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# Solvent Effects on Ion-Pair Distribution and Dimerization of Tetraalkylammonium Salts

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**Summary.** The distribution of tetraalkylammonium ions $(C_nH_{2n+1})_4N^+$ ($R^+$, $TAAn^+$, $n = 4$–7) with picrate ion ($pic^-$) and inorganic anions $X^-$, ($Cl^-$, $Br^-$, $ClO_4^-$), into various inert organic solvents was studied at 25.0°C. The distribution data were analyzed by taking into consideration the distribution of ion pairs, $R^+ \cdot X^-$, and the dimerization of the ion pairs, $(R^+ \cdot X^-)_2$, in the organic phase. The ion-pair, distribution constant, $K_{dist}$, increases with increasing chain length of the tetraalkylammonium ion and with increasing ionic radius of the anion. The values of $K_{dist}$ show a good correlation with the $E_T$ value of solvent, *i.e.* the solvation ability with respect to the anion, and smoothly increase with increasing $E_T$. The effect of the solvent on the dimerization constants, $K_{dim}$, is markedly different between the ion pairs of picrate ion and inorganic anions. In the case of picrate, $K_{dim}$ significantly decreases with decreasing length of the alkyl chain of the tetraalkylammonium ion, but hardly changes by changing the solvent. On the other hand, in the case of ion pairs of inorganic anions the value of $K_{dim}$ decreases with decreasing $E_T$ and is almost constant for all anions. These results were reasonably explained by the difference of the solvation of the anion moieties of the monomeric and dimeric ion pairs.

**Keywords.** Anions; Cations; Electrolytes; Equilibrium; Solvent effect.

## Introduction

Tetraalkylammonium ($TAAn^+$) salts with short alkyl chains, such as methyl and ethyl groups, are the most common electrolytes for non-aqueous solvents, and their thermodynamic properties in a variety of solvents have been studied. $TAAn^+$ salts with long alkyl chains are quite popular as cationic surfactants and ion-pair extraction reagents. Various kinds of $TAAn^+$ salts have been used for the separation and determination of anionic compounds and complexes [1], and the fundamental data of the distribution equilibria and the thermodynamic properties of these ion pairs have extensively been collected [2]. It has been reported that the logarithmic distribution constants of ion pairs, $\log K_{dist}$, is approximately given by the sum of the contributions of cation and anion and that $\log K_{dist}$ linearly correlates with the number of the methylene groups of the tetraalkylammonium ion [3–5]. The mechanism of ion-pair distribution, however, is not so simple. Although the electrolytes are present in a form of ion pair in low permittivity ($\varepsilon$) solvents, the

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dissociation of the ion pair must be taken into consideration even in relatively low permittivity solvents such as 1,2-dichloroethane ($\varepsilon = 10.4$) [6–11]. Thus, the distribution of ion pairs has been reasonably rationalized by two elemental steps: the distribution of each ion from aqueous phase to organic phase and the ion-pair formation in the organic phase [9, 10].

In addition to ion-pair dissociation, the formation of higher aggregates of ions such as triple and quadruple ions is important in low $\varepsilon$ solvents [6, 7, 10]. In a previous paper, we have studied the dimerization of ion pairs (quadruple ions) of a series of tetraalkylammonium salts in xylene and reported the effects of the chain length of $TAAn^+$ and of the ion size of counter anions [10]. Thus, the elucidation of side reactions of electrolytes in organic solvents, such as ion-pair dissociation and aggregation, is quite important not only from the viewpoint of solution thermodynamics but also for the exact treatment of the distribution data.

In the present investigation, the distribution of tetraalkylammonium salts into various organic solvents was studied, and the effects of the solvent and of the structure of the electrolyte on the distribution and dimerization equilibria of ion pairs are discussed.

## Results and Discussion

### *Distribution equilibria*

The distribution equilibrium of monomeric ion pairs of tetraalkylammonium ion $TAAn^+$ ($R^+$) with counter anions ($X^-$) is given by

$$R^+ + X^- \overset{K_{\text{dist}}}{\rightleftharpoons} R^+ \cdot X^-_{,\text{org}} \tag{1}$$

where the subscript 'org' refers to the organic phase. The distribution constant, $K_{\text{dist}}$, of the ion pair $R^+ \cdot X^-$ is defined by

$$K_{\text{dist}} = \frac{[R^+ \cdot X^-]_{\text{org}}}{[R^+][X^-]} \tag{2}$$

where the square brackets denote the equilibrium concentration in solution. The distribution ratio of $R^+$, $D$, is obtained from the total concentrations of $R^+$ in the organic phase, $C_{R^+,\text{org}}$ and in the aqueous phase, $C_{R^+}$, as $D = C_{R^+,\text{org}}/C_{R^+}$. As the side reactions for $R^+$ and $X^-$ in the aqueous phase are negligible, the equilibrium concentrations $[R^+]$ and $[X^-]$ are given by the total concentrations $C_{R^+}$ and $C_{X^-}$, respectively. If we assume the distribution of a monomeric species $R^+ \cdot X^-$ into the organic phase, the equilibrium concentration of the ion pair, $[R^+ \cdot X^-]_{\text{org}}$, is equal to the total concentration of $R^+$ in the organic phase, $C_{R^+,\text{org}}$. Thus,

