Temperature Effect on the Selective Hydration of Sodium Ion in Nitrobenzene

Toshiyuki OSAKAI,*† Akiko TOKURA,* Hajime OGAWA,* Hiroki HOTTA,* Masaru KAWAKAMI,** and Kazuyuki AKASAKA***

*Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657-8501, Japan

**Department of Molecular Science, Graduate School of Science and Technology,
Kobe University, Nada, Kobe 657-8501, Japan

***Department of Biotechnological Science, School of Biology-Oriented Science and Technology,
Kinki University, Uchita-cho, Wakayama 649-6493, Japan

The effect of the temperature on the co-extraction of water molecules with Na⁺ from water to nitrobenzene (NB) in the presence of dipicrylamine ion has been studied. The number (*n*) of water molecules co-extracted with a Na⁺ ion, as measured by the Karl Fischer method, increased from 3.1 to 5.2 with increasing temperature (6–65°C). This observation is in apparent contradiction to the expectation from simple thermodynamics because hydration is generally an entropically unfavorable process. Additional ¹H NMR experiments for the selective hydration of Na⁺ in deuterated NB have confirmed that the association constants of water with Na⁺ indeed decrease with increasing temperature. On the other hand, however, it has been shown that water solubility into NB substantially increases with temperature. We conclude that the latter effect overwhelms the former unfavorable entropy effect, which results in a net increase of the *n*-value, as observed.

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Introduction

For many years much attention has been directed towards the co-extraction of water to water immiscible organic solvents with hydrophilic inorganic ions,^{1–9} including Li⁺, Na⁺, Ca²⁺, and Cl[–] and also with organic ions^{9–11} having dissociated groups, such as –CO₂[–] and –NH₃⁺. Even water-immiscible organic solvents, such as nitrobenzene (NB), usually dissolve a considerable amount of water (e.g. 168 mM H₂O in NB at 25°C;⁸ M = mol dm^{–3}). Accordingly, the co-extraction of water with ions can be elucidated in terms of the selective hydration of ions in mixed solvents.¹² This is a key concept intimately related to important ion-transfer processes, not only in separation and detection systems (e.g. solvent extraction, membrane transport, ion-selective electrodes), but also in biological systems (lipid membrane, ion channels, etc.). In recent years the co-transport of water by ions has been dealt with by molecular dynamic simulations.^{13–15}

In solvent-extraction studies,^{1–8,10,11} the number (*n*) of water molecules co-extracted with an ion was determined by the Karl Fischer method. However, it has frequently been asked whether the ion is really bound to water molecules in organic solvents. The answer was given by a ¹H NMR study¹⁶ on the selective hydration of anions (X[–] = Cl[–], Br[–], I[–], NO₃[–], ClO₄[–], SCN[–]) in deuterated NB (NB-d₅); the chemical shift of water protons changed to lower magnetic fields with the addition of X[–], giving evidence for ion-water interactions. It was also found that the

selective hydration of anions can be elucidated in terms of a successive reaction mechanism: X(H₂O)_{*m*–1} + H₂O ⇌ X(H₂O)_{*m*} (*m* = 1, 2, 3, ...). Thus, the observed hydration number (i.e. the *n* value) does not need to be an integer, since it is always given as an averaged value over several species in different hydration states.

The important role of water molecules in the Gibbs energy of transfer of hydrophilic ions between two immiscible liquids was discussed by Osakai and Ebina^{17,18} and Sánchez *et al.*¹⁹ based on a model in which a hydrophilic ion transfers across the organic solvent (O)/water (W) interface as a *hydrated* ion. The model gave a better account of the transfer energies of hydrophilic ions than the previous models in which the role of the hydrated water molecules was not taken into consideration. Recently, the entropy of ion transfer across the NB/W interface was accurately determined for various ions by means of a W/O/W thermocouple,²⁰ which showed the importance of hydrated water molecules in determining the transfer entropy of relatively hydrophilic ions (Na⁺, K⁺, Br[–], etc.).

For gaining further insight into the mechanisms of selective hydration of ions, it seems to be important to examine the temperature dependence. However, to the authors' knowledge, there has been only one report by Rais *et al.*,²¹ in which the temperature dependence of the extraction of alkali metal dipicrylaminates into NB is discussed in terms of the temperature dependence of the water solubility in NB.

In the present study we have focused on Na⁺ and have examined the temperature dependence of the number of co-transported water molecules per Na⁺ ion (i.e. the *n* value). Previous studies show that the Na⁺ ion co-transport as many as four water molecules at 25°C.^{1,2,8} In the present study, we found

† To whom correspondence should be addressed.
E-mail: osakai@kobe-u.ac.jp

that the n value increases with the temperature. This finding was unexpected in terms of an unfavorable entropy in ion solvation. However, additional ^1H -NMR measurements revealed that the strong increase in water solubility in NB actually overcomes the unfavorable entropy effect, and increases n with the temperature.

Experimental

Chemicals

Sodium dipicrylamine (NaDPA) was purchased from Tokyo Kasei Kogyo Co., Ltd. and dried under reduced pressure for at least 5 h before use. Analytical-grade NB was treated before use with activated alumina (Wako Pure Chemical Industries, Ltd.; 200 mesh for column chromatography). All other reagents were of analytical grade and used without further purification.

