

Hydration of Ions in Organic Solvent and Its Significance in the Gibbs Energy of Ion Transfer between Two Immiscible Liquids

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Various kinds of cations (alkali and alkaline earth metal ions, Me_4N^+ , Et_4N^+ , $n\text{-Bu}_4\text{N}^+$, and tetraphenylarsonium ion) and anions (halide ions, SCN^- , ClO_4^- , NO_3^- , and tetraphenylborate ion) have been extracted from water to nitrobenzene (NB) using several extractants: viz. tetraphenylborate and dipicrylamine for the cations; $n\text{-Bu}_4\text{N}^+$, $n\text{-Pen}_4\text{N}^+$, $n\text{-Hep}_4\text{N}^+$, and tris(1,10-phenanthroline)iron(II) for the anions. The determination of water content in NB by means of the Karl Fischer method has confirmed that some water molecules are coextracted by hydrophilic inorganic cations and anions. Accurate numbers (n) of the coextracted water molecules per ion have been established. On the basis of these findings, a new model has been proposed for a better understanding of the Gibbs energy ($\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$) of ion transfer at the organic solvent/water interface. If hydrated radii of ions evaluated from n are used, conventional (Born-type) electrostatic solvation models are invalid. A new approach recognizing short-range ion–solvent interactions (e.g. hydrogen bonds) has given a better account of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ for the hydrated ions.

Introduction

The standard Gibbs free energy ($\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$) of ion transfer at the organic solvent(O)/water(W) interface is a key concept intimately related to ion-transfer processes taking place in solvent extraction, membrane transport, ion-selective electrodes, cell membranes, etc. In theoretical treatments,¹ $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ has been generally evaluated on the basis of Born-type electrostatic solvation models.^{2–5} In the classical Born model,² the ion is considered as a hard sphere of a given radius r immersed in a continuous medium of constant permittivity; the transfer energy (i.e. resolution energy) of the ion is obtained as a difference between electrostatic energies for charging the ion up to ze (e the elementary charge) in O and W:

$$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{Born}) = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon^{\text{o}}} - \frac{1}{\epsilon^{\text{w}}} \right) \quad (1)$$

where N_A is the Avogadro constant, ϵ_0 is the permittivity of vacuum, and ϵ^{o} and ϵ^{w} are relative permittivities of O and W, respectively. In this Born model the effect of dielectric saturation (i.e. the lowering of the permittivity of solvents adjacent to an ion due to the high electric field) is not taken into account. So far, several modifications^{3–5} considering the dielectric effect have been proposed. In a recent paper,⁶ a non-Bornian approach to $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ has also been made by the authors, being based on quantum chemical considerations on short-range ion–solvent interactions of an ion with solvents.

In almost all theoretical studies described above, it is postulated or tacitly understood that when an ion is transferred across the O/W interface, it strips off solvated molecules completely, and hence the crystal ionic radius (r_c) is usually employed for the calculation of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$. Although Abraham and Liszi,^{4b} in considering the transfer between mutually

saturated solvents, were aware of the effects of hydration of ions in organic solvents in which water is quite soluble (e.g. 1-octanol, 1-pentanol, and methylisobutyl ketone), they concluded that in solvents such as 1,2-dichloroethane and nitrobenzene the solubility of water is rather small and most ions in the water-saturated solvent exist as unhydrated entities. However, solvent extraction studies since 1968 have demonstrated that water molecules are coextracted with ions into organic solvents such as nitrobenzene and 1,2-dichloroethane. Rais et al.⁷ and Iwachido and co-workers^{8–11} employed the Karl Fischer method to determine hydration numbers of alkali and alkaline earth metal ions in nitrobenzene (NB). Some inorganic anions (Cl^- , Br^- , I^- , SCN^- , ClO_4^- , and NO_3^-) have also been found to coextract water into NB.^{12–14} Similar phenomena have further been observed in solvents other than NB (e.g., 1,1- and 1,2-dichloroethane, 4-methyl-2-pentanone, chloroform, NB–benzene mixtures).^{14–17} If these observations are valid, we should reconsider the previous theories of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ of transfer of ions between mutually saturated solvents in which the hydration of ions in O is not properly taken into account. The purpose of this study is to reaffirm the hydration of ions in NB and determine accurate hydration numbers for a variety of common ions. A new model based on the postulated transfer of a hydrated ion will be proposed for $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$.

Experimental Section

Materials. Sodium tetraphenylborate (NaTPB; Dojindo Laboratories) was purified by recrystallization from 1:1 (v/v) acetone–chloroform upon heating. Lithium salt of TPB^- was prepared by the literature method.¹⁸ For preparing the calcium salt of TPB^- , a large excess of solid calcium chloride was added to an acetone solution of NaTPB; after stirring for several hours, the residue containing sodium chloride was removed by filtration. This operation was repeated three times. By evaporating the resulting solution to dryness, $\text{Ca}(\text{TPB})_2$ in crystalline form was obtained. Et_4N^+ , $n\text{-Bu}_4\text{N}^+$, $n\text{-Pen}_4\text{N}^+$, and tetraphenylarsonium (TPAs^+) salts of TPB^- were prepared by an equimolar mixing of a NaTPB solution with solutions of

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Et_4NCl , $n\text{-Bu}_4\text{NBr}$, $n\text{-Pen}_4\text{NCl}$, or TPAsCl , respectively, and then purified by recrystallization from 1:1 (v/v) acetone–ethanol.

Sodium dipicrylamine (NaDPA) was purchased from Tokyo Kasei Kogyo Co. Ltd. and used as received. The other alkali and alkaline earth metal salts of DPA^- were prepared by the reported procedures.¹⁷ Dipicrylamine (explosive; now unavailable in Japan) was kindly given by Prof. Sorin Kihara of Kyoto Institute of Technology. The Me_4N^+ , Et_4N^+ , and TPAs^+ salts of DPA^- were prepared by an equimolar mixing of a solution of NaDPA with a solution of the bromide of the corresponding cation, and the precipitate was recrystallized from the acetone solution by the addition of water.

$n\text{-Bu}_4\text{N}^+$ bromide (Wako Pure Chemical Industries, Ltd.), iodide (Tokyo Kasei), and thiocyanate (Tokyo Kasei) were used as received. $n\text{-Pen}_4\text{N}^+$ thiocyanate was prepared by the equimolar addition of a solution of $n\text{-Pen}_4\text{NCl}$ and a solution of sodium thiocyanate; the resulting precipitate was extracted into chloroform, and the desired salt was recrystallized by the addition of hexane. $n\text{-Pen}_4\text{N}^+$ perchlorate was likewise prepared from the sodium salt and recrystallized from the ethanol solution by the addition of water. $n\text{-Pen}_4\text{N}^+$ chloride, bromide, and iodide were purchased from Wako and used as received. $n\text{-Hep}_4\text{N}^+$ thiocyanate, perchlorate, and TPB^- were prepared by an equimolar addition of ethanol solution of $n\text{-Hep}_4\text{NBr}$ and aqueous solution of a sodium salt of each anion, and then purified by recrystallization from 1:1 (v/v) water–ethanol or 1:1 (v/v) acetone–ethanol (for the TPB^- salt). $n\text{-Hep}_4\text{N}^+$ bromide (Aldrich) and iodide (Tokyo Kasei) were used as received.