$$\log D - \log C_{X^-} = \log K_{\text{dist}} \tag{3}$$

The distribution ratio of the tetraalkylammonium ion $(C_nH_{2n+1})_4N^+$ ($R^+$, $TAAn^+$, $n = 4$–$7$) with an anion $X^-$ (picrate ion ($pic^-$) or inorganic anion ($Cl^-$, $Br^-$, $ClO_4^-$)) into an inert organic solvent (chloroform, bromobenzene, chlorobenzene, 1,1,1-trichloroethane, benzene, toluene, xylene, carbon tetrachloride, *n*-hexane) was measured as a function of $TAAn^+ \cdot X^-$ concentration. Results (plots of $\log D - \log C_{X^-}$ *vs.* $\log C_{R^+,\text{org}}$) are shown in Fig. 1 (distribution of various kinds of

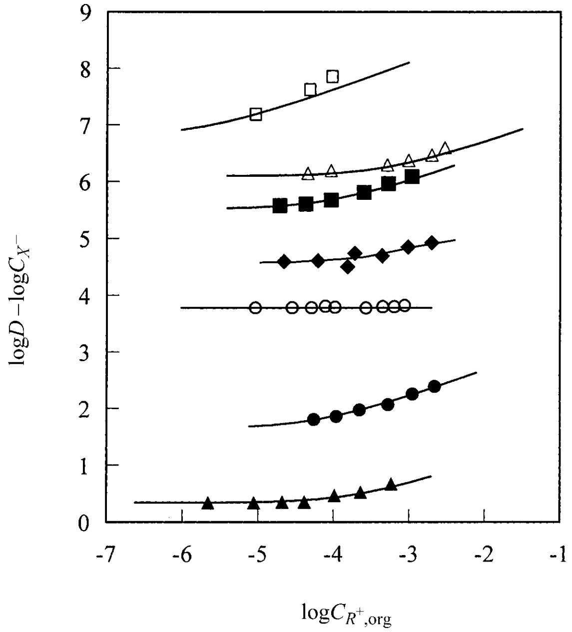

**Fig. 1.** Plot of $\log D - \log C_{X^-}$ as a function of $\log C_{R^+,\mathrm{org}}$ in benzene; $R^+ \cdot X^-$: □, *TAA*$6^+ \cdot$*pic*$^-$; △, *TAA*$5^+ \cdot$*pic*$^-$; ○, *TAA*$4^+ \cdot$*pic*$^-$; ■, *TAA*$6^+ \cdot \mathrm{ClO_4^-}$; ◆, *TAA*$7^+ \cdot \mathrm{Br}^-$; ●, *TAA*$6^+ \cdot \mathrm{Br}^-$; ▲, *TAA*$6^+ \cdot \mathrm{Cl}^-$; solid lines are the normalized curves (see text)

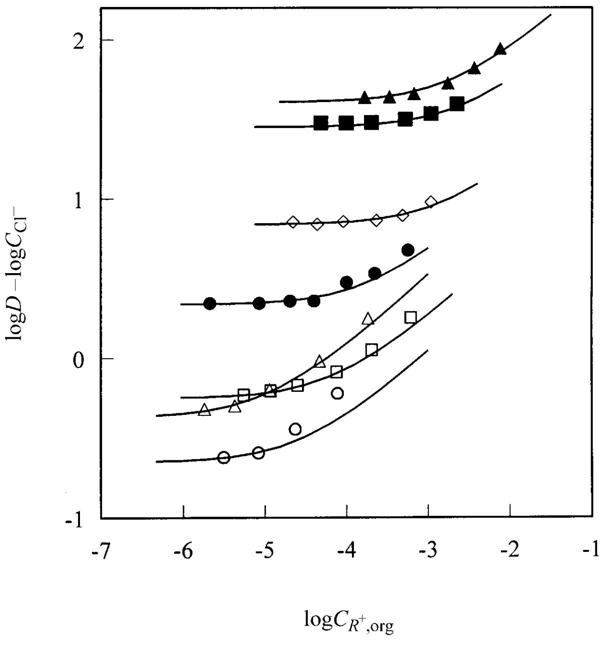

**Fig. 2.** Plot of $\log D - \log C_{\mathrm{Cl}^-}$ as a function of $\log C_{R^+,\mathrm{org}}$ for the *TAA*$6^+ \cdot \mathrm{Cl}^-$ system; □, toluene; △, xylene; ○, carbon tetrachloride; ◇, 1,1,1-trichloroethane; ■, chlorobenzene; ●, benzene; ▲, bromobenzene; solid lines are the normalized curves

$R^+ \cdot X^-$ into benzene) and Fig. 2 (distribution of $TAA6^+ \cdot \mathrm{Cl}^-$ into various solvents) as examples. Similar results were obtained for other $TAAn^+ \cdot X^-$ and solvent systems.

