# Solvent Extraction of Several Anions with Tetrabutylammonium Ion into 1,2-Dichloroethane and Hydration of Anions in the Organic Phase

**Satoshi Kusakabe*** **and Miwa Arai**

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

(Received May 2, 1995)

The partition equilibrium of tetrabutylammonium salts $Bu_4NX$, where $X^-$ is $N_3{}^-$, $NO_3{}^-$, $SCN^-$, $ClO_4{}^-$, and picrate ion, has been measured between water and 1,2-dichloroethane at 298 K. The distribution ratio of these salts can be explained in terms of the extraction of an ion pair (the extraction constant is defined as $K_{ex}=[Bu_4N^+X^-]_{org}/[Bu_4N^+]_{aq}[X^-]_{aq}f_\pm{}^2$) and the dissociation and dimerization of the ion pairs in the organic phase. The hydration number of the salt in the organic phase, $n_h$, seems similar among dissociated, ion-paired, and dimerized species. The free energy of phase transfer corrected for the hydration effect in the organic phase, $-RT(\ln K_{ex}-n_h)$, may be correlated with the Gibbs free energy of hydration of the anions in the aqueous phase.

The organic phase in solvent extraction systems often contains a certain amount of water transported by the extracts as well as the partitioned water according to its solubility in the solvent.[1—8] The chemical equilibria in the organic phase should be studied taking these waters into the account. In a previous paper, we reported about the extraction and hydration of tetrabutylammonium halides with respect to three organic solvents; 1,1- and 1,2-dichloroethane and 4-methyl-2-pentanone.[9] These extraction data were well explained in terms of extraction of an ion pair and its dissociation in the organic phase. In this study other tetrabutylammonium salts ($Bu_4NX$); azide, nitrate, thiocyanate, perchlorate, and picrate, have been extracted into 1,2-dichloroethane. Since Sawada, Sohara, and Kikuchi reported recently that ion pairs of tetraalkylammoniums dimerize in xylene,[10] the dimerization of the extracted ion pairs in the organic phase is taken into account in the analysis of this extraction data. The effects of hydration on these equilibria are of interest, especially in relation to the energy of phase transfer of ions, which can be estimated from the magnitude of the extraction constant.

## Experimental

**Materials.** A reagent grade 1,2-dichloroethane was shaken with concd sulfuric acid, 1% aqueous potassium hydroxide solution, and waters. All the $Bu_4NX$ salts but picrate were commercially available. The salts of azide, thiocyanate, and perchlorate were recrystallized from ethyl acetate and the nitrate from benzene. Stock solutions of the azide, thiocyanate, and nitrate were prepared by dissolving crystals of each in deionized and distilled water, while those of the perchlorate and picrate were prepared as the 1,2-dichloroethane solutions. The iodide was dissolved in the organic diluent just before use. A stock solution of the picrate was prepared as follows. An aqueous picric acid solution was neutralized with a small excess of aqueous $Bu_4NOH$ and agitated with a certain volume of 1,2-dichloroethane. The organic phase was stored after washing several times with an aqueous 0.01 $mol\,dm^{-3}$ sodium hydroxide solution. The $Bu_4N^+$ ion concentration of these stock solutions was measured by colorimetry of the picrate in chloroform solution.

**Extraction Procedures.** Experiments were done in a room thermostatted at 298 K. The aqueous phase for the iodide was 0.01 $mol\,dm^{-3}$ sodium thiosulfate and that for the picrate was 0.01 $mol\,dm^{-3}$ sodium hydrogencarbonate. For the perchlorate it was pure water and for the other salts the stock solution was diluted with water. A sample (usually 5 $cm^3$) of the aqueous phase and the same volume of the organic phase were placed in a stoppered glass tube of 20 $cm^3$, shaken mechanically for half an hour, and then separated by centrifuging. A portion of the aqueous phase was transferred to another tube. A sodium picrate solution and a certain volume of chloroform were added there and the $Bu_4N^+$ ion was extracted into the chloroform. The concentration of the $Bu_4N^+$ ion was measured from the optical absorbance of the chloroform solution at 370 nm ($\epsilon=1.75\times10^4$). The distribution ratio of the salts between two phases was calculated from the initial concentration and the equilibrated aqueous phase concentration.

**Measurements of the Water Content in the Organic Phase.** A $Bu_4N^+$ salt was partitioned between water and 1,2-dichloroethane. Then, the two phases were centrifuged for 5 min at about 2000 rpm. The two phases were kept standing for 2 h or longer in the thermostatted room. A portion of the organic phase was taken out with a dried syringe, weighed, and titrated by Hiranuma AQ6 type Aquacounter. The water in the sample was measured by the titration in combination with the weight and density of the sample, averaging three measurements for each sample.

## Results

The partition curves of the salts are shown in Fig. 1. For the iodide several points in the higher salt concentrations were added to those reported in our previous paper. These data are treated as follows. The chemical species in the organic phase is denoted by the subscript "org" and that in the aqueous phase without any subscript. The salts in this study, $Bu_4NX$, will be extracted mainly as an ion pair but in the aqueous phase the ion pair formation should be negligible.

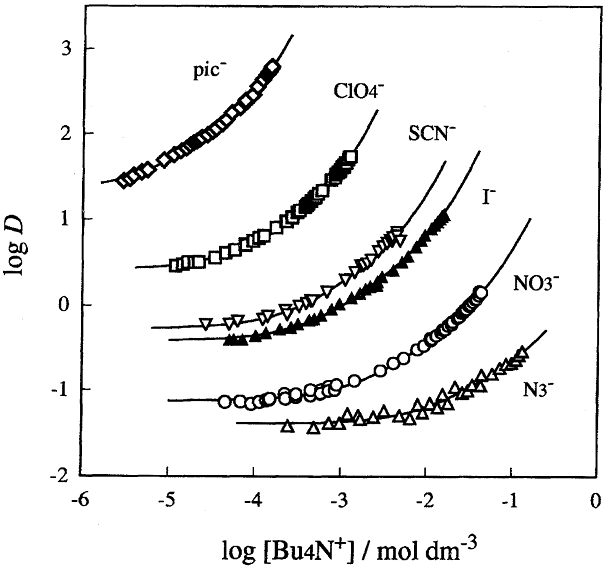

Fig. 1. Partition curves of $Bu_4NX$ between 1,2-dichloroethane and water. The solid curves were calculated by Eq. 6 using the constants in Table 1 assuming $f_{\pm org} = 1$.

