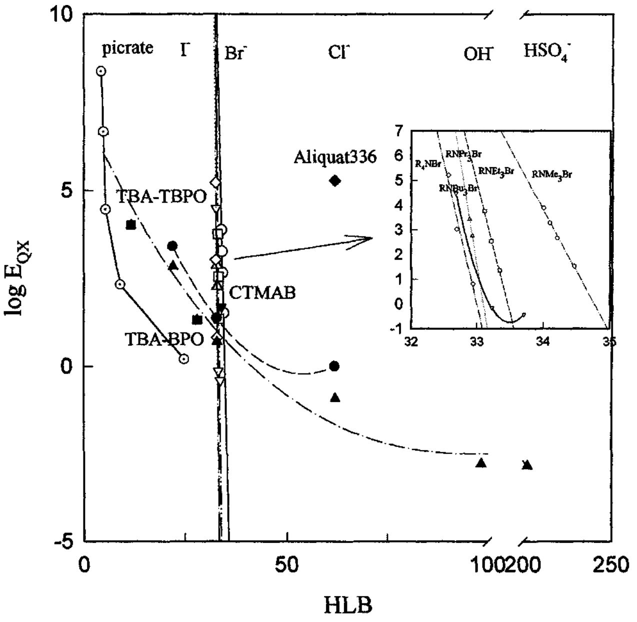

Figure 10. Log E_{QX} vs. HLB.

The experimental data were quoted from this study (● ▲ ■ ◆ ▼); Gustavii (1967) (⊙, R_4Npicrate); and Dehmlow and Dehmlow (1993) (○ □ △ ◇ ▽).

functional group of the unsymmetrical quaternary cation has one (or more) methyl (or hydrogen) group, the prediction error will be larger because the q-value is greater than one.

Free energy of transfer and dissociation constant

An extensive and self-consistent data set on the free energies of transfer of some inorganic salts has been reported (Abraham and de Namor, 1976). In this study, the free energy of the extraction constant, distribution constant, and dissociation constant are expressed as

$$\Delta G_i = -RT \cdot \ln(i); \qquad i = E_{QX}, E_{QX}^T, m, K_{da} \text{ or } K_{do} \quad (31)$$

Figure 11 displays ΔG_i values for various quaternary salts and four kinds of solvents. Figure 11a shows the data quoted from the report of Gustavii (1967). Bockries and Reddy (1980) indicated that the dissociation constant of quaternary salt increased when the dielectric constant of solvents is increased. Nagata (1975) reported that the logarithmic value of the association constant of quaternary salt was proportional to the reciprocal of the dielectric constant of the mixed solvent. According to Eq. 31 and Figure 11e, the dissociation constant was slightly decreased as the value of the reciprocal of the dielectric constant increased. Parker et al. (1978) demonstrated that the free energies of transfer are very useful in correlation with the solvent effects on S_N2 effects in phase-transfer catalysis. The free energies of transfer for the quaternary salts of dissociated ions from water to the solvent can be written as

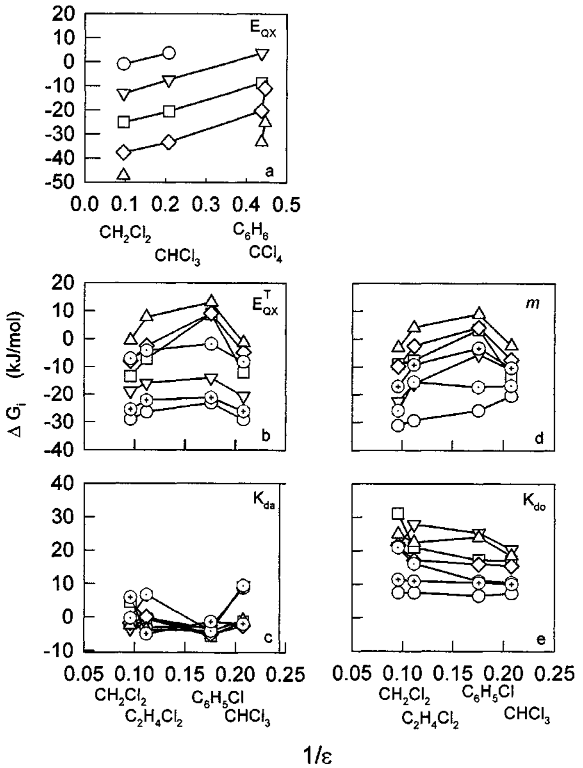

Figure 11. Transfer free energies and dissociated free energies on the reciprocal of dielectric constant.