By the assumption of the presence of only a monomeric species in the organic phase, the value of $\log D - \log C_{R^+}$ ($\log K_{\mathrm{dist}}$) must be constant, irrespective of $[R^+ \cdot X^-]$, *i.e.* $\log C_{R^+,\mathrm{org}}$ (Eq. (3)). Nevertheless, the slope of the plot increases with increasing $\log C_{R^+,\mathrm{org}}$, although it approaches zero at low $C_{R^+,\mathrm{org}}$. These facts indicate the formation of polymeric species of $R^+ \cdot X^-$ ion pairs in the organic phase at higher $C_{R^+,\mathrm{org}}$. By assuming a formation of dimeric species $(R^+ \cdot X^-)_2$ (quadruple ions) in the organic phase,

$$2(R^+ \cdot X^-)_{\mathrm{org}} \overset{K_{\mathrm{dim}}}{\rightleftharpoons} (R^+ \cdot X^-)_{2,\mathrm{org}} \tag{4}$$

the dimerization constant is defined by

$$K_{\mathrm{dim}} = \frac{[(R^+ \cdot X^-)_2]_{\mathrm{org}}}{[R^+ \cdot X^-]^2_{\mathrm{org}}}. \tag{5}$$

The total concentration of $R^+$ in the organic phase is given by

$$C_{R^+,\mathrm{org}} = [R^+ \cdot X^-]_{\mathrm{org}} + 2[(R^+ \cdot X^-)_2]_{\mathrm{org}} = [R^+ \cdot X^-]_{\mathrm{org}} + 2K_{\mathrm{dim}}[R^+ \cdot X^-]^2_{\mathrm{org}} \tag{6}$$

Solving the quadratic equation for $[R^+ \cdot X^-]_{\mathrm{org}}$, we obtain

$$[R^+ \cdot X^-]_{\mathrm{org}} = \frac{-1 + (1 + 8K_{\mathrm{dim}}C_{R^+,\mathrm{org}})^{1/2}}{4K_{\mathrm{dim}}} \tag{7}$$

The distribution ratio of $R^+$ can be rewritten as

$$D = \frac{[R^+ \cdot X^-]_{\mathrm{org}} + 2K_{\mathrm{dim}}[R^+ \cdot X^-]^2_{\mathrm{org}}}{[R^+]}. \tag{8}$$

Substitution of Eq. (2) into Eq. (8) leads to

$$D = K_{\mathrm{dist}}[X^-](1 + 2K_{\mathrm{dim}}[R^+ \cdot X^-]_{\mathrm{org}}). \tag{9}$$

Substitution of Eq. (7) into Eq. (9) finally affords

$$\log D - \log C_{X^-} = \log K_{\mathrm{dist}} + \log F \tag{10}$$

where $F = 1/2 + 1/2(1+y)^{1/2}$ and $y = 8K_{\mathrm{dim}}C_{R^+,\mathrm{org}}$.

The normalized curve $\log F$ *vs.* $\log y$ was compared with the experimental results, *i.e.* the plot of $\log D - \log C_{X^-}$ *vs.* $\log C_{R^+,\mathrm{org}}$. As shown in Figs. 1 and 2, the experimental results comply well with the normalized curve (solid lines); a similar fits was obtained for other systems. Thus, it was confirmed that the ion pairs of tetraalkylammonium salts in the organic phase are generally in equilibrium between the monomeric and dimeric species. The logarithmic distribution constant, $\log K_{\mathrm{dist}}$, and the logarithmic dimerization constant, $\log K_{\mathrm{dim}}$, evaluated by this curve fitting are listed in Tables 1 and 2, respectively. The values of distribution constant listed in Table 1 were converted to the mole fraction constants, $K_{\mathrm{dist}}(\mathrm{mf})$, because the mole fraction unit is the most suitable concentration unit to discuss thermodynamic constants among different solvents. These constants are the

**Table 1.** Logarithmic ion-pair distribution constants of $R^+ \cdot X^-$ ($\log K_{\mathrm{dist}}(\mathrm{mf})$)

| Solvent | $TAA4^+ \cdot pic^-$ | $TAA5^+ \cdot pic^-$ | $TAA6^+ \cdot pic^-$ | $TAA6^+ \cdot \mathrm{ClO}_4^-$ | $TAA7^+ \cdot \mathrm{Br}^-$ | $TAA6^+ \cdot \mathrm{Br}^-$ | $TAA6^+ \cdot \mathrm{Cl}^-$ |
|---|---|---|---|---|---|---|---|
| Chloroform | 8.24 | 10.24 | 11.03 | | | | |
| Bromobenzene | | | | | | 5.53 | 3.97 |
| Chlorobenzene | 7.39 | 9.68 | 10.90 | 9.50 | | 5.75 | 4.11 |
| 1,1,1-Trichloroethane | | | | | | 4.87 | 3.32 |
| Benzene | 6.20 | 8.53 | 9.89 | 7.98 | 6.76 | 4.06 | 2.77 |
| Toluene | | | | 7.67 | | 3.53 | 2.27 |
| Xylene | 5.69 | 8.06 | 9.88 | 7.27 | 5.83 | 3.42 | 1.93 |
| Carbon tetrachloride | 4.65 | 7.14 | 9.62 | 6.22 | 5.69 | 3.32 | 1.81 |
| *n*-Hexane | 2.31 | 4.91 | 7.63 | | | | |