The salts of tris(1,10-phenanthroline)iron(II) ($\text{Fe}(\text{phen})_3^{2+}$) with anions were prepared as follows: equimolar aqueous solutions of iron(II) sulfate and 1,10-phenanthroline monohydrate (Nacalai Tesque, Inc.) were mixed; the desired salt was precipitated by adding an excess amount of the sodium salt of each anion and then recrystallized from ethanol.

Analytical grade NB (Wako) was treated with activated alumina for column chromatography (Wako; 200 mesh) before use. All other reagents were of analytical grade and used without further purification.

Procedures. For distribution experiments, 5 mL of both the aqueous and NB phases were put in a glass bottle (25 mL) with a Teflon cap, shaken in a water bath thermostated at $25 \pm 0.1^\circ\text{C}$ for 1 h, and then separated by allowing to stand for at least 30 min. The aqueous phase was pipetted off from the glass bottle directly when placed in the water bath, and an aliquot of the aqueous solution was subjected to determination of ion(s) (for details, see below). Then an aliquot (500 μL) of the NB phase in the bottle was slowly drawn off using a microsyringe and subjected to the determination of water concentration by means of a Karl Fischer coulometer (Kishida Chemicals CA-20).

In distribution experiments of cations with TPB^- , the TPB^- salts of Li^+ , Na^+ , or Ca^{2+} were added to the aqueous phase, whereas the TPB^- salts of Et_4N^+ or $n\text{-Bu}_4\text{N}^+$ were added to the NB phase. The concentration of the TPB^- salts ranged from 0 to 20 mM. In the distribution experiments with Li^+ , Na^+ , and Ca^{2+} , the aqueous phase also contained 5.0 mM CaCl_2 in order to prevent formation of emulsions.¹⁹ In a distribution experiment of Ba^{2+} with TPB^- , BaCl_2 (20 mM) and NaTPB (0–20 mM) were added to the aqueous phase. As for the hydrophilic metal ions (Li^+ , Na^+ , Ca^{2+} , and Ba^{2+}), the concentration of the ion(s) that remained in the aqueous phase was measured using an inductively coupled plasma emission spectrometer (Shimadzu ICPS-5000). As for the hydrophobic

organic ions (Et_4N^+ and $n\text{-Bu}_4\text{N}^+$), the equilibrium concentrations of these ions in NB were considered to be equal to the initial concentrations, because these TPB^- salts are virtually insoluble in water. Distribution experiments of K^+ , Rb^+ , Cs^+ , and TPAs^+ with TPB^- could not be performed, since the TPB^- salts of these ions were not adequately soluble in both W and NB.

In distribution experiments of cations with DPA^- , DPA^- salts of Li^+ , Na^+ , Ca^{2+} , or Ba^{2+} were added to the aqueous phase, whereas the DPA^- salts of K^+ , Rb^+ , Me_4N^+ , or Et_4N^+ were added to the NB phase. The initial concentration of the DPA^- salts was 0–50 mM. In the distribution experiments of the metal ions, the nitrate or chloride salt of each ion was added to the aqueous phase (the ionic strength, $I = 0.1$) to prevent formation of emulsions. The pH of the aqueous phase was adjusted to 10 by using a hydroxide of the respective metal ion. The equilibrium concentration of DPA^- in the aqueous phase was determined from its absorbance at 428 nm ($\epsilon = 2.61 \times 10^4$), and the concentration of the cations was then calculated.

In distribution experiments of anions with R_4N^+ ($\text{R} = n\text{-Bu}$, $n\text{-Pen}$, and $n\text{-Hep}$), R_4N^+ salts of Cl^- or Br^- were added to the aqueous phase, while the R_4N^+ salts of I^- , SCN^- , or ClO_4^- were added to the NB phase (salt concentration = 0–100 mM). The equilibrium concentration of R_4N^+ (=the anion concentration) in the aqueous phase was determined by conductometric titration with a standard NaTPB solution.

In distribution experiments of anions with $\text{Fe}(\text{phen})_3^{2+}$, $\text{Fe}(\text{phen})_3^{2+}$ salts of Br^- or NO_3^- were added to the aqueous phase, while the $\text{Fe}(\text{phen})_3^{2+}$ salts of SCN^- , ClO_4^- , or TPB^- were added to the NB phase (salt concentration = 0–100 mM). The equilibrium concentration of $\text{Fe}(\text{phen})_3^{2+}$ in the aqueous phase (=the anion concentration)/2 was determined from its absorbance at 510 nm ($\epsilon = 1.058 \times 10^4$).

Results and Discussion

Distribution Behavior of Ions. Since NB has a relatively high permittivity ($\epsilon^0 = 34.8$), the ion-pair formation in NB is usually of less significance. Thus, in the “ion-pair” extraction systems using NB, the formation of ion pairs is not necessarily required to be considered for low overall concentrations of the salts. According to the proposed theory,^{20–23} the distribution equilibrium in such a system can be described in terms of the standard ion-transfer potential ($\Delta_{\text{O}}^{\text{W}}\phi_i^0 = -(\Delta G_{\text{tr}}^{\text{O} \rightarrow \text{W}}/z_i F$; F , the Faraday constant) as a measure of extractability (or hydrophobicity) of an individual ion. When m kinds of ions are distributed at equilibrium between the O/W interface, the Galvani potential difference ($\Delta_{\text{O}}^{\text{W}}\phi \equiv \phi^{\text{W}} - \phi^{\text{O}}$) across the O/W interface is given by^{20,21,23}

$$\sum_{i=1}^m \frac{z_i c_i^{0,\text{W}}}{1 + \exp\left[\frac{z_i F}{RT}(\Delta_{\text{O}}^{\text{W}}\phi - \Delta_{\text{O}}^{\text{W}}\phi_i^0)\right]} + \sum_{i=1}^m \frac{z_i c_i^{0,\text{O}}}{1 + \exp\left[\frac{z_i F}{RT}(\Delta_{\text{O}}^{\text{W}}\phi - \Delta_{\text{O}}^{\text{W}}\phi_i^0)\right]} = 0 \quad (2)$$

where z_i and $\Delta_{\text{O}}^{\text{W}}\phi_i^0$ are, respectively, the charge number (including the sign) and the standard ion-transfer potential of ion i ($i = 1, 2, 3, \dots, m$), $c_i^{0,\text{W}}$ and $c_i^{0,\text{O}}$ are the initial concentrations of the ion in W and O, and R and T have their usual meanings. In eq 2, it is assumed that the volume ratio of the two phases is 1. If the values of $\Delta_{\text{O}}^{\text{W}}\phi_i^0$ are known for all ions

