Equilibrium and extraction of quaternary salt in an organic solvent/alkaline solution: effect of NaOH concentration

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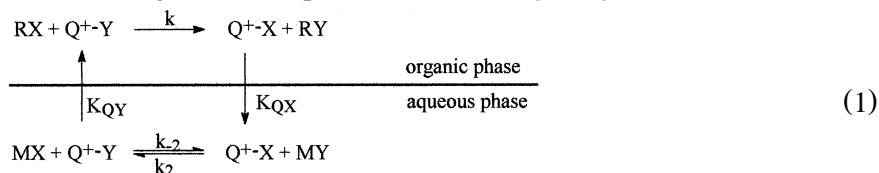
Abstract

This study measures the quaternary salt concentration in a dichloromethane (or chlorobenzene)/alkaline solution and determines the thermodynamic equilibrium data. The true extraction constant, distribution coefficient, dissociation constant in the aqueous phase and free energies of the true extraction constant, distribution coefficient and dissociation constant are obtained as well. The distribution coefficient increased and the real dissociation constant decreased with increasing NaOH concentration. The hydroxide ion concentration and the water content in the organic phase attain a maximum value when the NaOH concentration is around 6 M. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Phase-transfer catalysis; Thermodynamic equilibrium; Extraction; Distribution coefficient

1. Introduction

Phase-transfer catalysis (PTC) is an effective tool for synthesizing organic chemicals from two immiscible reactants [1,2]. Quaternary salts are in general used as phase-transfer catalysts. The reactivity in phase-transfer catalysis is controlled by (i) the reaction rate in the organic phase, (ii) the mass-transfer steps between the organic and aqueous phases, and (iii) the distribution equilibrium of the quaternary salts between the two phases. The distribution of quaternary salts between these two phases directly affects the entire system reactivity [3–5]. The extraction behavior and distribution coefficients of quaternary salts in various media have been investigated [6–15].

Starks et al. [2] offered a classical diagram of the phase-transfer catalytic cycle:

$$
\begin{array}{ccc}
RX + Q^+\text{-}Y & \xrightarrow{k} & Q^+\text{-}X + RY \\
\uparrow & & \downarrow \\
K_{QY} & & K_{QX} \\
MX + Q^+\text{-}Y & \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} & Q^+\text{-}X + MY
\end{array}
\qquad \text{organic phase} \atop \text{aqueous phase}
\tag{1}
$$

where Q is the phase-transfer catalyst and QY is an active catalyst.

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On the basis of the experimental data and earlier literature [1,2,16], a generalized approach describing the liquid–liquid phase-transfer catalyzed (LLPTC) reaction system uses a pseudo-first-order reaction. The rate expression is written as

$$-\frac{d\overline{[RX]}}{dt} = k_{app}\overline{[RX]} \tag{2}$$

$$k_{app} = k\overline{[QY]} \tag{3}$$

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

Previous works [16,17] indicated that the pseudo-steady-state LLPTC model could describe the complicated nature of LLPTC reaction. Hence, the catalysts are seen to be in both the organic phase and the aqueous phase in the pseudo-steady-state. That is,

$$\frac{d[QY]}{dt} \cong 0, \qquad \frac{d\overline{[QY]}}{dt} \cong 0, \qquad \frac{d[QX]}{dt} \cong 0, \qquad \frac{d\overline{[QX]}}{dt} \cong 0. \tag{4}$$

The rate equation from the report of Wu [16] is expressed as

$$d\frac{\overline{[RX]}}{dt} = \frac{k\overline{[RX]}Q_i/\overline{V}}{\dfrac{\alpha m_{QY}+1}{\alpha m_{QY}} + \left(\dfrac{Da_{QY}}{\alpha m_{QY}} + Da_{QX}\right) + (1+\alpha m_{QX})\left(\dfrac{Da_{QY}+1}{\alpha m_{QY}}\beta + \alpha\gamma\right)} \tag{5}$$

where Da_{QY} $(= k\overline{[RX]}/\{K_{QY}A/\overline{V}\})$ and Da_{QX} $(= k\overline{[RX]}/\{K_{QX}A/\overline{V}\})$ are Damkohler numbers of 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. (5), the parameters of kinetics, mass-transfer and thermodynamic equilibrium must be conducted. The aim of this work is to evaluate equilibrium and extraction of quaternary salt in an organic solvent/various alkaline solution.