**Table 2.** Logarithmic ion-pair dimerization constants for $(R^+ \cdot X^-)_2$ in the organic phase ($\log K_{\mathrm{dim}}$)

| Solvent | $TAA4^+ \cdot pic^-$ | $TAA5^+ \cdot pic^-$ | $TAA6^+ \cdot pic^-$ | $TAA6^+ \cdot \mathrm{ClO}_4^-$ | $TAA7^+ \cdot \mathrm{Br}^-$ | $TAA6^+ \cdot \mathrm{Br}^-$ | $TAA6^+ \cdot \mathrm{Cl}^-$ |
|---|---|---|---|---|---|---|---|
| Chloroform | $\sim 2$ | 3.1 | 3.9 | | | | |
| Bromobenzene | | | | | | 2.1 | 2.0 |
| Chlorobenzene | $\sim 2$ | 3.1 | 3.6 | 2.2 | | 2.1 | 2.1 |
| 1,1,1-Trichloroethane | | | | | | 2.2 | 2.3 |
| Benzene | $\sim 2$ | 2.9 | 3.8 | 3.3 | 3.2 | 3.7 | 3.3 |
| Toluene | | | | 3.5 | | 4.2 | 3.6 |
| Xylene | $\sim 2$ | 2.7 | 3.8 | 4.2 | 4.2 | 4.4 | 4.4 |
| Carbon tetrachloride | $\sim 2$ | 2.8 | 3.6 | 4.9 | 5.1 | 4.7 | 3.9 |
| *n*-Hexane | $\sim 2$ | | 3.7 | | | | |

thermodynamic constants, *i.e.* the activity coefficients of ions in the aqueous phase were corrected with the help of the *Davies* equation [12]. The results for systems in which the distribution of $TAAn^+ \cdot X^-$ is too high or too low are omitted from the Tables because of very large experimental errors. For some systems, no reliable results could be obtained because of the formation of an emulsion at the interface of the aqueous and organic phases.

Some plots of $\log D - \log C_{X^-}$ *vs.* $\log C_{R^+,\mathrm{org}}$ show a deviation from the normalized curve at high $C_{R^+,\mathrm{org}}$, *i.e.* the slope of the experimental plot is higher than predicted from the formation of dimeric species. These results suggest a formation of trimeric or higher polymeric species, $(R^+ \cdot X^-)_{m,\mathrm{org}}$ $(m > 2)$, in the higher $TAAn^+ \cdot X^-$ concentration region. On the other hand, in the case of $TAA4^+ \cdot pic^-$ the value of $\log D - \log C_{X^-}$ hardly changes with increasing $C_{R^+,\mathrm{org}}$ in any solvent system as can be seen from Fig. 1. This fact indicates that $TAA4^+ \cdot pic^-$ does not form the dimeric species under the present experimental conditions, *i.e.* the dimerization constant is very small. The dimerization constant of $TAA4^+ \cdot pic^-$ was tentatively determined as $\log K_{\mathrm{dim}} \approx 2$ from the small increase in $\log D - \log C_{X^-}$ at high $C_{R^+,\mathrm{org}}$. In the case of the solvents of relatively high relative permittivity such as 1,2-dichloroethane ($\varepsilon = 10.4$), the value $\log D - \log C_{X^-}$ decreases as $C_{R^+,\mathrm{org}}$ increases. This result can be reasonably interpreted by the dissociation of ion pair in the organic phase. In the present systems, as can be seen from Figs. 1 and 2 no dissociation of ion pairs was observed because of the low relative permittivity ($\varepsilon < 6$) of the solvents.

### *Distribution constant*

In order to elucidate the solvent effect on the distribution of $TAAn^+ \cdot X^-$, the correlation of $\log K_{\mathrm{dist}}$ with typical solvent parameters, such as the relative permittivity ($\varepsilon$), the *Dimroth-Reichardt* parameter of polarity ($E_{\mathrm{T}}$), and the *Hildebrand* solubility parameter ($\delta$), were examined. The values of these solvent parameters of water-saturated solvents are listed in Table 3. The values of $\varepsilon$ and $\delta$ are hardly changed by the saturation of solvent with water because of the relatively low solubility of water. The $E_{\mathrm{T}}$ values, however, are significantly affected by the presence of water as shown in Table 3 ($E_{\mathrm{T}}$, dry solvent; $E_{\mathrm{T}}$(WS), water-saturated solvent). The donating ability of the solvent used in the present study is very low (Donor Number = 0) [13]. The logarithmic distribution constants, $\log K_{\mathrm{dist}}$, are plotted as a function of $E_{\mathrm{T}}$(WS) in Fig. 3. Those values show a good correlation with $E_{\mathrm{T}}$(WS), *i.e.* it smoothly increases as $E_{\mathrm{T}}$ increases. The values of $\log K_{\mathrm{dist}}$ of chloride and bromide systems linearly increase with increasing $E_{\mathrm{T}}$, whereas the slopes of picrate systems decrease with increasing $E_{\mathrm{T}}$(WS). These results indicate that the solvent effect on the distribution of the ion pairs is mainly controlled by the polarity or acceptor nature of the solvent [13], *i.e.* the stability of the ion pair increases with increasing in the interaction of the solvent with the anion moiety of the ion pair. As can be seen from the plots of $\log K_{\mathrm{dist}}$ *vs.* $\varepsilon$ (Fig. 4a) and $\delta$ (Fig. 4b), $\log K_{\mathrm{dist}}$ shows no reasonable correlation with these parameters; thus, the electrostatic interaction (dipole–dipole interaction) and cohesive energy between the ion pair and solvent may not be a dominant factor of the difference in the stability of the ion pairs among the solvents.