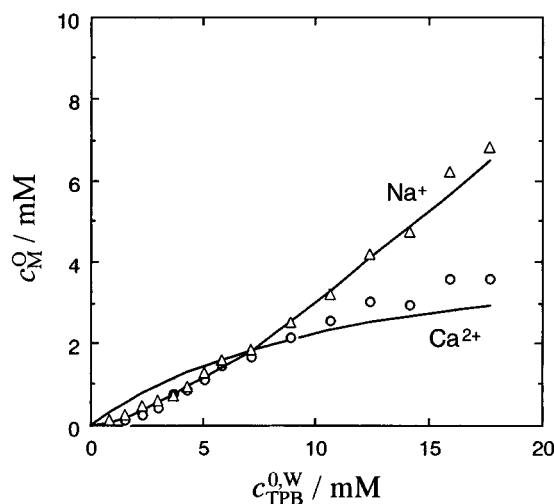


Figure 1. Plots of equilibrium concentrations of Na^+ and Ca^{2+} in NB against the initial concentration of TPB^- in W. To the aqueous phase, CaCl_2 (5.0 mM) as well as NaTPB was added at the beginning. Solid lines show regression curves obtained with eqs 2 and 3.

in the system of interest, the value of $\Delta_O^W\phi$ can be evaluated from eq 2. Then, the distribution ratio of each ion can be calculated from the Nernst equation:

$$D_i \equiv \frac{c_i^O}{c_i^W} = \exp\left[\frac{z_i F}{RT}(\Delta_O^W\phi - \Delta_O^W\phi_i^0)\right] \quad (3)$$

where c_i^O and c_i^W are the equilibrium concentrations of ion i in O and W, respectively. In this study, it is assumed for simplicity that the concentration of an ion is equal to the activity. As shown below, distribution equilibria in the present NB–W system have been well elucidated by using the above equations in which no ion-pair formation is considered.

Distribution of Cations with TPB^- . The extraction of Ca^{2+} into NB was performed by adding $\text{Ca}(\text{TPB})_2$ to the aqueous phase containing 5.0 mM CaCl_2 (for preventing emulsification). In this case, Ca^{2+} and TPB^- are distributed to NB, but Cl^- is hardly extracted to NB. This can readily be expected from eqs

2 and 3: Because the $\Delta_O^W\phi^0$ of Cl^- (ca. -0.45 V^{24}) is much more negative than that of TPB^- (0.372 V^{25}) or Ca^{2+} (0.349 V^{26}), the term pertaining to Cl^- in eq 2 can be neglected. At the equilibrium potential ($\Delta_O^W\phi$) thus determined by Ca^{2+} and TPB^- , all Cl^- ions remain in the aqueous phase. Under these conditions, it can be predicted from eqs 2 and 3 that the equilibrium concentration of Ca^{2+} in NB (c_{Ca}^O) depends linearly on the initial concentration of TPB^- in W ($c_{\text{TPB}}^{0,W}$). In practice, such a linear dependence was observed for $c_{\text{TPB}}^{0,W} < 25 \text{ mM}$; the regression line is expressed as $(c_{\text{Ca}}^O/\text{mM}) = 0.366(c_{\text{TPB}}^{0,W}/\text{mM})$ (correlation coefficient = 0.994). As a result of a regression analysis using eqs 2 and 3, a value of $\Delta_O^W\phi^0$ ($=0.355 \text{ V}$) for Ca^{2+} as an adjustable parameter is obtained in fair agreement with a literature value of 0.349 V^{26} . In this regression analysis, the $\Delta_O^W\phi^0$ value of TPB^- was fixed at the literature value²⁵ of 0.372 V , since the distribution ratio of an ion is determined by relative values of $\Delta_O^W\phi^0$, as can be seen from eqs 2 and 3.

Figure 1 shows the results obtained when CaCl_2 (5.0 mM) and NaTPB were added to the aqueous phase. In this case, both Ca^{2+} and Na^+ were extracted to NB. As shown by the plots in Figure 1, distribution ratios of the ions changed with the initial concentration of NaTPB in W. This can be well elucidated using eqs 2 and 3; solid lines in Figure 1 show regression curves obtained with eqs 2 and 3. A satisfactory agreement between experimental and theoretical values was obtained, although there are some deviations from the experimental values for Ca^{2+} (the deviations at lower concentrations may be ascribed to possible adsorption of Ca^{2+} onto emulsions slightly formed in W). In the fitting analysis, the $\Delta_O^W\phi^0$ value of Ca^{2+} was fixed to the value of 0.355 V obtained in the above regression analysis. The $\Delta_O^W\phi^0$ value of Na^+ as the only adjusting parameter was found to be 0.364 V , which was close to a literature value²⁵ (0.354 V). A similar regression analysis was successful for Li^+ . The $\Delta_O^W\phi^0$ value (0.375 V) of Li^+ thus obtained is shown with a literature value²⁵ (0.395 V) in Table 1, where the $\Delta_O^W\phi^0$ values of various ions being determined in other extraction systems are also shown with literature values.

Distribution of Cations with DPA^- . Figure 2 shows the results of distribution experiments of Li^+ , Na^+ , K^+ , Rb^+ ,

TABLE 1: Standard Ion-Transfer Potentials Obtained from Regression Analyses of Distribution Data in Several Extraction Systems at 25°C

ion	$\Delta_O^W\phi^0$ (V)				
	literature	TPB^- system ^a	DPA^- system ^b	$n\text{-Bu}_4\text{N}^+$ system ^c	$\text{Fe}(\text{phen})_3^{2+}$ system ^d
(cation)					
Li^+	0.395 ^e	0.375 (-0.020) ^j	0.420 ($+0.025$)		
Na^+	0.354 ^e	0.364 ($+0.010$)	0.347 (-0.007)		
K^+	0.242 ^e		0.237 (-0.005)		
Rb^+	0.201 ^e		0.190 (-0.011)		
Ca^{2+}	0.349 ^f	0.355 ($+0.006$)	0.364 ($+0.015$)		
Ba^{2+}	0.320 ^f		0.307 (-0.013)		
$n\text{-Bu}_4\text{N}^+$	-0.275 ^g			-0.275 (fixed)	
$\text{Fe}(\text{phen})_3^{2+}$	-0.228 ^h				-0.228 (fixed)
(anion)					
TPB^-	0.372 ^e	0.372 (fixed)			
DPA^-	0.407 ^e		0.407 (fixed)		
ClO_4^-	-0.094 ^h			-0.055 ($+0.039$)	-0.059 ($+0.035$)
SCN^-	-0.185 ^h			-0.147 ($+0.038$)	-0.139 ($+0.046$)
I^-	-0.210 ^h			-0.175 ($+0.035$)	-0.171 ($+0.039$)
Br^-	-0.340 ^h			-0.32 ^k	-0.36 ^k
Cl^-	-0.45 ⁱ			-0.36 ^k	
NO_3^-	-0.289 ^h				-0.30 ^k