(a) Extraction constant of quaternary ammonium picrates quoted from Gustavii, (1967) : (○) $N(CH_3)_4$; (△) $N(C_2H_5)_4$; (□) $N(n\text{-}C_3H_7)_4$; (▽) $N(n\text{-}C_4H_9)_4$; (◇) $N(n\text{-}C_5H_{11})_4$. (b)–(e) Calculated from this study: (○) Aliquat 336; (□) TBAI; (△) TBPB; (▽) TBAB; (◇) TBAC; (⊙) TBA-TBPO; (⊕) TBA-BPO.

$$\Delta G^t_{Q^+ + X^-} = -RT \cdot \ln\left(\frac{\bar{a}_{Q^+}}{a_{Q^+}} \frac{\bar{a}_{X^-}}{a_{X^-}}\right) = -RT \cdot \ln\left(E^T_{QX} \cdot K_{do}\right) \quad (32)$$

The free energies of transfer for free ions from water to the solvent can be written as

$$\Delta G^t_i = -RT \cdot \ln\left(\frac{\bar{a}_i}{a_i}\right) \qquad i = Q^+ \text{ or } X^- \quad (33)$$

Abraham (1971), Czapkiewicz et al. (1978), and Taft et al. (1985) have reported the free energies of transfer of $(C_nH_{2n+1})_4NX$ ($n = 1$–3) for ion pairs and dissociated ions. Table 2 lists the free energies of transfer for quaternary salts of ion pairs and dissociated ions from water to four kinds of organic solvents in this study. The free energies of transfer for ion pairs were smaller than those for dissociated ions. That is, the transfer ability of ion pairs was larger than that of dissociated ions. The result of the stronger cation–anion attraction in ion pairs significantly reduces the magnitudes of

Table 2. Free Energies of Transfer Data for Alkylammonium Halide of Ion Pairs and Dissociated Ions at 20°C

	ΔG_i^t (ion pairs, QX) (kJ/mol)							ΔG_i^t (dissociated ions, $Q^+ + X^-$) (kJ/mol)						
	Aliquat 336	TBPB	TBAI	TBAB	TBAC	TBA-TBPO	TBA-BPO	Aliquat 336	TBPB	TBAI	TBAB	TBAC	TBA-TBPO	TBA-BPO
CH_2Cl_2	−31.1	−8.95	−22.4	−9.74	−3.03	−25.7	−17	−21.55	17.7	2.5	13.72	24.394	−4.4	4.21
$C_2H_4Cl_2$	−29.3	−7.61	−16.1	−2.41	4.13	−15.4	−9.2	−18.89	13.81	12	14.57	30.27	−6	6.68
C_6H_5Cl	−25.7	3.38	−5.48	4.18	8.99	−25.2	−3.22	−16.49	26.1	11.31	36.95	37.1	−10.2	8.57
$CHCl_3$	−20.4	−13.3	−11	−7.36	−2.34	−16.7	−10.3	−21.86	4.9	−0.2	10.65	17.05	−15.6	8.57

Table 3. Free Energies of Transfer for Free Ions at 20°C

	Aliquat 336$^+$	TBA$^+$	TBP$^+$	I$^-$	Br$^-$	Cl$^-$	TBPO$^-$	BPO$^-$
CH_2Cl_2	−64.944 (−52.6)*	−19 (−19)*	−15.02	21.5 (23.7)*	32.72 (35.5)*	43.394 (43.6)*	14.6	23.21
$C_2H_4Cl_2$	−68.16	−19 (−23)**	−19.76	31 (25)†	33.57 (38)†	49.27 (52)†	13	25.68
C_6H_5Cl	−72.59	−19	−29.85	30.31	55.95	56.1	8.8	27.57
$CHCl_3$	−57.91	−19	−24.75	18.8	29.65	36.05	3.4	27.57

*Brändström (1982).

**Czapkiewicz et al. (1978).

†Marcus et al. (1988).

the endoergic solvent cavity terms, as well as the expergic anion−solvent attractive terms. The stability of quaternary salts for ion pairs was larger than that for dissociated ions from water to the organic phase. The result corresponds to that of Taft et al. (1985). The sequence of free energy of transfer for quaternary salts has three ways: (1) $P^+ > N^+$; (2) $TBPO^- < I^- < BOP^- < Br^- < Cl^-$; and (3) a long chain of the alkyl group is of low value (Aliquat 336 < TBAC). The stability of ion pairs in dichloromethane (or dissociated ions in chloroform) was the highest among the four kinds of solvents. These results reveal that the incremental charge localization in the anion and decrement in the cation increases the stability of quaternary salt in the organic phase. From Figure 2, the co-extracted water may stabilize ions and ion pairs through extensive interaction (Eqs. 25 and 26).