Among the vast range of phase-transfer catalysis applications, the largest sector involves reacting anions that are reacted and/or generated under PTC conditions by deprotonation of acidic or moderately acidic organic compounds. PTC uses inexpensive and relatively safe bases such as NaOH and KOH, instead of the classical organic alkoxides, amides and hydrides, to generate these anions. Approximately 40% of PTC patents involve the hydroxide ion, and it has been estimated that approximately 60% of commercial PTC application involve the hydroxide ion [2]. To date, the extraction behavior and distribution coefficient of quaternary salts in various media in the presence of base have been scarcely investigated.

Our previous work [15] designed a numerical method to calculate the distribution coefficient between two phases and the dissociation constant of quaternary salt in the aqueous phase. This work using this method indicates the free energy of transfer of some quaternary salts from aqueous solution to dichloromethane (or chlorobenzene) based on distribution data of quaternary ammonium salts and assesses the extraction behavior of quaternary salts in the presence of NaOH to comprehend the phase-transfer-catalyzed reaction system.

2. Experimental

2.1. Materials

Tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium hydrogen sulfate (TBAHS), tetra-*n*-butylammonium hydroxide (TBAOH), tetra-*n*-butylammonium iodide (TBAI), tetra-*n*-butylphosphonium bromide (TBPB), solvents and other reagents are all reagent-grade chemicals.

2.2. Procedure

Quaternary salt (0.1 M) was prepared and mixed with an equal volume (25 cm^3) of organic solvent/water in a flask (125 cm^3). The flask was immersed in a thermostatic constant temperature water bath shaker. The shaking was performed 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 concentrations of quaternary salts were determined by extractive titration method using sodium tetraphenylborate as the titrant and tetrabromophenolphthalein ethyl ester potassium salt as the indicator [18,19]. The water content in the organic phase was measured by potential meter (Karl Fischer Titration). The water difference in the organic phase ($\Delta\overline{(H_2O)}$) equals subtracting the measured water content in a solvent (blank content) from that in the organic solution at equilibrium state (actual content). The OH$^-$ in the organic phase was first extracted into another aqueous phase ($> 98\%$ extracted). The hydroxide ion concentration in the aqueous phase was measured by the acid–base titration method.

3. Theoretical

The distribution coefficients of quaternary cation D_Q were obtained by measuring concentrations of quaternary cation (Q^+) in the organic and aqueous phase, respectively.

$$D_Q = \frac{\overline{[Q^+]}_{obs}}{[Q^+]_{obs}} \tag{6}$$

At equilibrium, the extraction coefficient is generally expressed

$$E_{QX}^R = \frac{\overline{[QX]}}{[Q^+][X^-]} \tag{7}$$

Apparent extraction coefficients E_{QX} were generally calculated from the distribution of the quaternary salts between water and various solvents [20].

$$E_{QX} = \frac{\overline{[Q^+]}_{obs}}{[Q^+]_{obs}^2} \tag{8}$$

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

$$E_{QX}^T = \frac{\overline{[QX]}}{[Q^+][X^-]\gamma_\pm^2} \tag{9}$$

where $\gamma_{\pm}$ denotes the mean ionic activity coefficient of quaternary salts. E_{QX}^{T} value was determined by extrapolating the dependence of $\log E_{QX}$ on the ionic strength of the aqueous phase to its zero value.

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

$$m = \frac{\overline{[Q^+X^-]}}{[Q^+X^-]} \tag{10}$$

The dissolved Q^+X^- in the aqueous phase may dissociate to

$$Q^+X^- \rightleftharpoons Q^+ + X^- \tag{11}$$

Thus, the dissociation constant K_d of QX in the aqueous phase is written as

$$K_d = \frac{[Q^+][X^-]\gamma_{\pm}^2}{[Q^+X^-]} \tag{12}$$

The mass balances of quaternary cation Q^+ in both phases can be displayed as

$$\overline{[Q^+]}_{obs} = \overline{[Q^+X^-]} \tag{13}$$

$$[Q^+]_{obs} = [Q^+X^-] + [Q^+] \tag{14}$$

From Eqs. (9), (10), (12)–(14), we can obtain

$$\frac{\overline{[Q^+]}_{obs}}{\sqrt{[Q^+]_{obs}}} = \frac{\sqrt{[Q^+]_{obs}}}{m} + \frac{1}{\gamma_{\pm}}\sqrt{\frac{K_d}{m}} \tag{15}$$

or

$$\frac{\overline{[Q^+]}_{obs}}{\sqrt{[Q^+]_{obs}}} = \frac{\sqrt{[Q^+]_{obs}}}{m} + \frac{1}{\gamma_{\pm}\sqrt{E_{QX}^{T}}} \tag{16}$$

The true extraction constants on various quaternary salts can be calculated by obtaining the intercept of $\overline{[Q^+]}_{obs}/\sqrt{[Q^+]_{obs}}$ vs. $\sqrt{[Q^+]_{obs}}$ by least-squares regression (Fig. 5). From Eqs. (10), (12) and (16), the distribution coefficients m of quaternary salt between both phases and the dissociation constants K_d of quaternary salts in the aqueous phase are obtained.