The extraction constant is, then, defined by Eq. 1.

$$Bu_4N^+ + X^- \rightleftharpoons Bu_4N^+X^- \text{ (org)}$$

$$K_{ex} = [Bu_4N^+X^-]_{org}/[Bu_4N^+][X^-]f_{\pm}^2 \tag{1}$$

The mean activity coefficient can be calculated with Eq. 2:

$$\log f_{\pm} = -A\sqrt{I}/\left(1 + Ba\sqrt{I}\right)$$
$$= -0.5115\sqrt{I}/\left(1 + 0.3291 \times 6\sqrt{I}\right) \tag{2}$$

where $B=(8\pi N_A e_0{}^2/1000\epsilon kT)^{1/2}$ and $A=N_A e_0{}^2 B/4.606\epsilon RT$ for the 1 : 1 electrolyte solution and $I$ is the ionic strength of the aqueous solution. The contact distance of the anion and cation, $a$, is taken as 0.6 nm or $a=6/10^{-8}$ cm.[4,11)]

The ion pairs in the organic phase may partly dissociate. The dissociation constant $K_{dis}$ is the reciprocal of the association constant $K_{as}$.

$$K_{dis} = 1/K_{as} = [Bu_4N^+]_{org}[X^-]_{org} f_{\pm org}{}^2/[Bu_4N^+X^-]_{org} \tag{3}$$

The activity coefficient in the organic phase $f_{\pm org}$ is first assumed to be always unity. Afterwards, it is calculated as is mentioned in Discussion.

In higher concentrations of the salt, the extraction of some salts was better than expected from the ion-pair extraction only. Thus, dimerization of the ion pair is supposed in the organic phase. The dimerization constant $K_{dim}$ can be written as:

$$K_{dim} = [(Bu_4N^+X^-)_2]_{org}/[Bu_4N^+X^-]_{org}{}^2 \tag{4}$$

The distribution ratio of $Bu_4N^+$ ion is then written as:

$$D = \{[Bu_4N^+]_{org} + [Bu_4N^+X^-]_{org} + 2[(Bu_4N^+X^-)_2]_{org}\}/[Bu_4N^+] \tag{5}$$

Using the equilibrium constants above and the charge balance in both phases, Eq. 5 is changed to Eq. 6.

$$D = \sqrt{K_{dis}K_{ex}} f_{\pm}/f_{\pm org} + K_{ex}[Bu_4N^+]f_{\pm}{}^2 + 2K_{dim}K_{ex}{}^2[Bu_4N^+]^3 f_{\pm}{}^4 \tag{6}$$

Three constants in this equation can be obtained by a successive approximation on the basis of a least squares method. The constants obtained are listed in Table 1 together with those reported previously.

The increase of water content in the organic phase with the extraction of the salt should be due to the hydration of the salt in the organic phase. Then, the averaged number of water molecules on the salt in the organic phase will be expressed by Eq. 7.

$$n_h = ([H_2O]_{org,total} - [H_2O]_{org,0})/[Bu_4NX]_{org,total} \tag{7}$$

The term $[H_2O]_{org,0}$ is the concentration of background water, namely, water soluble in the pure solvent. It was found to be 0.128±0.003 mol dm$^{-3}$. The values in the literature are 0.1252 mol dm$^{-3}$,[12)] and 0.124±0.001 mol dm$^{-3}$.[13)] Although this value is changed by the addition of salts to the aqueous phase, it should be negligible in this study because the salt concentration was at most 0.17 mol dm$^{-3}$ at equilibrium. The hydration number was calculated from Eq. 7 and the results are shown in Fig. 2 against the total concentration of the salt in the organic phase. Since the value of $n_h$ was sensitive to the amount of measured background water in low salt concentrations, it was averaged weighting on the data in the higher concentration range. The averaged values are listed in Table 1.

## Discussion

In this study three forms of ions are considered in the organic phase; dissociated ion, ion pair, and its dimer. The

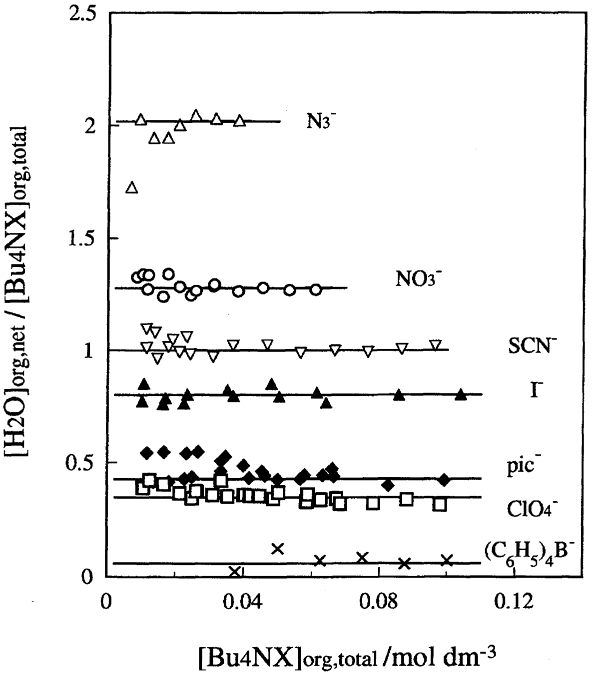

Fig. 2. Hydration number of tetrabutylammonium salts in relation to the total salt concentration in the organic phase.