^a The TPB^- salt of Li^+ , Na^+ , or Ca^{2+} and CaCl_2 (5.0 mM) were added to W. ^b The DPA^- salt of each metal ion was added to W ($I = 0.1$; pH = 10). ^c The $n\text{-Bu}_4\text{N}^+$ salt of each anion was added to W or NB. ^d The $\text{Fe}(\text{phen})_3^{2+}$ salt of each anion was added to W or NB. ^e Reference 25. ^f Reference 26. ^g Reference 27. ^h Reference 21. ⁱ Reference 24. ^j The values in parentheses show deviations from the literature values. ^k Roughly determined.

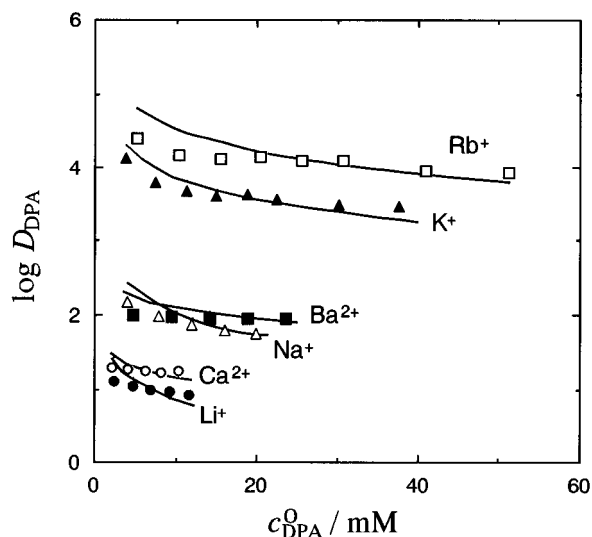


Figure 2. Dependencies of distribution ratios of alkali and alkaline earth metal ions on the initial concentration of DPA^- in W ($I = 0.1$; pH = 10) or NB. Each solid line shows a regression curve obtained with eqs 2 and 3.

Ca^{2+} , and Ba^{2+} with DPA^- (the data for Cs^+ and organic cations have been omitted in the figure, since the distribution ratios of these ions could not accurately be determined because of their high extractabilities to NB). In the figure, the logarithm of the distribution ratio of DPA^- is plotted against the initial concentration of DPA^- in W or NB. Each solid line shows the regression curve which was calculated using eqs 2 and 3. In the fitting analysis, the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ value of each cation was an adjusting parameter, whereas the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ value of DPA^- was fixed to the literature value²⁵ (0.407 V). As shown in Table 1, the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ values of the metal ions obtained in the regression analysis are consistent with the literature values. Thus, eqs 2 and 3 which were obtained by assuming no ion-pair formation were available for this system, suggesting that the metal ions were mostly unassociated in NB. These results are in harmony with the previous observation.⁷

Distribution of Anions. In distribution experiments of anions, only a single electrolyte was distributed in the NB–W system. If no ion-pairs are formed in both phases, the distribution ratio of an ion, D ($\equiv c_{\text{ion}}^{\text{O}}/c_{\text{ion}}^{\text{W}}$), given by eq 3 can be expressed as

$$\ln D = \left(\frac{z_{\text{c}} z_{\text{a}}}{z_{\text{a}} - z_{\text{c}}} \right) \frac{F}{RT} (\Delta_{\text{O}}^{\text{W}}\phi_{\text{anion}}^{\circ} - \Delta_{\text{O}}^{\text{W}}\phi_{\text{cation}}^{\circ}) \quad (4)$$

where z_{c} and z_{a} are the charge numbers of the cation and the anion, respectively. In this way, the distribution ratio should depend on the difference in standard ion-transfer potential between the cation and the anion and not on the concentration of the electrolyte. In practice, it was found that in the extraction systems with $n\text{-Bu}_4\text{N}^+$ and $\text{Fe}(\text{phen})_3^{2+}$, the equilibrium concentration of an anion in NB was proportional to the initial concentration of the anion in W. In the extraction systems with $n\text{-Pen}_4\text{N}^+$ and $n\text{-Hep}_4\text{N}^+$, however, no accurate distribution ratios of anions could be determined because the anions were quantitatively extracted to NB.

As seen from eq 4, the more positive the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ value of an anion is, or the more hydrophobic the anion is, the larger the value of D . In the $n\text{-Bu}_4\text{N}^+$ system, the value of D increased in the order $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{SCN}^- < \text{ClO}_4^- < \text{TPB}^-$. In the $\text{Fe}(\text{phen})_3^{2+}$ system, the order was $\text{Br}^- < \text{NO}_3^- < \text{I}^- < \text{SCN}^- < \text{ClO}_4^- < \text{TPB}^-$. These orders are in agreement with

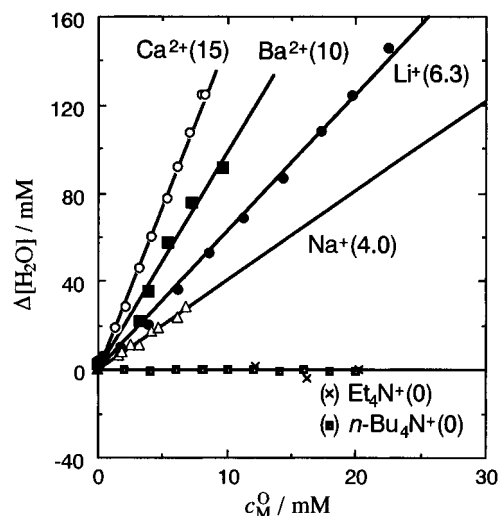


Figure 3. Plots of the increase of water concentration in NB ($\Delta[\text{H}_2\text{O}]$) with extraction of cations with TPB^- against the equilibrium cation concentration in NB. The $\Delta[\text{H}_2\text{O}]$ values of Li^+ and Na^+ were corrected for the contribution from Ca^{2+} . The $\Delta[\text{H}_2\text{O}]$ value of Ba^{2+} was corrected for the contribution from Na^+ . Each value in the parentheses shows the number (n) of coextracted water molecules per ion.

the order of $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ (see Table 1). By using literature values of $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ for $n\text{-Bu}_4\text{N}^+$ (-0.275 V²⁷) and $\text{Fe}(\text{phen})_3^{2+}$ (-0.228 V²¹), the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ values of the anions were evaluated from distribution ratios (see also Table 1). Because Br^- , I^- , and NO_3^- were only slightly extracted to NB, their $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ values being determined from rather small distribution ratios should contain large experimental errors. The more reliable values of $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ for three other anions (I^- , SCN^- , and ClO_4^-) have been found to be more positive than the literature values by ca. 0.04 V. If the literature values of $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ for $n\text{-Bu}_4\text{N}^+$ and $\text{Fe}(\text{phen})_3^{2+}$ are correct, the $\Delta_{\text{O}}^{\text{W}}\phi^{\circ}$ values of the anions should perhaps be revised and further studies seem to be needed. Apart from this point, the above results clearly show that the anions studied as well as the metal ions are unassociated in NB.