The equilibrium state of the ion-exchange reaction in the two-phase system is expressed as

$$\overline{Q^+X^-} + Y^- \rightleftharpoons \overline{Q^+Y^-} + X^- \tag{17}$$

The selectivity coefficient $K_{Y|X}^{sel}$ is defined as

$$K_{Y|X}^{sel} = \frac{\overline{[Q^+Y^-]}[X^-]}{\overline{[Q^+X^-]}[Y^-]} \tag{18}$$

4. Results and discussion

The functional groups of the quaternary salts generally influence the dissolution of the catalyst in the organic phase. Furthermore, the phase transfer of the anion also influences the reaction rate in PTC. Therefore, properly selecting the quaternary salt is crucial in promoting the reaction rate. Five

types of phase-transfer catalysts (TBPB, TBAB, TBAI, TBAOH and TBAHS) are frequently employed in PTC. The abbreviations of quaternary salts are defined in experimental section. The extremely lipophilic or hydrophilic groups of quaternary cations are discussed in future work.

Polar solvents, e.g., dichloromethane, 1,2-dichloroethane, chlorobenzene, chloroform, toluene and *n*-hexane, are normally used as the solvent in PTC. The organic reaction rate increases with increasing polarity of solvent. Hence, dichloromethane and chlorobenzene usually are used in PTC.

The base can play four crucial roles in PTC (i) reactant; (ii) deprotonating the aqueous reactant to become the reactive form; (iii) salting out the intermediate product of catalyst QY from aqueous phase to organic phase; or (iv) reducing the solvation of catalyst and water to upgrade the reactivity of active catalyst in the organic phase. The base concentration influences and determines the PTC reaction rate. Therefore, we discuss the extractive behavior of quaternary salt between two phases with the base concentration in the following.

Fig. 1 presents the hydroxide ion concentration and water content in the organic phase at various initial NaOH concentrations in the range of 0 to 10 M in the absence of quaternary salt in a dichloromethane (Fig. 1a and b) and chlorobenzene (Fig. 1c)/alkaline solution. The water content in the organic phase decreased with increasing initial NaOH concentration. The water content in dichloromethane exceeded that in chlorobenzene. The hydroxide ion concentration in the organic phase was too low to measure unless the concentration of NaOH was in the range from 5 to 10 M in the dichloromethane/alkaline solution. The hydroxide ion concentration was low, ranging between 10^{-4} and 10^{-5} M. In addition, the hydroxide ion concentration and water content were slightly increased with a temperature increase.

Figs. 2 and 3 display the distribution coefficient of quaternary cation, water difference ($\Delta\overline{[H_2O]}$) and hydroxide ion concentration in the organic phase vs. the initial NaOH concentration for various phase-transfer catalysts in a dichloromethane and chlorobenzene/aqueous system, respectively. The water difference in the organic phase ($\Delta\overline{[H_2O]}$) equals subtracting the measured water content in a solvent (blank content) from that in the organic solution at equilibrium state (actual content). The quaternary salt concentration remains constant (0.1 M). In dichloromethane, the orders for the
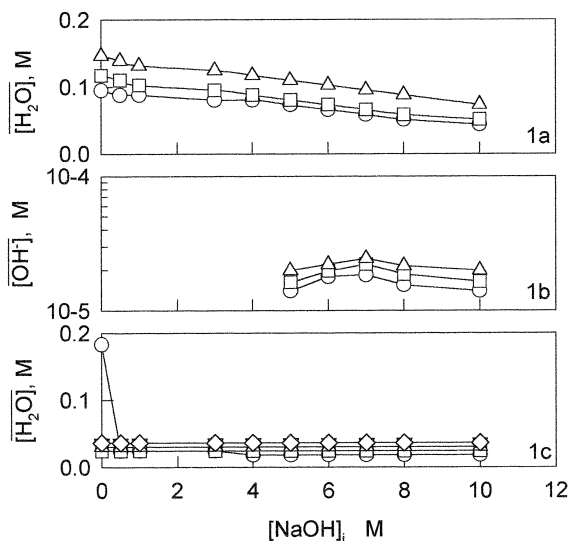

Fig. 1. Distribution coefficients and water contents on the initial concentration of NaOH for various temperatures [(a,b) dichloromethane; (c) chlorobenzene]: (○) 10℃; (□) 20℃; (△) 30℃.