Table 1. Ion-Pair Extraction Constant of $Bu_4NX$ and Equilibrium Constants in 1,2-Dichloroethane at 298 K
Literature values for the hydration number are given in parentheses.

| $X^-$ | $f_{\pm org}=1$ is assumed | | | $f_{\pm org}\neq 1$ is assumed | | | $n_h$ |
|---|---|---|---|---|---|---|---|
| | $\log K_{ex}$ | $-\log K_{dis}$ | $\log K_{dim}$ | $\log K_{ex}$ | $-\log K_{dis}$ | $\log K_{dim}$ | |
| $Cl^-$ [a)] | −0.54 | 3.78 | nil | −0.68 | 3.72 | | 2.7 (2.4) [f)] |
| $Cl^-$ [b)] | 0.21 | 3.67±0.4 | 1.39±0.2 | 0.18 | 3.67±0.3 | 1.42±0.2 | |
| $N_3^-$ | 0.53±0.1 | 3.28±0.4 | 0.7 | 0.17±0.3 | 3.22±0.5 | | 2.05 |
| $Br^-$ [a)] | 0.86 | 3.76 | nil | 0.70 | 3.69 | | 2.0 |
| $NO_3^-$ | 1.57 | 3.81 | 0.6 | 1.45 | 3.76 | | 1.28 |
| $I^-$ [c)] | 2.82 | 3.65 | 0.3 | 2.67 | 3.67 | | 0.80 |
| $SCN^-$ | 3.16 | 3.70 | 0.5 | 3.03 | 3.72 | | 1.00 |
| $ClO_4^-$ | 4.50 | 3.67 | 0.67 | 4.38 | 3.64 | 0.38 | 0.35 (0.33) [g)] |
| $Pic^-$ [d)] | 6.46 | 3.80 | 0.49 | 6.37 | 3.79 | 0.27 | 0.40 |
| $Tpb^-$ [e)] | | | | | | | 0.06 (0.05) [h)] |

The limit of error is 0.06 for $\log K_{ex}$, 0.2 for $\log K_{dis}$ both $f_{\pm org}=1$ and $f_{\pm org}\neq 1$ other than given in the Table. That for $n_h$ is 0.02. a) Ref. 9. b) Aqueous phase is 2 mol dm$^{-3}$ LiCl solution, see text. c) Revised value by this study. d) Picrate ion. e) Tetraphenylborate ion. f) Ref. 4. g) Ref. 3. h) Ref. 3, in nitrobenzene.

total salt concentration in the organic phase in these experiments fell mostly between $1\times10^{-5}$ and 0.1 mol dm$^{-3}$ so that from the magnitude of $K_{dis}$ and $K_{dim}$ the predominant species should be the dissociated ion in the lower concentration and the ion pair in the higher concentration. The dimer of ion pairs should be found in the highest salt concentrations.

**Activity of Ions in the Organic Phase.** The activity coefficient of ions in the organic solution may be calculated by the Debye–Hückel equation. The distribution data was treated taking into account the activity of ions in the organic phase. By using $\epsilon_{aq}=78.3$, $\epsilon_{org}=10.3$ for 1,2-dichloroethane,[14] and $a=5/10^{-8}$ cm Eq. 2 is changed to Eq. 2′.

$$\log f_{\pm org} = -0.512(\epsilon_{org}/\epsilon_{aq})^{3/2}\sqrt{I_{org}} \Big/ \left(1+0.329a\sqrt{\epsilon_{org}/\epsilon_{aq}\sqrt{I_{org}}}\right) \tag{2'}$$

$$I_{org} = \sqrt{K_{dis}K_{ex}}f_{\pm}/f_{\pm org} \tag{8}$$

The value of $f_{\pm}$ in Eq. 8 is calculated by Eq. 2 using a certain salt concentration in the aqueous phase. The value of $f_{\pm org}$ is obtained by successive approximations through Eqs. 8 and 2′ starting with $f_{\pm org}=1$ until the value of $I_{org}$ accords with that of the previous iteration within 1%.

The values of equilibrium constants obtained are compared in Table 1 with those obtained by assuming $f_{\pm org}=1$. For the aqueous phase the least value of $f_{\pm}$ was 0.8 and the correction with the activity coefficient was negligible when the ionic concentration was less than 0.05 mol dm$^{-3}$. On the contrary, for the organic phase the least value of $f_{\pm org}$ reached about 0.1 in some salts. Thus, from the magnitude of the activity coefficients the correction of activity seems more necessary in the organic phase. However, as is seen from the results in Table 1, the effect of correction on the equilibrium constants seems not very decisive. By introducing $f_{\pm org}$ the extraction constants was reduced by 0.1 in logarithm units but the dissociation constant changed only within experimental errors. The dimerization constant became less reliable and in some salts needless to use. The standard deviations (SD) were similar except the azide, in which the fit was not satisfactory upon introducing $f_{\pm org}$ (SD=0.0958 against 0.0356 with $f_{\pm org}=1$).

In this study the reliability of calculated constants can be estimated by the limit of error, which is obtained in such a manner that the value of the constant in question is diminished by little bits until the standard deviation reaches three times that of the least one on keeping the other constants at their best fit values. For example, for the perchlorate the results are $\log K_{ex}=4.50\pm0.02$, $\log K_{dis}=-3.67\pm0.13$, and $\log K_{dim}=0.67\pm0.23$ with the least SD=0.00835 under the assumption of $f_{\pm org}=1$. As for $K_{dim}$, when it was diminished from $10^{0.67}$ to $10^{0.44}$ the SD reached 0.0250 and thus, the limit of error was taken as 0.23. On the contrary, when $f_{\pm org}$ was used in the calculation, the least SD decreased to 0.00767 but the limit of error was not obtained for $\log K_{dim}$ because even when $K_{dim}$ was reduced to zero the SD was still double the least one.

The Debye–Hückel equation may be valid to some extent for the estimation of the activity coefficient in the solutions, however, we have no idea about the activity of the electrically neutral species. Although the ionic concentration in the aqueous phase was experimentally measured, that in the organic phase was supposed by a mathematical treatment. Not to go so far from the experimental results, we preferred to take the values of constants on the hypothesis of $f_{\pm org}=1$ for the further discussion since the difference in the values of constants was not decisive and the standard deviation were scarcely improved by using $f_{\pm org}$. As for the ions in the aqueous phase, we use the activity coefficient because we failed to realize the experimental distribution curves by the calculations only with the stoichiometric concentrations.

**Dimerization of the Ion Pair.** Calculations assuming any triple ion formation in the organic phase did not improve the fit of the partition curves. This may be because the concentration of the dissociated ion cannot be enough to form triple ions even in higher salt concentrations in this solvent.