**Table 3.** Solvent parameters

| Solvent | $E_T$[a] kcal · mol$^{-1}$ | $E_T$(WS)[b] kcal · mol$^{-1}$ | $\varepsilon$[c] | $\delta$[d] cal$^{1/2}$ · cm$^{-3/2}$ |
|---|---|---|---|---|
| Chloroform | 39.1 | 40.2 | 4.81 | 9.94 |
| Bromobenzene | 36.6 | 39.0 | 5.45 | 9.87 |
| Chlorobenzene | 36.8 | 38.9 | 5.69 | 9.97 |
| 1,1,1-Trichloroethane | 36.2 | 36.9 | 7.24 | 8.50 |
| Benzene | 34.3 | 35.5 | 2.28 | 9.51 |
| Toluene | 33.9 | 35.2 | 2.38 | 8.90 |
| Xylene | 33.1 | 34.3 | 2.40 | 9.13 |
| Carbon tetrachloride | 32.4 | 33.4 | 2.24 | 8.93 |
| *n*-Hexane | 31.0 | 32.2 | 1.89 | 7.57 |

[a] *Dimroth-Reichardt* parameter of pure solvent; [b] $E_T$ value of water-saturated solvent; [c] relative permittivity; [d] solubility parameter

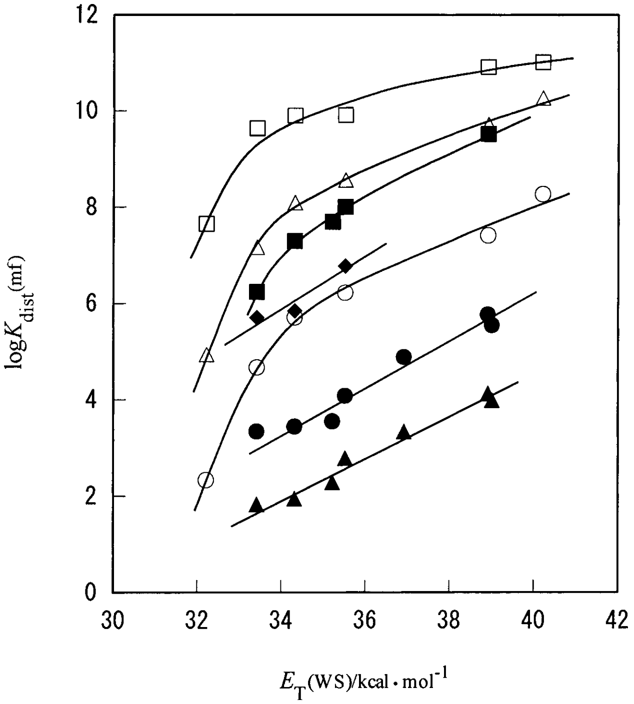

**Fig. 3.** Plot of the logarithmic ion-pair distribution constant ($\log K_{dist}$(mf)) as a function of $E_T$; for symbols, see Fig. 1

As can be seen from Table 1, the values of $\log K_{dist}$ of the *TAA*$6^+$ systems decrease as the ionic radius of the anion decreases. Similar results have been obtained for the *TAA*$4^+ \cdot X^-$–*TAA*$7^+ \cdot X^-$ systems in xylene [10]. A linear correlation of $\log K_{dist}$ with the reciprocal crystal radius of $X^-$ has been reported, and these results were reasonably explained by the hydration energy of the anion in the aqueous phase. The value of $K_{dist}$ increases with increasing in the chain length ($n$) of the alkyl group of *TAAn*$^+$ and a linear correlation of $\log K_{dist}$ with $n$ has been observed.