Fig. 2. Distribution coefficients, water differences and hydroxide ion concentration on the initial concentration of NaOH for various kinds of quaternary salts and temperatures in dichloromethane (catalyst = 0.1 M): (○) 10°C; (□) 20°C; (△) 30°C.

distribution coefficient of quaternary cation, water difference and hydroxide ion concentration are TBAI > TBPB > TBAB > TBAOH > TBAHS, TBAHS > TBAOH > TBAB > TBPB > TBAI, and TBAHS > TBAOH > TBAB ≈ TBPB ≈ TBAI, respectively. In chlorobenzene, the orders for the
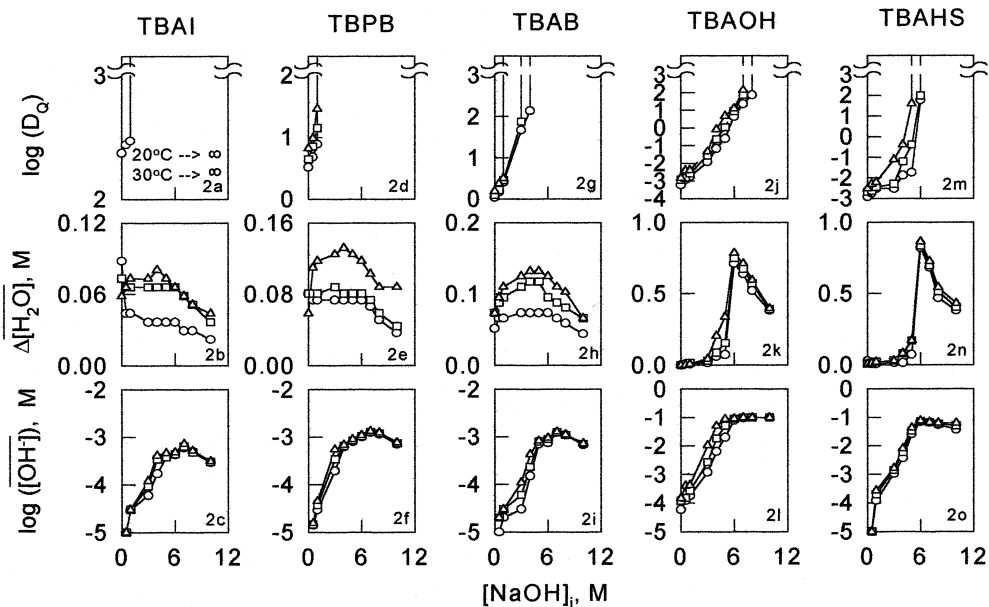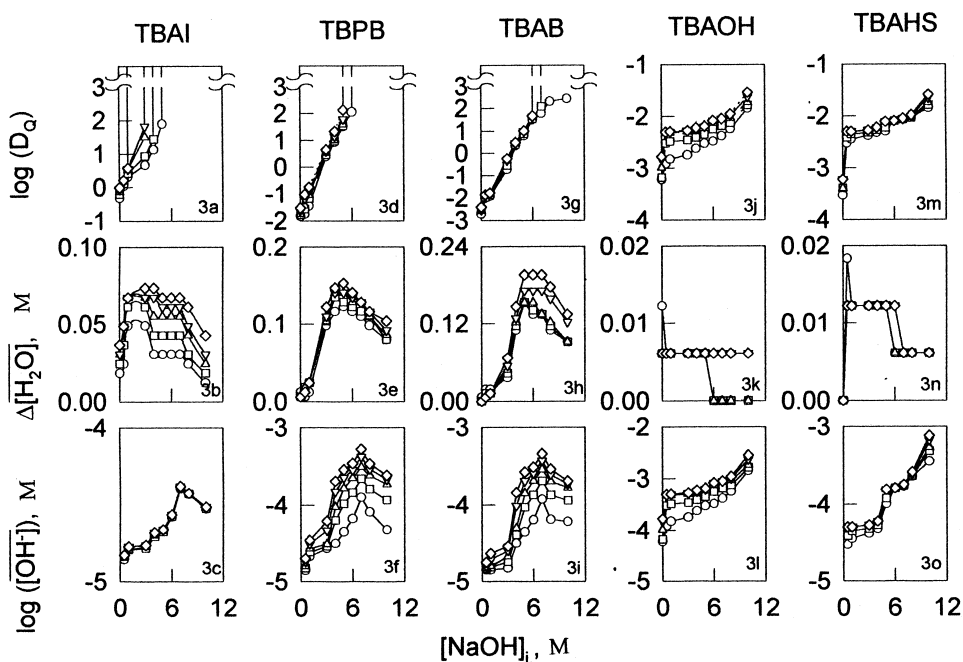