Sawada et al. have reported the dimerization constant of ion pairs of tetraalkylammonium salts in xylene by the magnitude of $10^3$ to $10^4$.[10] Since this magnitude does not depend on the number of carbon atoms among symmetric tetraalkylammonium salts, the salts of $\mathrm{Bu_4N^+}$ may have similar magnitudes of $K_{\mathrm{dim}}$ in xylene. In this study the dimerization of ion pairs was supposed, however, the constant seemed to be $<10$ and was not always obtained with enough reliability. This may be because the permittivity of the solvent is larger than that of xylene ($\epsilon$=2.3 to 2.6).[14] The reason for the poor reliability is, in other words, that the molar ratio of the dimerized species under the experimental conditions is not enough to contribute to the standard deviation in the curve-fitting calculation.

To establish the formation of a dimer, $\mathrm{Bu_4NCl}$ was extracted from aqueous 2 mol dm$^{-3}$ lithium chloride solution into 1,2- and 1,1-dichloroethane. Since the extraction of lithium ion was found to be negligible, $[\mathrm{Bu_4N^+}]_{\mathrm{org}}=[\mathrm{Cl^-}]_{\mathrm{org}}$ should be valid. The ion-pair formation of $\mathrm{Bu_4N^+Cl^-}$ in the aqueous phase should now be considered and the equation for the distribution ratio of $\mathrm{Bu_4NCl}$ is modified to Eq. 9.

$$D=\left\{\sqrt{K_{\mathrm{dis}}K_{\mathrm{ex}}[\mathrm{Cl^-}]/[\mathrm{Bu_4N^+}]}\,f_{\pm}/f_{\pm\mathrm{org}}+K_{\mathrm{ex}}[\mathrm{Cl^-}]\,f_{\pm}{}^2 +2K_{\mathrm{dim}}K_{\mathrm{ex}}{}^2[\mathrm{Cl^-}]^2[\mathrm{Bu_4N^+}]\,f_{\pm}{}^4\right\}\Big/\left(1+K_{\mathrm{pair}}[\mathrm{Cl^-}]\,f_{\pm}{}^2\right) \quad (9)$$

The $K_{\mathrm{pair}}$ is the formation constant of an ion pair in the aqueous phase, which is defined as $[\mathrm{Bu_4N^+Cl^-}]/[\mathrm{Bu_4N^+}][\mathrm{Cl^-}]f_{\pm}{}^2$. Although in this extraction system the activity coefficient of chloride ion in the aqueous phase changes little, the mean activity coefficients are calculated with a modification of Eq. 2 where the value of $a$ was used $4.3/10^{-8}$ cm for LiCl. The term of $[\mathrm{Cl^-}]$ can be replaced with $2+[\mathrm{Bu_4N^+}]$ and Eq. 9 rewritten as a function of $[\mathrm{Bu_4N^+}]$. The experimental results and fitted curves with Eq. 9 are shown in Fig. 3. Marked increase in the distribution ratio in higher concentrations of $\mathrm{Bu_4N^+}$ suggests the aggregation of extracts, however, the behavior may be explained well by the dimerization of the ion pair only. The values of constants obtained with 1,2- (and 1,1-) dichloroethane on the hypothesis of $f_{\pm\mathrm{org}}=1$ are:

$$\log K_{\mathrm{ex}} = 0.21 \pm 0.05\ (-0.76 \pm 0.05);$$
$$-\log K_{\mathrm{dis}} = 3.67 \pm 0.38\ (4.91 \pm 0.46);$$
$$\log K_{\mathrm{dim}} = 1.39 \pm 0.20\ (1.72 \pm 0.23);$$
$$\log K_{\mathrm{pair}} = 0.55 \pm 0.08\ (0.48 \pm 0.07),$$

respectively. The values of $K_{\mathrm{pair}}$ from extraction systems are both approximately 3. This is of similar magnitude to that for $\mathrm{Bu_4NI}$ by Evans and Kay, 3.1 and 2.0.[15] The reason why the values of $\log K_{\mathrm{ex}}$ are larger than those in our previous study[9] ($-0.54$ and $-1.49$ in 1,2- and 1,1-dichloroethane, respectively) would be explained by a salting-out effect of LiCl. When the same experimental data were treated using the activity of ions in the organic phase, the values of $f_{\pm\mathrm{org}}$ changed in the range from 0.97 to 0.30 for 1,2-dichloroethane but the resulting constants changed little, e.g., $\log K_{\mathrm{dim}}=1.42\pm0.23$. Although the $K_{\mathrm{dim}}$ was obtained with a reasonable limit of error from these extraction systems and, consequently, the dimerization of ion pairs seems to be recognizable for the chloride in the higher concentration in 1,2-dichloroethane, we should say that the dimerization in 1,2-dichloroethane is, as a whole, better to be considered in the calculation of equilibrium constants in this extraction system to get a good fit with the experimental results.

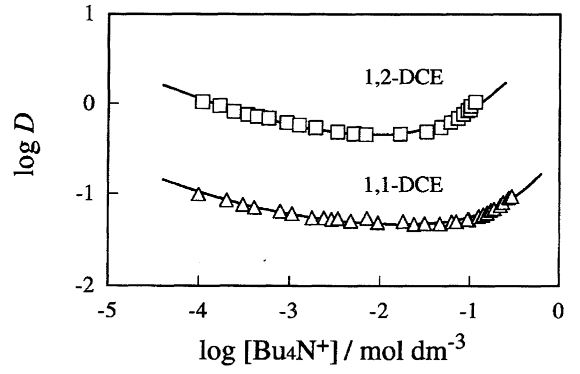

Fig. 3. Extraction of $\mathrm{Bu_4NCl}$ in aqueous 2 mol dm$^{-3}$ LiCl solution into 1,1- and 1,2-dichloroethane. The solid curves are calculated by Eq. 9 using the values of constants in the text assuming $f_{\pm\mathrm{org}}=1$.