Number of Coextracted Water Molecules. It has been found that pure NB dissolves water at a concentration of 0.168 ± 0.004 M at 25 °C (literature value,¹¹ 0.178 M). The increase in water concentration in NB ($\Delta[\text{H}_2\text{O}]$) with extraction of an ion was evaluated as a function of equilibrium concentration of the ion in NB. A typical example, obtained in the TPB^- system, is shown in Figure 3. The $\Delta[\text{H}_2\text{O}]$ values of Li^+ and Na^+ have been corrected for the contribution from Ca^{2+} being simultaneously extracted to NB. Similarly, the $\Delta[\text{H}_2\text{O}]$ value of Ba^{2+} has been corrected for the contribution from Na^+ . As seen in Figure 3, hydrophobic organic cations (Et_4N^+ and $n\text{-Bu}_4\text{N}^+$) showed no increase in water concentration, indicating that these cations as well as TPB^- had no ability to transport water to NB. In contrast, hydrophilic metal ions showed a distinguishing increase. The slope of each linear plot should correspond to the number (n) of water molecules coextracted to NB with a metal ion, which are listed in Table 2 together with those determined in other systems. As shown in Figure 4, a similar result was obtained in the DPA^- system. Hydrophobic organic cations (Me_4N^+ , Et_4N^+ , and TPAs^+) showed no increase in water, while metal ions showed a more or less distinguishing increase. As shown in Table 2, the n values determined from the slopes of linear plots were in fair agreement with the literature values.^{7,8} Thus, it has been reaffirmed that alkali and alkaline earth metal ions coextract 0.4–6.0 water molecules to NB.

It has also been confirmed that inorganic anions studied have an ability to transport 0.2–4.0 water molecules to NB. In all

TABLE 2: Numbers (n) of Coextracted Water Molecules in NB and Radii (r_h) of Hydrated Ions at 25 °C

cation	n			r_h (nm)	r_c^a (nm)
	TPB ⁻ system	DPA ⁻ system	av		
Li ⁺	6.3	5.7 (4.2 ^b ; 5.5 ^c)	6.0 ± 0.4	0.351	0.073 ^g
Na ⁺	4.0	3.6 (3.6 ^b ; 3.5 ^c)	3.8 ± 0.3	0.307	0.116 ^g
K ⁺		1.0 (1.0 ^b ; 1.3 ^c)	1.0	0.220	0.152 ^g
Rb ⁺		0.7 (0 ^b ; 0.7 ^c)	0.7	0.212	0.166 ^g
Cs ⁺		0.4 (0 ^b ; 0.7 ^c)	0.4	0.206	0.181 ^g
Ca ²⁺	15	12 (13 ^c)	14 ± 2	0.467	0.114 ^g
Ba ²⁺	10	11 (9.4 ^c)	11 ± 1	0.435	0.149 ^g
Me ₄ N ⁺		0	0		0.279 ^h
Et ₄ N ⁺	0	0	0 ± 0		0.337 ^h
<i>n</i> -Bu ₄ N ⁺	0 (~0 ^d)	0	0		0.413 ^h
TPAs ⁺		0	0		0.426 ⁱ

anion	n				av	r_h (nm)	r_c^a (nm)
	<i>n</i> -Bu ₄ N ⁺ system	<i>n</i> -Pen ₄ N ⁺ system	<i>n</i> -Hep ₄ N ⁺ system	[Fe(phen) ₃] ²⁺ system			
Cl ⁻		4.0 (3.3 ^c)			4.0	0.322	0.167 ^g
Br ⁻	2.1 (1.8 ^e)	2.1	2.0	<i>j</i> (5.5 ^f)	2.1 ± 0.1	0.276	0.182 ^g
I ⁻	0.9	0.8	1.0	1.0 ^k (2.1 ^f)	0.9 ± 0.1	0.248	0.206 ^g
SCN ⁻	1.1	1.1	1.0	1.1 ^k (1.9 ^f)	1.1 ± 0.1	0.260	0.213 ⁱ
ClO ₄ ⁻	0.3	0.2	0.2	0.1 ^k (0.64 ^f)	0.2 ± 0.1	0.244	0.236 ⁱ
NO ₃ ⁻	(~1.4 ^d)			1.7 ^k	1.7	0.267	0.189 ⁱ
TPB ⁻	0 (~0 ^d)	0	0	0 ^k	0		0.421 ⁱ

^a Crystal ionic radius. ^b Reference 7. ^c Reference 8. ^d Reference 14. ^e Reference 15. ^f Reference 13. ^g Reference 28. ^h Calculated from the van der Waals volume of the ion.²⁹ ⁱ Reference 30. ^j No reliable value could be obtained due to the extremely low extractability ($D < 0.03$). ^k Corrected for the contribution ($n = 0.3$) from [Fe(phen)₃]²⁺.

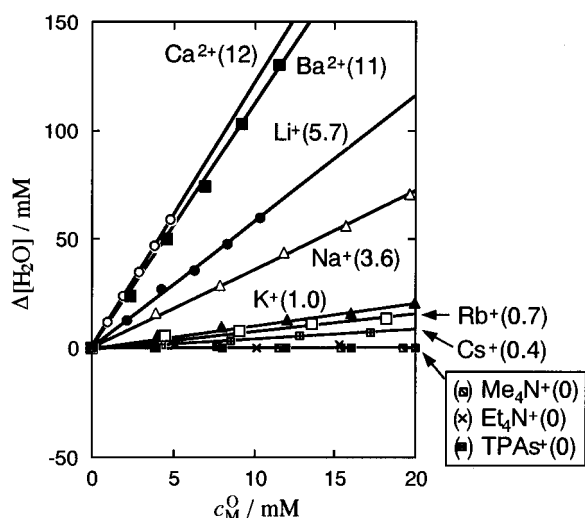


Figure 4. Plots of the increase of water concentration in NB ($\Delta[\text{H}_2\text{O}]$) with extraction of cations with DPA⁻ against the equilibrium cation concentration in NB. Each value in the parentheses shows the number (n) of coextracted water molecules per ion.