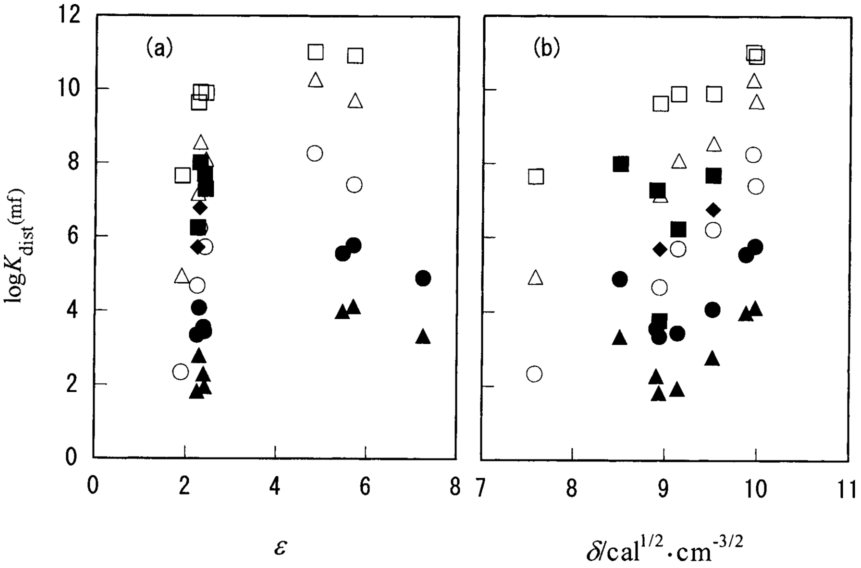

**Fig. 4.** Plot of the logarithmic ion-pair distribution constant ($\log K_{\text{dist}}$(mf)) as a function of $\varepsilon$ (a) and $\delta$ (b); for symbols, see Fig. 1

The increment of $\log K_{\text{dist}}$ ($\Delta\log K_{\text{dist}}$) by increasing $n$ by 1 (*i.e.* the total number of methyl groups of $TAAn^+$ is increased by 4) has been reported as 2.5–3.2, irrespective of $X^-$ [10] and solvent [3].

In order to discuss the effect of the solvent on this increment, the difference of $\log K_{\text{dist}}$ between two systems of $TAAn^+ \cdot X^-$, $\Delta\log K_{\text{dist}}$, was plotted as a function of $E_T$ in Fig. 5. The values of $\Delta\log K_{\text{dist}}$ between the inorganic anions are almost the same, irrespective of solvent, although the value of $K_{\text{dist}}$ of $ClO_4^-$ in carbon tetrachloride is very small compared with those of other systems. On the other hand, the values of $\Delta\log K_{\text{dist}}$ between different $TAAn^+$ of picrates (*i.e.* between $TAAn^+ \cdot pic^-$ and $TAA(n-1)^+ \cdot pic^-$) decrease with decreasing $E_T$; in particular, $\Delta\log K_{\text{dist}}$ between $TAA6^+ \cdot pic^-$ and $TAA5^+ \cdot pic^-$ shows a significant decrease. The values of $\Delta\log K_{\text{dist}}$ between $TAAn^+ \cdot X^-$ and $TAA(n-1)^+ \cdot X^-$ are almost the same among the low $E_T$ solvents, and these results agree with those determined for various kinds of inorganic anions in xylene ($\Delta\log K_{\text{dist}} = 2.6$). Consequently, it is concluded that the effect of chain length on the distribution is diminished for high $E_T$ solvents, although it hardly changes for low $E_T$ solvents.

### *Dimerization constant*

The logarithmic dimerization constants, $\log K_{\text{dim}}$, of $TAAn^+ \cdot X^-$ are plotted as a function of $E_T$ of the solvent in Fig. 6. In the same manner as the extraction constants, the dimerization constants show a good correlation with $E_T$ value, whereas they do not show a reasonable correlation with the parameters $\delta$ and $\varepsilon$. The changes of $\log K_{\text{dim}}$ by changing the cation, anion, and solvent are significantly different between the picrate ion and inorganic anion systems. In the case of picrate, the value of $K_{\text{dim}}$ hardly differs when changing the solvent, and it deceases