**Hydration Number of Ion in Dichloroethane.** As is seen in Fig. 2, the apparent hydration number of the salts does not change over the higher concentrations. Thus, it can be said that no water leaves nor enters on the dimerization of ion pairs. On the other hand, if the points in the left side in Fig. 2 deviate upward from the flat lines in the figure, a larger hydration number is expected on the dissociated ions than on the ion pairs. This is, however, not clear because of the lack of experimental accuracy. From the extraction of tetraalkylammonium salts to nitrobenzene in which the ions are almost dissociating, the hydration number of the extracted salts is reported as 3.3 ($\mathrm{Cl^-}$), 1.8 ($\mathrm{Br^-}$), 1.0 ($\mathrm{I^-}$),[4] 1.4 ($\mathrm{NO_3{}^-}$), and 0.33—0.40 ($\mathrm{ClO_4{}^-}$).[3] Most of these values are a little larger than those given in Table 1. Since the acceptor number[16] of 1,2-dichloroethane (16.7) is similar to that of nitrobenzene (14.8), the degree of solvation by the organic solvent should not be very different in these two solvents. Moreover, both the permittivity and the solubility of water of 1,2-dichloroethane are less than those of nitrobenzene. The hydration of the dissociated ions in 1,2-dichloroethane might be, consequently, less than those in nitrobenzene cited above. Therefore, the hydration number of a dissociated ion should not be very much different from those given in Table 1. The value of $n_{\mathrm{h}}$ for tetrabutylammonium tetraphenylborate were obtained as 0.06. Since the anion and cation of this salt are both hydrophobic, the hydration number on the $\mathrm{Bu_4N^+}$ should be less than 0.06. Thus, the most part of the $n_{\mathrm{h}}$ given in Table 1 can be attributed to hydration on the anions.

**Dissociation of Ion Pair in Dichloroethane.** The values of $\log K_{\mathrm{dis}}$ in Table 1 are mostly of similar magnitude in spite of the anionic size being different. Jalhom and

Siekierski have reported similar results in the extraction of tetraalkylammoniums to chloro- and dichlorobenzene with a series of anions from chloride to perchlorate.[17] This seems curious because the degree of association of ions should be mainly decided by the distance between the cation and anion. In a previous paper[9] we estimated the distance of ions, *a* for $Bu_4N^+$-halides ion pair by the Fuoss equation[18,19] to be approximately 0.5 nm. Since the values of association constants of polyatomic anions are similar to those of halides, this distance may be also applicable to the ion pairs treated in this study. Assuming the shape of $Bu_4N^+$ to be spherical, we can estimate the cationic radius as 0.49 nm from its limiting molar volume of 298.6 $cm^3 mol^{-1}$ in organic solvents.[20] The share of distance for the anion, then, remains very short. This distance suggests at least that the formed ion pairs are not the water-inserted but directly contacted ones. In other words, the hydrating water may not prevent the direct contact of the ions.

The similarity in the magnitude of association constants has also been found among the values from dry 1,2-dichloroethane obtained by conductivity measurements; 3.91 ($NO_3^-$),[21] 3.90[22] and 3.83[6] ($I^-$), 3.81 ($ClO_4^-$),[23] and 3.64 (picrate ion).[21] This fact suggests that the role of water is small in the similarity of $K_{dis}$.

This may be explained by the model that the $Bu_4N^+$ ion is composed of a rigid core as large as the tetraethylammonium ($Et_4N^+$) ion and two flexible outer carbon atoms in each butyl group.[24] The radius of $Et_4N^+$ ion is estimated to be 0.40 nm from the volume of 160.8 $cm^3 mol^{-1}$ in the organic phase.[20] The association constant for $Et_4N^+$ salts in dry 1,2-dichloroethane have been filed by Abraham and Danil de Mamor[25] in logarithms as 4.29 ($Cl^-$), 4.16 ($Br^-$), 4.13 ($NO_3^-$), 4.04 ($I^-$), 3.97 ($ClO_4^-$), and 3.79 (picrate ion). These values clearly show that the smaller the anion, the more associating. If $Bu_4N^+$ ion allows the anion to stay in its soft sphere, the effect of anionic size should diminish, whatever the hydration enlarges the size or not. A more drastic effect of hydration on the association constant is reported for the alkali metal ions and dipicrylamide [bis(2,4,6-trinitrophenyl)amide] anion.[26] In dry nitrobenzene the ion-pair formation constant $K_{as}$ is in the order $Li^+(52.6) > Na^+(13.9) > K^+(9.5) > Rb^+(7.7) > Cs^+(5.2)$ though the values are 2—4 in nitrobenzene almost saturated with water.

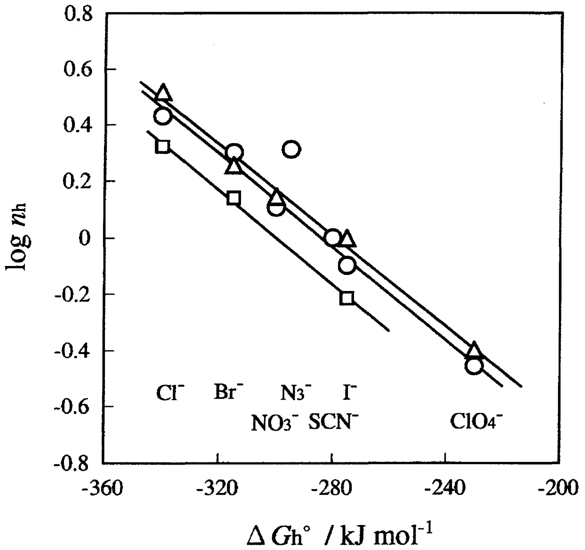

Fig. 4. Hydration number of anions in the organic solvents and the Gibbs free energy of hydration.[27] The solvent is 1,2-dichloroethane (circle), 1,1-dichloroethane (square, Ref. 9), and nitrobenzene (triangle, Refs. 3 and 4). The regression equation for 1,2-dichloroethane is given by Eq. 10.