extraction systems for anions, linear dependences of $\Delta[\text{H}_2\text{O}]$ on the equilibrium anion concentration in NB were also observed (plots not shown). As shown in Table 2, the n values obtained in the n -R₄N⁺ (n -Bu₄N⁺, n -Pen₄N⁺, and n -Hep₄N⁺) systems coincided well with each other. Also, some of the values are in harmony with the literature values.^{14,15} In the [Fe(phen)₃]²⁺ system, however, the n values of all anions including TPB⁻, which were determined directly from the slopes of $\Delta[\text{H}_2\text{O}]$ vs anion concentration plots, were larger by ca. 0.3 than those obtained in the above n -R₄N⁺ systems. Since TPB⁻ has no ability to transport water as shown above, the value of 0.3 should be allotted to [Fe(phen)₃]²⁺. This may be supported by the previous observation,³¹ in which [Fe(phen)₃]²⁺ formed an adduct with as much as 6 water molecules when it was extracted to nitromethane. However, this view was later criticized by Yamamoto et al.,¹³ who concluded that water was transported exclusively by the anion (e.g. ClO₄⁻ in ref 31) and the chelate cation took no part in the transference. On the whole,

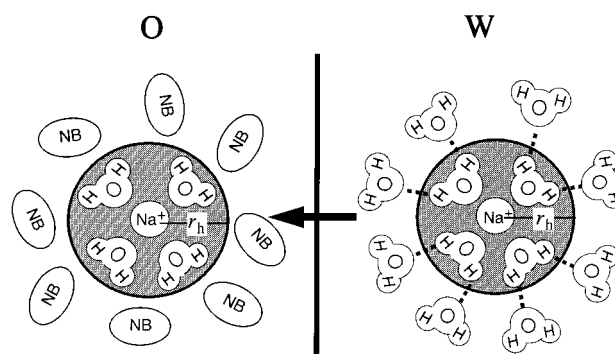


Figure 5. Proposed model of the transfer of a hydrophilic ion across the O/W interface. The illustration shows the transfer of Na⁺ from water (W) to nitrobenzene (NB) as a typical example.

Yamamoto et al.'s conclusion is in line with the present result, but the contribution from the chelate cation should not be excluded completely. In this study, by subtracting 0.3 from the observed n values for anions, their net values have been estimated. The estimated values, however, are somewhat smaller than literature values,¹³ even if the literature values are corrected for the contribution ($n = 0.3$) from [Fe(phen)₃]²⁺. The origin of this discrepancy has not been elucidated.

For both cations and anions, the n values determined were only slightly dependent on the nature of extractant (i.e. co-ion). This is an additional proof that ion-pair formation in NB is of less significance or that the ions are almost dissociated. Thus we could determine accurate numbers of water molecules being certainly associated with individual ions.

Proposed Model of Interfacial Transfer of a Hydrophilic Ion. On the basis of the above experimental findings, we propose a new model, as depicted in Figure 5. In this model, the hydrophilic ion transfers from W to O with some water molecules associated with the ion. A typical example in the figure shows that a sodium ion transfers across the NB/W interface with 4 water molecules. In theoretical treatment of transfer energy of such a hydrophilic ion, therefore, the transferring species should be regarded as the "hydrated" ion. Accordingly, the radii (r_h) of hydrated ions in NB were estimated

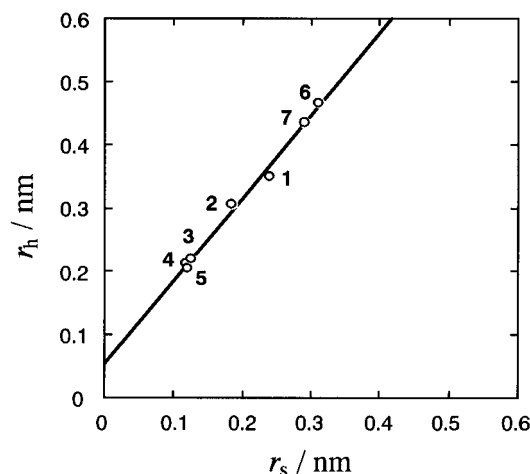


Figure 6. Correlation of the hydrated radius (r_h) with the Stokes radius (r_s) for alkali and alkaline earth metal ions: (1) Li^+ , (2) Na^+ , (3) K^+ , (4) Rb^+ , (5) Cs^+ , (6) Ca^{2+} , (7) Ba^{2+} . The solid line represents the regression line which is given by $(r_h/\text{nm}) = 1.310(r_s/\text{nm}) + 0.055$.

from hydration numbers (n) and crystal ionic radii^{28–30} (r_c) by

$$r_h = \sqrt[3]{\frac{3}{4\pi\rho}n + r_c^3} \quad (5)$$

where ρ is the density of water in the hydration shell (here, the value of ρ is assumed to be the same as that of bulk water, i.e., $3.33 \times 10^{28} \text{ molecule m}^{-3}$). The estimated values of r_h are shown in Table 2.

The correlations of r_h with the Stokes radius³² (r_s) have been investigated. Although there has been no clear correlation for anions, r_h for alkali and alkaline earth metal ions has been found to show good correlation with r_s , as shown in Figure 6; the regression line is expressed as $(r_h/\text{nm}) = 1.310(r_s/\text{nm}) + 0.055$ (correlation coefficient = 0.997). This correlation suggests the similarity of transfer processes of these metal ions at the O/W interface to the properties in bulk water. The water molecules which are strongly bound to the metal ions in W appear to be undissociated even in the ion transfer across the O/W interface.

Invalidity of Bornian Electrostatic Models. As seen in Table 2, the order of the magnitude of r_h for alkali metal ions is the reverse of that of the magnitude of r_c . This means that a more hydrophilic ion has a larger r_h . However, this fact does contradict the expectation from Bornian electrostatic theories. As can be seen in the Born equation (eq 1), it is expected that the larger radius an ion has, the more positive $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ value the ion has, that is, the more hydrophobic it becomes. For example, this would show that Li^+ is more hydrophobic than Cs^+ , but this is of course not the case. An invalidity of the Born model will be also confirmed by the following more quantitative analysis.

So far it has been customary to divide $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ into two (or three) parts corresponding to electrostatic and nonelectrostatic (and specific) ion–solvent interactions.^{1,3,5,6,33} Such a division is to a certain degree arbitrary since different effects may overlap. However, here it is useful to evaluate the individual effects. In this analysis we divided $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ into two terms:

$$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}} = \Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep}) + \Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-indep}) \quad (6)$$

where $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ is the charge-dependent term which comprises the electrostatic (long-range) ion–solvent interaction (i.e. charging energy) and/or the specific (short-range) interactions of an ion with solvents in its immediate vicinity (i.e.