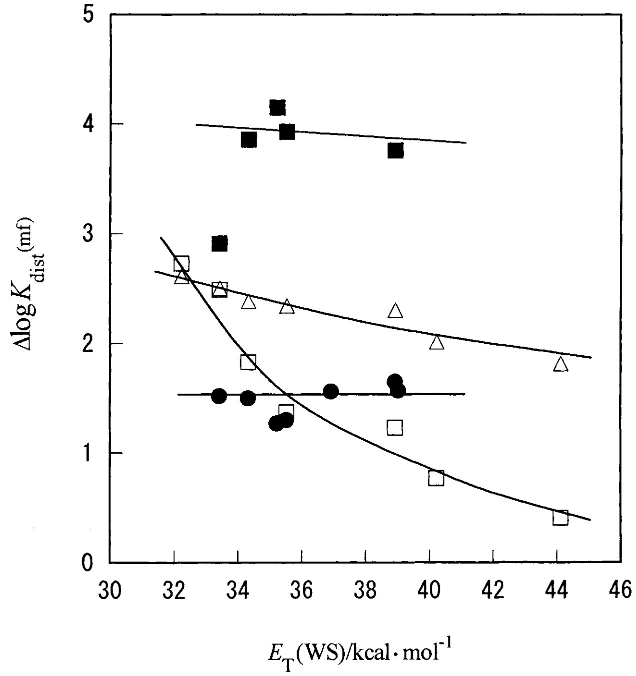

**Fig. 5.** Plot of the difference of the logarithmic ion-pair distribution constant between two $R^+ \cdot X^-$ species ($\Delta\log K_{dist}$(mf)) as a function of $E_T$; □, $TAA6^+ \cdot pic^-$ – $TAA5^+ \cdot pic^-$; △, $TAA5^+ \cdot pic^-$ – $TAA4^+ \cdot pic^-$; ■, $TAA6^+ \cdot ClO_4^-$ – $TAA6^+ \cdot Br^-$; ●, $TAA6^+ \cdot Br^-$ – $TAA6^+ \cdot Cl^-$

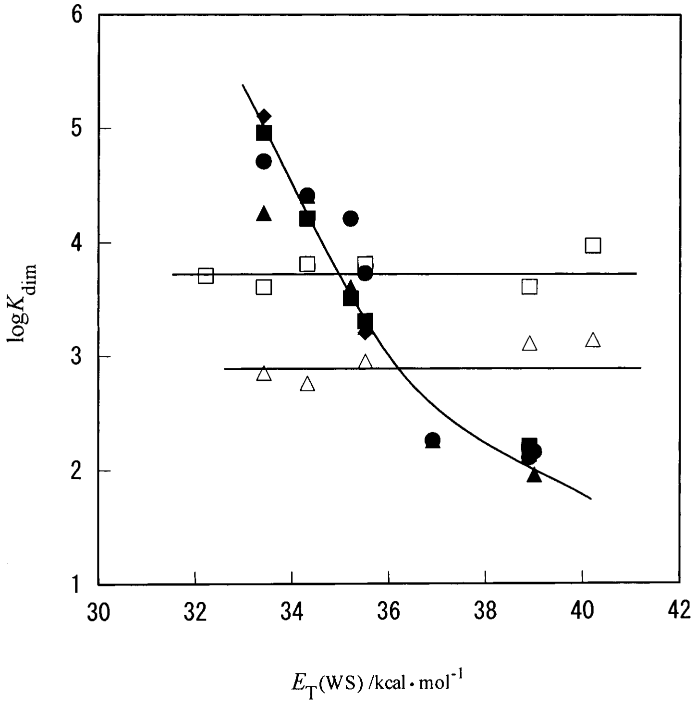

**Fig. 6.** Plot of the logarithmic dimerization constant ($\log K_{dim}$) as a function of $E_T$; for symbols, see Fig. 1

by decreasing chain length. On the other hand, $\log K_{\mathrm{dim}}$ values of $TAAn^{+}\cdot X^{-}$ significantly decrease as the $E_{\mathrm{T}}$ value of the solvent decreases, and the changes are almost the same for a given solvent. As can be seen from the results of $TAA7^{+}\cdot X^{-}$, the dimerization constant of inorganic $X^{-}$ hardly changes by changing chain length of $TAAn^{+}$. It also has been confirmed for the xylene system [10] that $K_{\mathrm{dim}}$ scarcely changes in the series $TAA4^{+}$–$TAA7^{+}$ for any inorganic anion.

The markedly different behaviour of the dimerization constant between the picrate and inorganic ions might be explained by the structure of the ion pairs. The structures of the monomeric ion pairs in the organic solvents have been estimated by means of electroconductivity and distribution equilibria as shown in Figs. 7a (inorganic anion) [8] and 7b (picrate ion) [14]. That is, the interionic distance of $TAAn^{+}\cdot X^{-}$ indicates that the counter anion directly contacts with the positive charge of the central nitrogen atom of $TAAn^{+}$ in the non-solvating solvents. MO calculation and electronic spectra of the picrate ion suggest that the phenolate oxygen site of the picrate ion approaches to the cation because the highest negative electrostatic potential exists in the vicinity of the phenolate $O^{-}$ [14], although the negative charge is delocalized to the nitro groups. Molecular models of the dimeric species estimated by molecular mechanics calculation with the help of CS Chem 3D® [15] are shown in Fig. 7c ($(TAA6^{+}\cdot \mathrm{Cl}^{-})_2$) and 7d ($(TAA6^{+}\cdot pic^{-})_2$). In the case of inorganic anions of relatively small ion size, the anions of the dimeric form are mostly surrounded by the alkyl groups of the $TAAn^{+}$ ion. The solvent molecules solvated to the anion of the monomeric $TAAn^{+}\cdot X^{-}$ have to be desolvated for dimer formation. Thus, the formation of the dimer of $TAAn^{+}\cdot X^{-}$ is