**Hydration Number and Gibbs Free Energy of Hydration.** The hydration tendency of an ion in aqueous solutions may be measured by the Gibbs free energy of hydration, $\Delta G_h°$, which is defined as the difference in the free energy between gaseous ions and ions in the aqueous solution. Since the ions are also hydrated in the organic solution saturated with water, the value of $n_h$ should have some relations with $\Delta G_h°$. The values of $n_h$ in Table 1 are plotted against $\Delta G_h°$ in Fig. 4 for the anions from $Cl^-$ to $ClO_4^-$. The values in the literature, in nitrobenzene[3,4] and in 1,1-dichloroethane[9] are also shown in the figure. The values of $\Delta G_h°$ are taken from Ref. 27. That for $ClO_4^-$ was calculated from the enthalpy and entropy of hydration in the other papers of the same author[28,29] because that given in Ref. 27, −430 $kJ mol^{-1}$, is incredibly negative compared with the values of other anions. In Fig. 4 the plot of 1,2-dichloroethane seems to give a straight line given by:

$$\log n_h = -0.00825\Delta G_h° - 2.344 \quad (n = 6,\ R^2 = 0.990) \qquad (10)$$

Among the anions shown in Fig. 4, azide ion was excluded from the regression calculation because of its extensive deviation. This deviation might be caused by the uncertain value of $\Delta G_h°$. Marcus's value, −295 $kJ mol^{-1}$, seems to be obtained from two experimental data of the standard enthalpy of hydration,[28] $\Delta H_h° = -302$ and −359 $kJ mol^{-1}$. From these, $\Delta G_h°$ is calculated as −278 and −335 $kJ mol^{-1}$, respectively. The value calculated by Eq. 10 with $n_h=2.05$ is −320 $kJ mol^{-1}$. The $\Delta G_h°$ of hydroxide ion is −430 $kJ mol^{-1}$ and this gives $n_h=16$ by Eq. 10 though the value obtained by a preliminary experiment was approximately 2.5. The $\Delta G_h°$ of picrate ion can be estimated as −215 $kJ mol^{-1}$ from the literature[30] and this ion also does not fit well to Eq. 10. Therefore, Eq. 10 may be valid only among limited anions. Although no theoretical explanation is given, this linear relationship may be available to deduce the hydration number of the ions in other solvents for some ions shown in Fig. 4 since the slopes for these three solvents seem to resemble each other.

**Extractability and Hydration of Anions.** Extractability of anion can be evaluated by the magnitude of $K_{ex}$ in this study. The extraction constant is replaced by the energy term of phase transfer of the ion pair, $-RT\ln K_{ex}$. This means the smaller the energy of phase transfer, the more easily the ions are extracted. The values of this term are calculated from the values of $K_{ex}$ in Table 1 ($f_{org}=1$) and plotted against the $\Delta G_h°$ of the anion in Fig. 5 with the open circles. As is seen

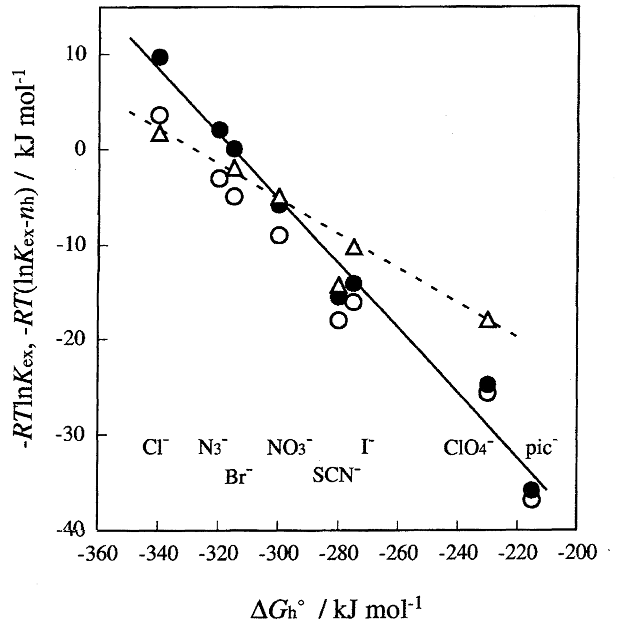

Fig. 5. Energy of phase transfer and the Gibbs free energy of hydration of the anion. Among the value of $\Delta G_h°$ (Ref. 27) that for pic⁻ is estimated value ($-215$ kJ mol$^{-1}$) from Ref. 30 and that for $N_3^-$ ($-320$ kJ mol$^{-1}$) by Eq. 10. Open circles are points for $-RT\ln K_{ex}$ and the closed circles for $-RT(\ln K_{ex}-n_h)$. Triangles (broken line) are for $-RT\ln K_{ex}(HX)$ in the extraction of acids with trioctylphosphine oxide in hexane (Ref. 33).

in the figure, the more negative the $\Delta G_h°$ is, the larger is the $-RT\ln K_{ex}$. In other words, the stronger the hydration, the less extractable. Since the hydration of ions in the aqueous phase should interfere with the extraction of the ion pair, this correlation should be reasonable. Does the hydration in the organic phase, then, also interfere with the extraction? The hydrated ions in the organic phase will have less lipophilic tendency which may lead to a poorer extraction. On the other hand, from the thermodynamic standpoint, they can save the dehydration energy on transferring from water to the organic phase. This idea will lead to a better extraction of the hydrated species. This problem will be solved on the basis of Ivanov and Zaitsev's discussion[5] about the relation between the energy of phase transfer and hydration energy. They extracted a series of salts of quaternary ammonium from the fluoride to the perchlorate with toluene. They compared the extraction constants with $\Delta G_h°$ of the anion in the following manner.

Suppose we have two organic solutions containing $X^-$; one is saturated with water but the other contains no water. The chemical potential of $X^-$ in these solutions may be written as $\mu_{x,wet}=\mu_{x,wet}°+RT\ln a_{x,wet}$, and $\mu_{x,dry}=\mu_{x,dry}°+RT\ln a_{x,dry}$, respectively. The $a_{x,wet}$ and $a_{x,dry}$ represent the activity of $X^-$ in wet and dry solvents. If $\mu_{x,wet}°=\mu_{x,dry}°$ is supposed, the difference between these chemical potential is:

$$\mu_{x,wet}-\mu_{x,dry}=RT\ln(a_{x,wet}/a_{x,dry})\approx -RTn_h \qquad (11)$$

This relation was derived from the studies of Mikhailichenko et al. about the effects of hydration on the activity of extractants such as amines[31] and tributyl phosphate[32] on the basis of Gibbs–Duhem equation for three-component systems of solvent–solute–water and the depression of the freezing point of the solvent; the activity of extractant $a_2$ should be reduced to $a_2^*$ in the wet solvents and the reduction can be approximated as Eq. 12 by using the hydration number of the extractant $h$.