Fig. 3. Distribution coefficients, water differences and hydroxide ion concentration on the initial concentration of NaOH for various kinds of quaternary salts and temperature in chlorobenzene (catalyst = 0.1 M): (○) 10°C; (□) 20°C; (△) 30°C; (▽) 40°C; (◇) 50°C.

distribution coefficient of quaternary cation, water difference and hydroxide ion concentration are TBAI > TBPB > TBAB > TBAOH ≈ TBAHS,   > TBAB > TBPB > TBAI > TBAHS ≈ TBAOH, and TBAHS ≈ TBAOH > TBAB ≈ TBPB > TBAI, respectively. For TBAI, TBPB and TBAB, the distribution coefficients of quaternary cation dramatically increased with increasing NaOH concentration. Moreover, the quaternary salt is almost entirely in the organic phase when the NaOH concentration exceeds 3 M in dichloromethane or 5 M in chlorobenzene. The water difference and the hydroxide ion concentration increased up to 6 M [NaOH], and decreased when the NaOH concentration exceeded 6 M. For TBAOH and TBAHS, the distribution coefficients of quaternary salts increased with increasing NaOH concentration. Moreover, the quaternary salt is almost entirely in the organic phase when the NaOH concentration exceeded 6 M. The water difference attained a maximum value at 0.8 M in dichloromethane, and a lower value in chlorobenzene when the NaOH concentration increased. The hydroxide ion concentration increased when the NaOH concentration increased. It did not have a maximum value. The distribution coefficient, hydroxide ion concentration and water difference in dichloromethane (more polar solvent) surpassed those in chlorobenzene. The operating temperature for dichloromethane and chlorobenzene ranged from 10–30°C and 10–50°C, respectively. According to Figs. 2 and 3, the temperature only slightly influenced this two-phase equilibrium system. The orders of influencing extraction capability are $I^- > Br^- > OH^- > HSO_4^-$ and $P^+ > N^+$ for anion and central cation, respectively. The lipophilicity of anion was crucial in promoting the extraction of quaternary salt. Previous works [9,11] has discussed reasons for these behaviors.

The significance of the selectivity coefficient in phase-transfer catalyzed-reaction system has been discussed [5,20–24]. The concentration of quaternary salt distributed between these two phases directly reflects the reactivity of the entire systems, e.g., concentration distribution is related to the distribution of the anions Y^- and X^- competing for the cation Q^+ in the aqueous-organic two-phase system (Eq. (17)). According to Fig. 4, the $K_{OH|X}^{sel}$ values are extremely small and lower then 10^{-3}.
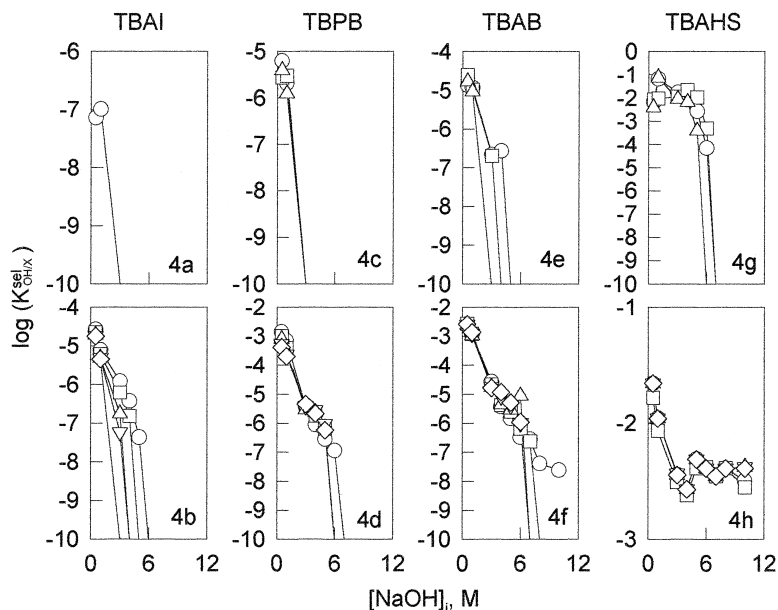

Fig. 4. $K_{OH|X}^{sel}$ values on the initial concentration of NaOH for various kinds of quaternary salts and temperature (above, dichloromethane; below, chlorobenzene): catalyst = 0.1 M; (○) 10°C; (□) 20°C; (△) 30°C; (▽) 40°C; (◇) 50°C.