TABLE 3: Gibbs Energies of Transfer of Ions at the NB/W Interface and Its Charge-Independent and -Dependent Components at 25 °C

ion	$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$ (kJ mol ⁻¹)	$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-indep})^a$ (kJ mol ⁻¹)	$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ (kJ mol ⁻¹)
(cation)			
Li^+	-38.2 ^b	23.6	-61.8
Na^+	-34.2 ^b	17.9	-52.1
K^+	-23.5 ^b	9.2	-32.7
Rb^+	-19.4 ^b	8.6	-28.0
Cs^+	-15.4 ^b	8.1	-23.5
Ca^{2+}	-67.3 ^c	41.6	-108.9
Ba^{2+}	-61.8 ^c	36.0	-97.8
Me_4N^+	-3.4 ^b	14.8	-18.2
Et_4N^+	5.3 ^d	21.7	-16.4
$n\text{-Bu}_4\text{N}^+$	26.5 ^e	32.5	-6.0
TPAs^+	35.9 ^b	34.6	1.3
(anion)			
Cl^-	-44 ^f	19.8	-63.8
Br^-	-32.8 ^g	14.6	-47.4
I^-	-20.3 ^g	11.7	-32.0
SCN^-	-17.9 ^g	12.9	-30.8
ClO_4^-	-9.1 ^g	11.4	-20.5
NO_3^-	-27.9 ^g	13.5	-41.4
TPB^-	35.9 ^b	33.8	2.1

^a Evaluated by the Uhlig equation (eq 7) with $r = r_h$ (for the inorganic ions) or r_c (for the organic ions). ^b Reference 25. ^c Reference 26. ^d Reference 36. The value is revised by employing Me_4N^+ as a reference ion in the place of $n\text{-Bu}_4\text{N}^+$. ^e Reference 27. ^f Reference 24. ^g Reference 21.

donor–acceptor effects or hydrogen bonds), and $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-indep})$ is the charge-independent term corresponding to the solvophobic interaction or the energy of the formation of a cavity in solvents. Although several formulas have been proposed for the theoretical calculation of the cavity formation energy, Volkov and co-workers^{1,5} successfully employed the semiempirical Uhlig formula³⁴ to evaluate the solvophobic contribution to the resolution energy of large organic cations. When the surface tension at the boundary of O with air is smaller than that of W, the Uhlig formula is written as

$$\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-indep}) = 4\pi N_A r^2 \sigma_{\text{O,W}} \quad (7)$$

where $\sigma_{\text{O,W}}$ is the interfacial tension at the plane interface between two solvents. Since the Uhlig formula is supposed to be valid for $\sigma_{\text{O,W}} > 10 \text{ mN m}^{-1}$ and $r > 0.2 \text{ nm}$,¹ it may be applied to the hydrated ions ($r_h > 0.21 \text{ nm}$) in the present NB–W system ($\sigma_{\text{O,W}} = 25.2 \text{ mN m}^{-1}$ ³⁵). Then we have tentatively employed the Uhlig formula to evaluate $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-indep})$ for the hydrated ions with $r = r_h$. By subtracting $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ from the literature values of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$, $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ are evaluated (see Table 3). If the Born equation (eq 1) is valid, $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ should be proportional to (z^2/r_h) . In practice, however, the plot of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}(\text{z-dep})$ against (z^2/r_h) has not shown a straight line (Figure 7). Although several modifications^{3–5} of the Born equation, in which the dielectric effect is taken into consideration, have been proposed, there is no essential difference between the simple Born equation and its modifications in the r -dependence of $\Delta G_{\text{tr}}^{\text{o},\text{o}-\text{w}}$. Accordingly, any modification could not serve as a rational explanation of the dispersed plots in Figure 7. We conclude that, if the hydrated ion is regarded as the transferring species at the O/W interface, Bornian electrostatic models are invalid.

A New Approach Based on Quantum Chemical Considerations. The invalidity of Bornian electrostatic models seems to be due to the neglect of the important contribution of short-

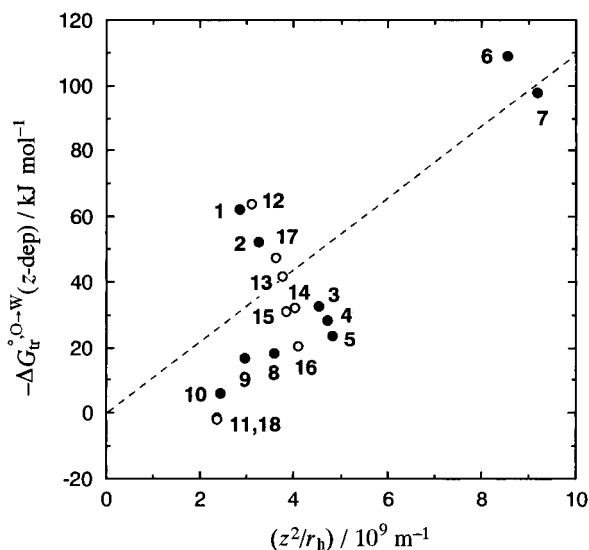


Figure 7. Plots of $\Delta G_{tr}^{o,o-w}(z\text{-dep})$ against (z^2/r_h) based on the simple Born model, for cations (●) (1) Li^+ , (2) Na^+ , (3) K^+ , (4) Rb^+ , (5) Cs^+ , (6) Ca^{2+} , (7) Ba^{2+} , (8) Me_4N^+ , (9) Et_4N^+ , (10) $n\text{-Bu}_4\text{N}^+$, (11) TPAs^+ , and for anions (○) (12) Cl^- , (13) Br^- , (14) I^- , (15) SCN^- , (16) ClO_4^- , (17) NO_3^- , (18) TPB^- . For the organic ions, (8), (9), (10), (11), (18), $\Delta G_{tr}^{o,o-w}(z\text{-dep})$ is plotted against z^2/r_c . The dashed line represents the dependence expected from the Born equation (eq 1) with $\epsilon^o = 34.8$ and $\epsilon^w = 78.5$.

range (i.e. chemical) interactions between an ion and solvents. For a better account of $\Delta G_{tr}^{o,o-w}$ for the hydrated ions, we have made a new approach which recognizes the short-range interactions, or allows for some overlap of the electron orbitals of the ion and the solvent molecule in its immediate vicinity. In ab initio molecular orbital studies,³⁷ the self-consistent field (SCF) energy of the ion–molecule interaction, U_{SCF} , is partitioned into several terms, e.g., Coulomb (COU), exchange (EX), polarization (POL), and charge-transfer (CT) terms:

$$U_{\text{SCF}} = U_{\text{COU}} + U_{\text{EX}} + U_{\text{POL}} + U_{\text{CT}} \quad (8)$$