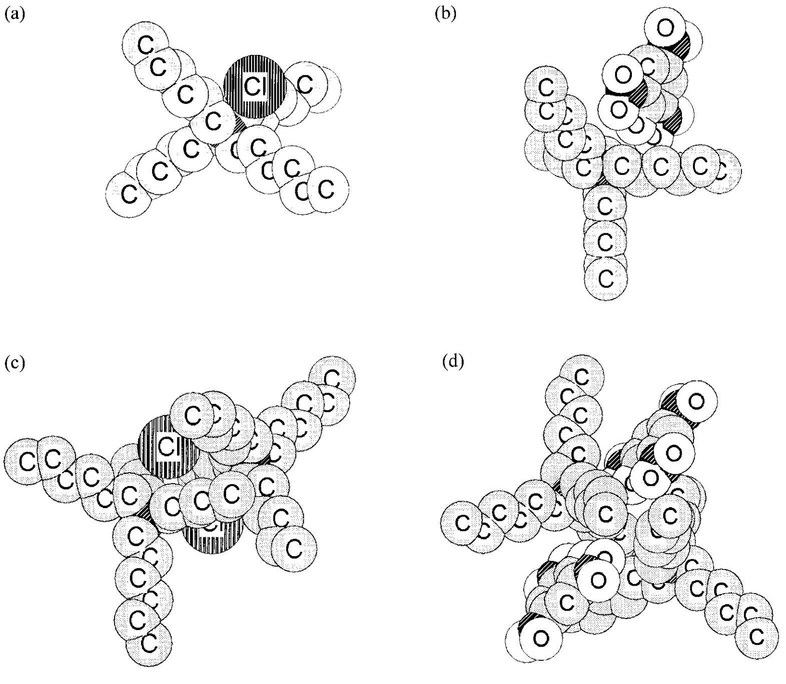

**Fig. 7.** Structures of the monomeric ion pairs of $TAA6^{+}\cdot \mathrm{Cl}^{-}$ (a) and $TAA6^{+}\cdot pic^{-}$ (b) and their dimeric ion pairs (c, d) estimated by molecular mechanics; nitrogen atoms are depicted by black circles, hydrogen atoms are omitted

unfavourable in solvents having a higher solvating ability to the anion, *i.e.* of higher $E_T$ value. On the other hand, the picrate ion is largely exposed to the solvent even in the dimeric form. Consequently, the number of the solvent molecules released by dimerization is small, and the dimerization constant is hardly affected by changing the solvent. The increase in the dimerization constant of inorganic ion systems by increasing the chain length *n* of the tetraalkylammonium ion may indicate that a peculiar intermolecular interaction operates between the alkyl groups of another $TAAn^+$.

## Experimental

### *Reagents*

Reagent grade $TAAn^+ \cdot Br^-$ and $TAA6^+ \cdot Cl^-$ were purchased from Nakarai Tesque and Aldrich Chemicals, respectively. Picric acid and organic solvents were purchased from Wako Pure Chemicals. Sodium picrate was prepared from picric acid by neutralization with sodium hydroxide. Other tetraalkylammonium salts ($TAAn^+ \cdot X^-$) were prepared from $TAAn^+ \cdot Br^-$. An aliquot of a $0.1\,mol \cdot dm^{-3}$ $TAAn^+ \cdot Br^-$ solution in $C_6H_6$ ($100\,cm^3$) was shaken with $100\,cm^3$ of $1.0\,mol \cdot dm^{-3}$ aqueous $Na^+ \cdot X^-$ solution ($X^- = ClO_4^-$ or $pic^-$). After separation by centrifugation, the aqueous solution was discarded. By three repetitions of this treatment, the bromide ion in the organic phase was completely replaced by $X^-$. The organic solvent was washed five times with an equivalent volume of deionized water (Puric Z, Organo).

In order to determine the *Dimroth-Reichardt* $E_T$ values of the water-saturated solvents, the UV/Vis absorption spectra of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenoxide (Aldrich Chemicals) in these solvents were measured using a Shimadzu UV-1600 spectrophotometer. $E_T$(WS) values of organic solvents were calculated from the wavelengths of the absorption maximum [16].

### *Procedure*

A quantity of organic solution containing $10^{-2}$–$10^{-5}\,mol \cdot dm^{-3}$ $TAAn^+ \cdot X^-$($20\,cm^3$) was shaken for 30 min with $20\,cm^3$ of distilled $H_2O$ or a 0.01 *M* aqueous $Na^+ \cdot X^-$ solution in a thermostatted water bath (25.0±0.05°C). This shaking time is sufficient for equilibrium to be reached. After the separation by centrifugation, the organic and aqueous phases were evaporated to dryness at 70°C under reduced pressure. After dissolving the residue in a proper amount of benzene, it was shaken with an aqueous $0.1\,mol \cdot dm^{-3}$ sodium picrate solution. It was confirmed that the $TAAn^+$ ion was quantitatively extracted in the benzene phase as $TAAn^+ \cdot pic^-$. The concentration of the picrate ion, *i.e.* the concentration of $TAAn^+$, was determined spectrophotometrically (absorption maximum: 362.0 nm, molar extinction coefficient: $1.77 \times 10^4\,mol \cdot dm^{-3}$). It was confirmed that the sodium ion is not extracted in any of the systems and that any anions are not extracted in the absence of $TAAn^+$.

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