The concentration of QX in the organic phase is nearly 100-times larger than that of hydroxide ion in the organic phase (Figs. 2 and 3). Hence, the hydroxide ion associated with the quaternary cation in the organic phase can be neglected in PTC when the lipophilic anion is added in the two phases.

Landini et al. [25] indicated that the solvation of quaternary salts and water could reduce the reactivity of quaternary salts in the organic phase in a PTC reaction. This finding is confirmed in previous work [3,11]. In our previous study, the water content in the organic phase was around 1.3 mole per mole quaternary salt when the concentration of quaternary salt was 0.1 M in the absence of NaOH. From Figs. 2 and 3, the water contents for TBAHS and TBAOH dramatically increased with NaOH concentration rise. The water content per mole quaternary salt exceeded 5. This finding reveals that the capability of solvation between TBAOH and water is large. However, the water contents per mole quaternary salt for TBAI, TBPB and TBAB were slightly decreased although the hydroxide ion concentration in the organic phase increased.

Previous works [3,19,26] reported that increasing free concentration of NaOH with respect to aqueous reactant increased the apparent reaction rate constant. A decrease in the apparent reaction rate constant was, however, observed when the concentration of NaOH was more than 7 M. According to this experimental result (Figs. 2 and 3), the water difference and hydroxide ion concentration in the organic phase have maximum values when the NaOH concentration is around 6 M. The organic environment is altered by the NaOH concentration. Hence, the decreasing phenomenon in PTC is clearly accounted for when the NaOH is more than 7 M.

From Eq. (9), Table 1 depicts the true extraction constants on various quaternary salts and temperatures in dichloromethane and chlorobenzene, respectively by obtaining the intercept of $[Q^+]_{obs}/\sqrt{[Q^+]_{obs}}$ vs. $\sqrt{[Q^+]_{obs}}$ in Fig. 5 by least-squares regression. The relationship of E_{QX} and $\sqrt{[Q^+]_{obs}}$ is obtained and expressed as

$$E_{QX} = \left(\frac{\sqrt{[Q^+]_{obs}}}{[Q^+]_{obs}} \right)^2 = \left(p\sqrt{[Q^+]_{obs}} + q \right)^{-2} \qquad (19)$$

Table 1 lists the p, q and E_{QX}^T values. The p values are all negative. The experimental data was carried out when the NaOH concentration was smaller than 1 M. The linear relationships of Eq. (19) for TBAHS and TBAOH are not good for each case. The quaternary salt's concentration was too low

Table 1
True extraction constants on various quaternary salts and temperatures in a chlorobenzene/aqueous solution

Solvent	T (°C)	TBAI		TBPB		TBAB		TBAHS	
		p	E_{QX}^T [a]	p	E_{QX}^T [a]	p	E_{QX}^T [a]	p	E_{QX}^T [a] ($\times 10^{-3}$)
CH$_2$Cl$_2$	10	−2.81	1.27	−2.21	2.05	−2.35	1.69	−529.6	4.58
	20	–	–	−2.15	2.16	−2.34	1.81	−520.8	4.78
	30	–	–	−2.09	2.28	−2.48	1.84	−254.6	9.75
C$_6$H$_5$Cl	10	−2.80	1.34	−59.6	0.041	−213.2	0.010	–	–
	20	−2.61	1.51	−29.0	0.085	−166.8	0.013	–	–
	30	−2.55	1.58	−23.8	0.099	−156.1	0.014	–	–
	40	−2.46	1.68	−21.5	0.107	−151.2	0.014	–	–
	50	−2.59	1.56	−16.2	0.146	−126.9	0.018	–	–