We supported setting set the free energy of TBA$^+$ ((n-$C_4H_9)_4N^+$) of −19.0 kJ/mol, calculated by Brändström (1982), as a starting point in the calculation of individual ΔG_i^t values. Meanwhile, assuming the free energy of TBA$^+$ is −19.0 kJ/mol in various kinds of solvents (may be different), we have given the result of such a calculation in Table 3. The results in this study correspond to those of Brändström (1982) when the solvent is dichloromethane. The free energy transfer for the tetra-n-butylphosphonium ions was larger than that for the tetra-n-butylammonium ion. The transfer ability of the quaternary cation or anion was different from remaining in various solvents.

Conclusion

Thermodynamic equilibrium parameters were obtained by a numerical iteration method. The calculated results compared well with the experimental results in the literature. The amount of coextracted water was related to the solubility of water in the organic phase. The extraction capability of quaternary salts was increased by decreasing the charge-volume ratio for the anion and increasing the charge-volume ratio for the central cation. The extraction of quaternary salts varied, and was without any obvious trend when temperature is increased. Most degrees of dissociation for quaternary salts in the organic and aqueous phases were less than 50%, and more than 98%, respectively, except for higher lipophilic quaternary salts (Aliquat 336, and TBA-TBPO). The equation of hydrophile−lipophile balance was developed to observe the extraction of quaternary salts between two phases based on the molecular weights of the hydrophilic and lipophilic groups. A linear relationship between the extraction constant and HLB was observed for ammonium cations. An average decrease in log E_{QX} is about 10.5 ± 2 units per HLB for various counteranions. The free energies of transfer for ion pairs and dissociated ions were determined and correspond to the experimental data in the literature.

Acknowledgment

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Notation

a = activity of quaternary salt in a solution
A = interfacial area between the organic and aqueous phase, m^2
Aliquat 336 = tricaprylmethylammonium chloride
C = concentration of quaternary salt
$C\#$ = number of carbon atoms in each of the four alkyl chains in the quaternary cation
D_Q = distribution coefficient of quaternary cation defined by Eq. 3
E_{QX} = apparent extraction constant defined by Eq. 4, (kmol/m^3)$^{-1}$
E_{QX}^T = true extraction constant defined by Eq. 5, (kmol/m^3)$^{-1}$
j = hydration number per quaternary salts in the organic phase
k = reaction-rate constant of the organic phase defined by Eq. 2, (kmol/m^3·s)$^{-1}$
k_{app} = apparent first-order reaction-rate constant defined by Eq. 1, s^{-1}
k_2 = forward reaction-rate constant of the aqueous phase defined by Eq. 2, (kmol/m^3·s)$^{-1}$

k_{-2} = reverse reaction-rate constant of the aqueous phase defined by Eq. 2, (kmol/m^3·s^{-1})
K_{da} = dissociation constant of QX in the aqueous phase, kmol/m^3
K_{do} = dissociation constant of QX in the organic phase, kmol/m^3
K_{QX} = overall mass-transfer coefficient of QX defined by Eq. 2, kmol/m^3·s^{-1}
m = distribution coefficient of onium salt defined by Eq. 6
M_H = molecular weight of hydrophilic group in quaternary salt (such as N^+X^-, OH)
M_{NX} = molecular weight of ionic group in quaternary salt (such as N^+X^-)
M_T = molecular weight of quaternary salt
$\mathrm{M_{TBAB}}$ = molecular weight of TBAB
MX = side product in the aqueous solution
MY = aqueous reactant
Q^+ = quaternary cation
QX = quaternary salt
RX = organic reactant
TBAB = tetra-*n*-butylammonium bromide
TBA-BPO = tetra-*n*-butylammonium 4-bromophenoxide
TBAC = tetra-*n*-butylammonium chloride
TBAI = tetra-*n*-butylammonium iodide
TBA-TBPO = tetra-*n*-butylammonium 2,4,6-tribromophenoxide
TBPB = tetra-*n*-butyl phosphonium bromide
V = volume of aqueous phase, m^3
X^- = anion

Greek letters

α = volume ratio (organic phase/aqueous phase)
ΔG = Gibbs free energy
δ = Hildebrand parameters
$\gamma_{\pm}$ = mean activity coefficient

Superscripts and subscripts

$\underline{T}$ = true value
$\overline{\quad}$ = the species in an organic phase
i = ith compound
I = initial value
obs = observe value

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