The term U_{COU} is identical with the empirical energy of ion–dipole interaction. If a solvent molecule is fixed on the ion, U_{COU} is given by³⁸

$$U_{\text{COU}} = -\mu E \cos \theta \quad (9)$$

where μ is the dipole moment of the solvent molecule, θ is the angle between the dipole axis and the line connecting point dipole and point charge, and E is the surface field strength of the ion which is given by

$$E = \frac{ze}{4\pi\epsilon_0 r^2} \quad (10)$$

Similarly, the term U_{POL} is identical with the semiclassical electrostatic energy of ion–induced dipole interaction, being given by³⁸

$$U_{\text{POL}} = -\frac{1}{2}\alpha E^2 \quad (11)$$

where α is the electronic polarizability of the solvent. The term U_{EX} represents the nonclassical repulsion term. Its major part, which probably arises from the kinetic energies of electrons, is inherently independent of z or E . The remaining term U_{CT} in eq 8 is the energy for the intermolecular electron transfer between the ion and the solvent. Although the dependence of U_{CT} on ionic charge and size had been considered very hard to

derive, Osakai and Ebina⁶ recently made a model Hamiltonian approach to show that U_{CT} ($= -\Delta W$ in ref 6) per primary solvent, for an ion such as the polyoxometalate anion, is a function of E , approximately a quadratic equation:

$$U_{\text{CT}} = -\zeta_0 - \zeta_1 E - \zeta_2 E^2 \quad (12)$$

The coefficients ζ_0 , ζ_1 , and ζ_2 (denoted as α_0 , α_1 , and α_2 in ref 6) are influenced by various molecular properties which include, e.g. in the case of the anion–solvent interaction, the ionization potential of the surface atoms of the ion, the electron affinity of the solvent, and the charge-transfer distance. However, these coefficients may be considered as common to a family of ions such as polyanions. Accordingly, eq 12 seems to be also applicable to a series of hydrated cations or anions. Although eq 12 was derived on the condition that the radius of the ion is much larger than that of the solvent molecule, this condition may also be fulfilled, on the whole, regarding the hydrated ions which have relatively large hydrated radii (0.21–0.48 nm).

On the basis of the above considerations, we conclude that the short-range interaction energy per primary solvent, U_{SR} , can be given by a quadratic function of E :

$$U_{\text{SR}} (= U_{\text{SCF}}) = -A - BE - CE^2 \quad (13)$$

with $A = \zeta_0 + U_{\text{EX}}$, $B = \mu \cos \theta + \zeta_1$, and $C = \alpha/2 + \zeta_2$. In the proposed model shown in Figure 5, a hydrated ion in the W phase transfers to the O phase after breaking some hydrogen bonds which are formed between the hydrated ion and the water molecules in its immediate vicinity. Since the resolution energy of hydrated ions cannot be elucidated in terms of the electrostatic (i.e. long-range) interaction energy, short-range interactions between a hydrated ion and solvents (especially, hydrogen bonds in W) probably play the most significant role in the resolution energy. Using eq 13, the contribution of short-range interactions to $\Delta G_{tr}^{o,o-w}$ is given as the difference between U_{SR} 's in O and W:

$$(\Delta G_{tr}^{o,o-w})_{\text{SR}} \text{ per primary solvent} = (U_{\text{SR}})^{\text{W}} - (U_{\text{SR}})^{\text{O}} = -\Delta A - \Delta BE - \Delta CE^2 \quad (14)$$

In Figure 8, the estimated values of $\Delta G_{tr}^{o,o-w}(z\text{-dep})$ divided by n (i.e. per coextracted water molecule) are plotted against E (with $r = r_h$) for the hydrated ions. As seen, the plots for either cations or anions lie on a single curve. In this way, it has been found that the charge-dependent part of $\Delta G_{tr}^{o,o-w}$ can be expressed by a function of E . Because E is proportional to r_h^{-2} , this finding seems to suggest again that the *short-range* (i.e. specific) interactions play much more important roles than the *long-range* electrostatic interaction (the energy is generally proportional to r_h^{-1} ; see eq 1). As shown in Figure 8, it has further been revealed that $\Delta G_{tr}^{o,o-w}(z\text{-dep})$ per coextracted water molecule becomes progressively greater as E is enhanced. This is in accord with the expectation from eq 14. Since the contribution from the interaction in W to $\Delta G_{tr}^{o,o-w}(z\text{-dep})$ is probably more significant than that from the interaction in O, the dependence shown in Figure 8 seems to suggest that the hydrogen bonds formed around a hydrated ion in W are strengthened by the surface field of the ion.

The above new approach based on quantum chemical considerations has given a better account of $\Delta G_{tr}^{o,o-w}$ for hydrated ions than conventional electrostatic approaches. However, we should recognize that the Bornian electrostatic energy should contribute to a considerable extent to the solvation energy of an ion in each phase. It can be thought that electrostatic

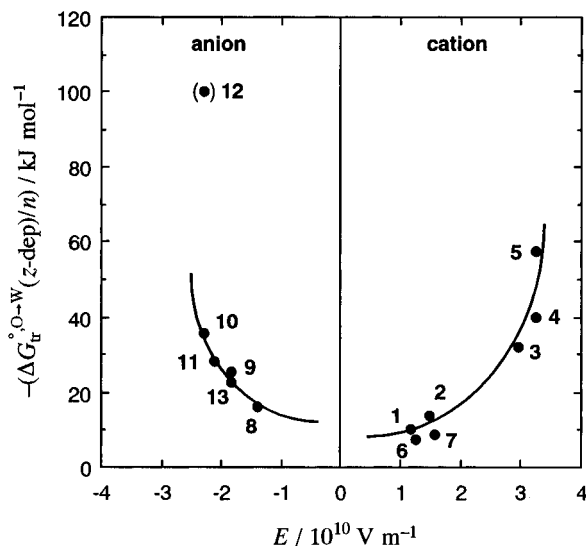


Figure 8. Plots of $\Delta G_{tr}^{o, O \rightarrow W}$ (z -dep) divided by n (i.e. per coextracted water molecule) against E (with $r = r_h$), for hydrated cations (1) Li^+ , (2) Na^+ , (3) K^+ , (4) Rb^+ , (5) Cs^+ , (6) Ca^{2+} , (7) Ba^{2+} , and for hydrated anions (8) Cl^- , (9) Br^- , (10) I^- , (11) SCN^- , (12) ClO_4^- , (13) NO_3^- . The plot of (12) ClO_4^- has a large experimental error because of the small value of n ($=0.2 \pm 0.1$).

solvation energies of the ion in the respective phases are for the most part canceled out in $\Delta G_{tr}^{o, O \rightarrow W}$ as the *difference* in the solvation energy between the two phases. This will result in the predominant contribution of short-range interactions to $\Delta G_{tr}^{o, O \rightarrow W}$. Finally, we would like to add that at the present stage our new approach has still not replaced the qualitative analysis. Further experimental and theoretical studies seem to be required to establish the analytical equation of $\Delta G_{tr}^{o, O \rightarrow W}$, by which the Born equation (or its modification) can be replaced.

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