[a] E_{QX}^T ($= q^{-2}$) values were determined by Eq. (10) and Fig. 5.
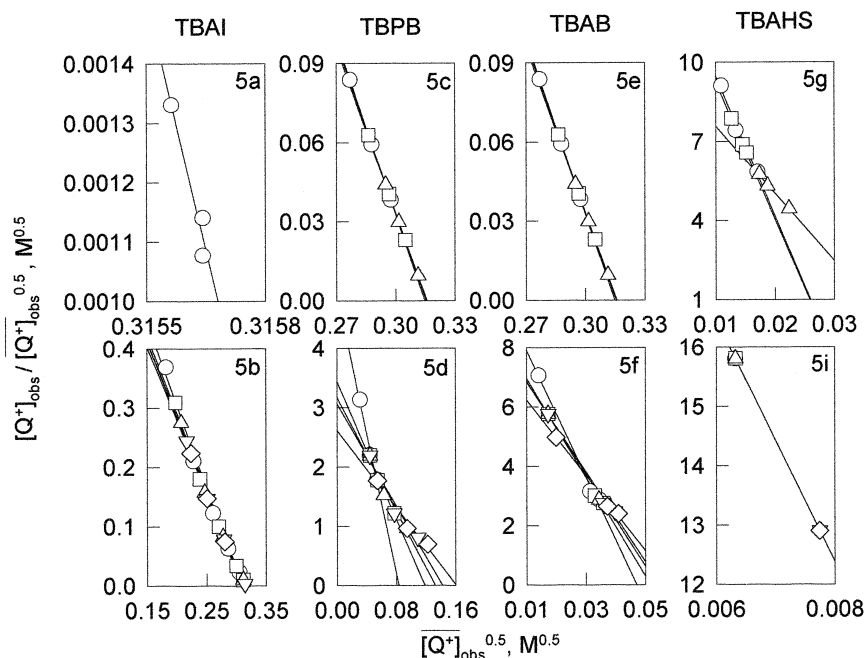
Fig. 5. Plot of $[Q^+]_{obs}/\sqrt{[Q^+]_{obs}}$ vs. $\sqrt{[Q^+]_{obs}}$ for various kinds of quaternary salts and temperatures: (○) 10°C; (□) 20°C; (△) 30°C; (▽) 40°C; (◇) 50°C.

to calculate the equilibrium data. The E_{QX}^T in this study are at least 10-fold larger than those in the absence of NaOH in previous work [15].

An extensive and self-consistent set of data on free energies, enthalpies and entropies of transfer of some inorganic salts has been reported [27]. In this study, the free energy of transfer of quaternary salt from one phase to another is related to E_{QX}^T through the expression

$$\Delta G_E = -RT \ln E_{QX}^T \tag{20}$$

Table 2 lists ΔG_E values for various quaternary salts in dichloromethane and chlorobenzene. Above results in general indicate that the free energies of both anion and cation in dichloromethane are smaller than that in chlorobenzene.

Eq. (15) is identical to that derived by Asai et al. [8] based on the ideal solution, i.e., $\gamma_\pm = 1$. If the method of Asai et al. was used to describe this equilibrium system, the results are presented in Fig. 5 that the slopes are negative. However, the mean activity coefficient $\gamma_\pm$ is not equal to one in the real solution, even in an alkaline solution. In addition, as well known, the slope must be positive ($m > 0$) and quaternary salt nearly dissociated in the aqueous phase. Hence, the slope in Fig. 5 cannot directly represent the distribution coefficient reciprocally. The calculated method for real system has been

Table 2
Free energies for true extraction constants on various quaternary salts at 20°C

Solvent	ΔG_E			
	TBAI	TBPB	TBAB	TBAHS
CH_2Cl_2	–	−1.3	−1.02	9.1
C_6H_5Cl	−0.7	4.23	7.45	–

Table 3
True dissociation constants and distribution coefficients on various temperatures

Solvent	T (°C)	TBAI		TBPB		TBAB		TBAHS	
		m	K_d	m	K_d	m	K_d	m	K_d ($\times 10^3$)
CH_2Cl_2	10	1 337 822	1 056 126	291.7	142.0	243.0	133.9	0.087	18.97
	20	–	–	405.8	187.3	322.7	175.3	0.091	19.10
	30	–	–	805.0	352.6	486.9	288.3	0.099	10.14
C_6H_5Cl	10	45.45	33.92	0.17	4.34	0.27	27.5	–	–
	20	86.47	57.27	0.12	1.47	0.21	15.5	–	–
	30	191.4	121.3	0.18	1.84	0.205	14.6	–	–
	40	255.5	152.3	0.29	2.68	0.202	14.1	–	–
	50	294.9	189.1	0.42	2.88	0.197	11.1	–	–

studied in our previous work [15], which considered $\gamma_{\pm} \neq 1$. The method can easily solve the distribution coefficient of a catalyst between both phases and the dissociation constant of quaternary salt in the aqueous phase using the relationship of Eqs. (16) and (19), and p and q values. This study employed the method to solve the distribution coefficient and dissociation constant. The true extraction constants of hydrophilic quaternary salts TBAHS are larger than one. The apparent extraction constant dramatically increases with an increasing initial NaOH concentration. Thus, the concentration of quaternary salt is gradually saturated in the aqueous phase (Figs. 2 and 3). The true extraction constants increase when the temperature increases.