$$RT\ln(a_2^*/a_2)\approx -RTh \qquad (12)$$

The approximation in Eq. 11 seems not always valid, so that we examined its adequacy for several supposed cases; see Appendix. Depending on Eq. 11, Ivanov and Zaitsev compared the solvation energy of $X^-$ in the wet and dry organic solvents as:

$$\Delta G_{s,wet}(X^-)=\Delta G_{s,dry}(X^-)-RTn_h \qquad (13)$$

This is because the change in chemical potentials for one molar substances are equal to the change in the Gibbs free energy. Extraction constant of a salt BX in their study is defined by Eq. 14 and related to the energy of phase transfer $\Delta G_{tr,wet}$ by Eq. 15.

$$K_{ex,i}=[B^+]_{org}[X^-]_{org}f_{\pm org}^2/[B^+][X^-]f_{\pm}^2 \qquad (14)$$

$$-RT\ln K_{ex,i}=\Delta G_{tr,wet}(B^+)+\Delta G_{tr,wet}(X^-) \qquad (15)$$

This extraction constant is replaced with that in this study as $K_{ex,i}=K_{ex}K_{dis}$. The $\Delta G_{tr,wet}$ can be also expressed as the difference between the solvation energy of the ion in the wet solvent and the hydration energy in the aqueous phase:

$$\Delta G_{tr,wet}(X^-)=\Delta G_{s,wet}(X^-)-\Delta G_h° \qquad (16)$$

If the discussion is limited to the extraction of a series of salts of a certain cation $B^+$, the energy terms concerning the cation can be bound to a certain constant. Furthermore, since solvation and hydration are similar phenomena around the ion, it may be assumed that the magnitude of $\Delta G_{s,dry}(X^-)$ is proportional to that of $\Delta G_h°$. Then, Eq. 17 is obtained from Eqs. 13, 14, 15, and 16.

$$-RT(\ln K_{ex}-n_h)=(C_1-1)\Delta G_h°+C_2 \qquad (17)$$

$C_1$ and $C_2$ can be regarded as constant terms; $C_1=\Delta G_{s,dry}(X^-)/\Delta G_h°$, which is expected to be similar among different anions so long as the solvent is the same, and $C_2$ is composed of the terms on the cation $\Delta G_{tr,wet}(B^+)$ and $RT\ln K_{dis}$, which is probably of similar magnitude among the anions.

Equation 17 indicates that the energy of phase transfer would be linearly correlated with $\Delta G_h°$ after the correction with the hydration term. Pointing out this linear correlation, Ivanov and Zaitsev have closed their discussion. If $n_h=0$ is assumed, we obtain from Eq. 17 $-RT\ln K_{ex}=\Delta G_{s,dry}(X^-)-\Delta G_h°+C_2$. Since this equation represents the energy of phase transfer of the anion from water to the *dry* solvent, this extraction constant should be distinguished from that obtained by experiments and we discribe it as $K_{ex,0}$. Furthermore, if it is allowed to assume that the hydration of the cation is negligible and that the value of $K_{dis}$ remains nearly constant in spite of the different concentration of water, the energy of phase transfer is given from Eq. 17 as:

$$-RT\ln K_{ex} = -RT\ln K_{ex,0} - RTn_h \qquad (18)$$

Now, it may be obvious from Eq. 18 that the hydration in the organic phase reduces the energy of phase transfer, or improves the extraction. The correlation given by Eq. 17 is illustrated in Fig. 5 with the closed circles. The $\Delta G_h{}^\circ$ value for azide ion is regarded as $-320$ kJ mol$^{-1}$ by the reasons mentioned for Eq. 10. The experimental results, shown by the open circles, situate below the filled ones. This indicates that the $-RT\ln K_{ex}$ is smaller than $-RT\ln K_{ex,0}$ by $RTn_h$ as is given by Eq. 18. This may be also explained from the principle of chemical equilibrium that any addition of new species in the organic phase always increases the distribution ratio in any extraction equilibria.

In such a case in which the hydration of the extracted species is very small, the linear correlation between $-RT\ln K_{ex}$ and $\Delta G_h{}^\circ$ should be realized by experimental data. One of such examples is the extraction of several inorganic acids with trioctylphosphine oxide (TOPO) into hexane,[33)] where the hydration scarcely occurs in the organic phase, since the background water molecules in hexane are very few ($4\times10^{-3}$ mol dm$^{-3}$ at 293 K[14)]). In this extraction the cation is supposed to be a bulky solvate of $H^+$ (or $H_3O^+$) with TOPO to form an ion pair with anion in the organic phase. The extraction constant is defined as $K_{ex}(HX)=[H(TOPO)_nX]_{org}/[H^+][X^-][TOPO]^n_{org}$ where $n=1$ or 2. In Fig. 5 the triangles are the values of this $-RT\ln K_{ex}$ (HX) plotted against $\Delta G_h{}^\circ$. This linear relationship is given by the broken line though the point for $SCN^-$ still deviates. This deviation should be due to other reasons than the hydration tendency of thiocyanate ion.

As the conclusion, the energy of phase transfer of ions may be proportional to the hydration energy of the ions after the correction of the hydration in the organic phase. This hydration in the organic phase may improve the extraction of the ion pair.

## Appendix

The approximation in Eq. 11 can be rewritten as Eq. 19 and numerically examined by the following treatment.

$$\ln(a_{x,dry}/a_{x,wet}) \approx n_h \qquad (19)$$

The $n_h$ is expressed by Eq. 20 as the function of the stability constants of the hydrate $X(H_2O)_i{}^-$, $b_i$, and the activity of water $q$ in the organic solvent.

$$n_h = \frac{b_1q + 2b_2q^2 + 3b_3q^3 + \cdots}{1 + b_1q + b_2q^2 + b_3q^3 + \cdots} \qquad (20)$$

The activity of $X^-$ is $a_{x,dry}=\gamma[X^-]_{org}$ in the dry solvent and $a_{x,wet}=\gamma'[X^-]_{org,total}/(1+b_1q+b_2q^2+b_3q^3+\cdots)$ in the wet one. Supposing $\gamma=\gamma'$, we obtain Eq. 21 for the same amount of anion:

$$\ln(a_{x,dry}/a_{x,wet}) = \ln(1 + b_1q + b_2q^2 + b_3q^3 + \cdots) = \ln\phi \qquad (21)$$

where $\phi=1+b_1q+b_2q^2+b_3q^3\cdots$.