By using the relationship of Eqs. (16) and (19), and p and q values, we can easily obtain the distribution coefficients m of quaternary salt between both phases and the dissociation constants K_d of quaternary salts in the aqueous phase. The calculated results are listed in Table 3. The distribution coefficients m for lipophilic quaternary salts (TBAI, TBPB and TBAB) are much larger than those for hydrophilic quaternary salts (TBAHS). The tendency of QX to extract into the organic phase and the tendency of QX to dissociate into $Q^+ + X^-$ go in opposite directions when QX is a hydrophilic compound. However, the tendency would change when QX is a more lipophilic compound or the organic solvent is of more polarity. Ansari and Islam [28] reviewed the conductimetric studies of ionic association of tetraalkylammonium halides in isopropanol/water mixtures. They obtained that the overall association behavior of quaternary salts has been found to increase with decrease in dielectric constant of the medium, and the order of the dissociation constant of quaternary salt was around 10^{-1} in 10 wt.% isopropanol/water mixture. Hence, the experimental results in Table 3 are reasonable. The true dissociation constants on various quaternary salts in the absence of NaOH are smaller than those in the presence of NaOH. However, the real dissociation constants on various quaternary salts in the absence of NaOH are larger than those in the presence of NaOH. The degree of dissociation of quaternary salt decreased with a NaOH concentration rise. In addition, the degree of dissociation of quaternary salt exceeded 98% herein when the NaOH concentration was low (< 1 M). Quaternary salt

Table 4
Free energies for distribution coefficients and dissociation constants on various quaternary salts at 20°C

Solvent		TBAI	TBPB	TBAB	TBAHS
CH_2Cl_2	ΔG_m (kcal/mol)	–	-10.3	-9.9	4.12
	ΔG_{K_d} (kcal/mol)	–	-8.98	-8.87	6.80
C_6H_5Cl	ΔG_m (kcal/mol)	-7.66	3.64	2.68	–
	ΔG_{K_d} (kcal/mol)	-6.95	-0.66	-4.7	–

nearly dissociates in the aqueous phase. ΔG_m and ΔG_{K_d} values on various quaternary salts in dichloromethane and chlorobenzene were calculated by Eq. (20) and listed in Table 4

5. Conclusion

The concentration of QX in the organic phase is nearly 100-times larger than that of hydroxide ion concentration in the organic phase. The water contents for TBAHS and TBAOH were dramatically increased with a NaOH concentration rise. The water content per mole of quaternary salt exceeded 5. The water difference and the hydroxide ion concentration in the organic phase have maximum values when the NaOH concentration was around 6 M. These results can explain the complicate phenomenon in PTC reaction. The equilibrium data (distribution coefficient, dissociation constant, extraction constant, selectivity and free energy) is obtained to understand the availability of phase-transfer catalyst in PTC. In addition, they can be seen as parameters to establish the reaction modeling in PTC.

6. Nomenclature

A	interfacial area between the organic and aqueous phase (m^2)
D_Q	distribution coefficient of quaternary cation defined by Eq. (6)
E_{QX}	apparent extraction constant defined by Eq. (8) (M^{-1})
E_{QX}^R	real extraction constant define by Eq. (7) (M^{-1})
E_{QX}^T	true extraction constant defined by Eq. (9) (M^{-1})
K_d	dissociation constant of QX in the aqueous phase (M)
K_{QY}	overall mass transfer coefficient of QY $(1 \, min^{-1})$
m	distribution coefficient of quaternary salt defined by Eq. (10)
p	slope of Eq. (19)
q	intercept of Eq. (16)
Q^+	quaternary cation
RX	chemical reactant
RY	chemical product
TBAB	tetra-*n*-butylammonium bromide
TBAHS	tetra-*n*-butylammonium hydrogen sulfate
TBAOH	tetra-*n*-butylammonium hydroxide
TBAI	tetra-*n*-butylammonium iodide
TBPB	tetra-*n*-butyl phosphonium bromide
X^-	anion

Greeks

α	volume ratio (oil/water)
$\gamma_{\pm}$	mean activity coefficient

Superscripts

T	true value
‾ (overbar)	species in the organic phase

Subscripts

cal	calculated value
i	ith compound
I	initial value
obs	observed value
QX	quaternary salt for anion X
QY	quaternary salt for anion Y

Acknowledgements

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