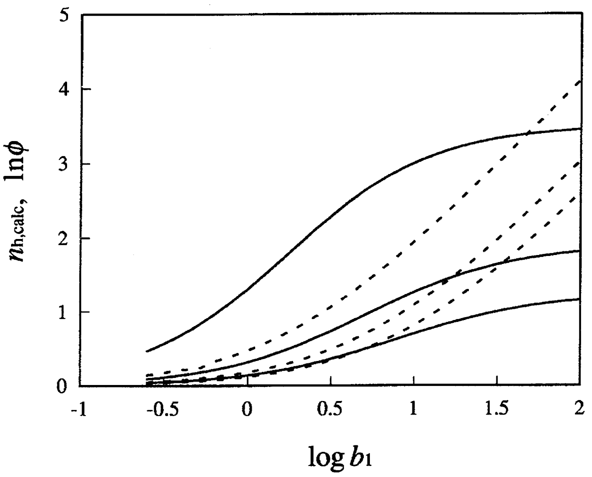

Fig. 6. Comparison of the hydration number (solid lines) and $\ln\phi$ (broken lines) calculated by Eqs. 20 and 21, respectively, assuming the activity of water $q=0.1$ and the stability constants of the hydrates $b_{n+1}=pb_n$ ($n=1$ to 5), where $p$ is supposed to be 2, 5, and 10 from the bottom to the top.

Since $b_i$ is the over-all stability constant for the $i$'th hydrate of $X^-$ ion, the numerical order should be $b_1<b_2<b_3\cdots$ except when saturation of the hydration site or any steric hindrance happens. For practical purposes, let us suppose $b_{n+1}/b_n=p$ where $p$ is a certain constant. The activity of water $q$ can be rounded to 0.1 mol dm$^{-3}$ because the concentration of water is 0.12 mol dm$^{-3}$. Then, the values of $n_h$ and $\ln\phi$ can be calculated by Eqs. 20 and 21, respectively, for the cases $p=2$, 5, and 10 using the terms up to $b_6$. The results are shown in Fig. 6. The solid and broken lines represent Eq. 20 and Eq. 21, respectively. From Fig. 6 it may be concluded that the approximation in Eq. 11 or Eq. 19 will be valid under certain restricted occasions decided by the combination of $b_i$ values. For more precise discussion, statistic treatments on the concentration of hydrates in the organic phase will be necessary, since the values of hydration numbers have been obtained only as the averaged value.

## References

1) M. Kawasaki, K. Toei, and T. Iwachido, *Chem. Lett.*, **1972**, 417.

2) J. F. Desreux, *Anal. Chim. Acta*, **52**, 207 (1970).

3) T. Kenjo and R. M. Diamond, *J. Phys. Chem.*, **76**, 2454 (1972).

4) T. Kenjo and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **36**, 183 (1974).

5) I. M. Ivanov and V. P. Zaitsev, "Proceedings of International Solvent Extraction Conference 1980," Abstr., 80-54.

6) K. Ito, E. Iwamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 2143 (1982).

7) S. Lis, J. N. Mathur, and G. R. Choppin, *Solvent Extr. Ion Exch.*, **9**, 637 (1991).

8) Y. Kikuchi, M. Kubota, T. Suzuki, and K. Sawada, *Bull. Chem. Soc. Jpn.*, **67**, 2111 (1994).

9) S. Kusakabe, M. Shinoda, and F. Kusafuka, *Bull. Chem. Soc. Jpn.*, **62**, 333 (1989).

10) K. Sawada, T. Sohara, and Y. Kikuchi, *J. Chem. Soc., Faraday Trans.*, **91**, 643 (1995).

11) E. Iwamoto, K. Ito, and Y. Yamamoto, *J. Phys. Chem.*, **85**,

894 (1981).

12) T. F. Lin, S. D. Christian, and H. E. Affsprung, *J. Phys. Chem.*, **69**, 2980 (1965).

13) C. Klofutar, S. Paljk, M. Senegacnik, and B. Jerkovic, *J. Inorg. Nucl. Chem.*, **34**, 3873 (1972).

14) J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents," 4th ed, John Wiley & Sons, New York (1986).

15) D. F. Evans and R. L. Kay, *J. Phys. Chem.*, **70**, 366 (1966).

16) U. Mayer, *Pure Appl. Chem.*, **51**, 1697 (1979).

17) M. G. Jalhoom and S. Siekierski, *Pol. J. Chem.*, **53**, 2319 (1979).

18) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

19) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770 (1975).

20) B. S. Krumgalz, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1887 (1980).

21) A. D'Aprano and R. M. Fuoss, *J. Solution Chem.*, **4**, 175 (1975).

22) R. L. Benoit and C. Louis, *Inorg. Nucl. Chem. Lett.*, **6**, 817 (1970).

23) Y. H. Inami, H. K. Bodenseh, and J. B. Ramsey, *J. Am. Chem. Soc.*, **83**, 4745 (1961).

24) Y. Nagano, H. Mizuno, M. Sakiyama, T. Fujiwara, and Y. Kondo, *J. Phys. Chem.*, **95**, 2536 (1991).

25) M. H. Abraham and A. F. Danil de Namor, *J. Chem. Soc., Faraday Trans. 1*, **72**, 955 (1976).

26) S. Motomizu, K. Toei, and T. Iwachido, *Bull. Chem. Soc. Jpn.*, **42**, 1006 (1969).

27) Y. Marcus, *J. Chem. Soc., Faraday Trans. 1*, **87**, 2995 (1991).

28) Y. Marcus, *J. Chem. Soc., Faraday Trans. 1*, **82**, 233 (1986).

29) Y. Marcus, *J. Chem. Soc., Faraday Trans. 1*, **83**, 339 (1987).

30) M. H. Abraham and J. Liszi, *J. Inorg. Nucl. Chem.*, **43**, 143 (1981).

31) V. V. Sergievski and Yu. G. Frolov, *Sov. Radiochem.* (*Engl. Transl.*), **16**, 278 (1974).

32) V. V. Sergievski, A. P. Zuev, Nguen Suan Ngok, and Yu. G. Frolov, *Sov. Radiochem.* (*Engl. Transl.*), **16**, 272 (1974).

33) M. Niitsu and T. Sekine, *Bull. Chem. Soc. Jpn.*, **50**, 1015 (1977).