Distribution experiments

Aqueous solutions of 0–20 mM NaDPA, which contained 0.1 M NaCl to prevent the formation of microemulsions, were prepared; the pH was adjusted to 10 with NaOH. A 10 mL aqueous solution and pure NB of the same volume were put in a glass bottle (25 mL) with a Teflon cap, shaken in a water bath thermostated at 6, 15, 25, 35, 45, 55, or 65°C for 3 h, and then separated by allowing to stand for at least a half day. A preliminary experiment showed that these operations achieved the distribution equilibrium. The aqueous phase was pipetted off from the glass bottle directly when placed in a water bath, and an aliquot of the aqueous solution was subjected to a spectrophotometric determination of DPA^- ($\epsilon = 2.61 \times 10^4$ at 428 nm);⁸ the aqueous solution was appropriately diluted in advance to prevent the solution from becoming turbid, probably due to microemulsion formation. Then, an aliquot (0.5 mL) of the NB phase in the bottle was slowly drawn off using a microsyringe and subjected to a determination of the water concentration by means of a Karl Fischer coulometer (Kishida Chemicals CA-20).

^1H NMR measurements

Dried NaDPA was dissolved in NB- d_5 (supplied by Isotec Inc.; 99.5% atom D) at different concentrations (0–20 mM); the solvent was dried in advance with a molecular sieve (4A; Wako). Using these solutions, sample solutions containing more than 10 different water concentrations were prepared, as described previously.¹⁶ For each sample solution, the ^1H NMR spectrum was measured at 25, 35, and 45°C at 400 MHz on a JEOL λ -400 NMR spectrometer. The proton chemical shifts were recorded in ppm with tetramethylsilane (TMS) as an internal reference. Other details were described previously.¹⁶

Results

Distribution experiments

The pioneering work of Rais *et al.*^{1,21,22} showed that in the extraction of 1:1 salts into sufficiently polar solvents, such as NB, the ionic association is not significant and the extraction equilibrium is given essentially by the distribution of ionic forms between the two phases. This is the case for the extraction of NaDPA, as also shown by our previous study,⁸ where the ionic association was completely ignored. By way of precaution, however, previous rigorous treatments^{1,21,23} considering a possible ion pair (Na^+DPA^-) in the O phase were performed. The distribution ratio of dipicrylamine is

expressed as

$$D_{\text{DPA}} = \frac{[\text{DPA}^-]_{\text{O}} + [\text{Na}^+\text{DPA}^-]_{\text{O}}}{[\text{DPA}^-]_{\text{W}}} \\ = \left(\frac{K_{\text{ex}}[\text{Na}^+]_{\text{W}}}{[\text{DPA}^-]_{\text{W}}} \right)^{1/2} + K_{\text{ex}}[\text{Na}^+]_{\text{W}}/K_{\text{D}}, \quad (1)$$

where K_{ex} and K_{D} are the extraction constant of NaDPA and the dissociation constant of the ion pair, respectively, which are defined by

$$K_{\text{ex}} = \frac{[\text{Na}^+]_{\text{O}}[\text{DPA}^-]_{\text{O}}}{[\text{Na}^+]_{\text{W}}[\text{DPA}^-]_{\text{W}}} \quad (2)$$

and

$$K_{\text{D}} = \frac{[\text{Na}^+]_{\text{O}}[\text{DPA}^-]_{\text{O}}}{[\text{Na}^+\text{DPA}^-]_{\text{O}}} \quad (3)$$

In the above equations, the brackets, $[\]_{\text{O}}$ and $[\]_{\text{W}}$, denote the equilibrium concentrations of a free ion or the ion pair in the O and W phases, respectively.

In this study, D_{DPA} was evaluated from the spectrophotometrically determined value of $[\text{DPA}^-]_{\text{W}}$ by considering the material balance,

$$G_{\text{DPA}} = [\text{DPA}^-]_{\text{W}}v_{\text{W}} + D_{\text{DPA}}[\text{DPA}^-]_{\text{W}}v_{\text{O}}, \quad (4)$$

where G_{DPA} is the molar quantity of dipicrylamine initially added to the W phase, and v_{W} and v_{O} are the volumes of the W and O phases, respectively (here, $v_{\text{W}} = v_{\text{O}} = 25$ mL). The value of $[\text{Na}^+]_{\text{W}}$ in the right-hand-side of Eq. (1) can be obtained from $[\text{DPA}^-]_{\text{W}}$ by considering the addition of 0.1 M NaCl and the electroneutrality principle for the W phase,

$$[\text{Na}^+]_{\text{W}} = 0.1 + [\text{DPA}^-]_{\text{W}} \text{ (in M)}. \quad (5)$$

According to Eq. (1), therefore, D_{DPA} divided by $[\text{Na}^+]_{\text{W}}$ should show a linear dependence on the quantity $([\text{Na}^+]_{\text{W}}[\text{DPA}^-]_{\text{W}})^{-1/2}$. In practice, we observed a linear $D_{\text{DPA}}([\text{Na}^+]_{\text{W}})^{-1}$ vs. $([\text{Na}^+]_{\text{W}}[\text{DPA}^-]_{\text{W}})^{-1/2}$ plot for each temperature, as shown in Fig. 1. This plot is essentially the same as that of Rais *et al.*,²¹ though the ionic strength is different for the two studies.

From the slopes of the linear plots in Fig. 1, K_{ex} was evaluated to be 6.9, 4.7, 4.5, 2.9, 2.3, 2.3, and 1.9 at 6, 15, 25, 35, 45, 55, and 65°C, respectively. The intercepts of the linear plots (*i.e.*, $K_{\text{ex}}/K_{\text{D}}$) gave ion-pair formation constants, $K_{\text{A}} (= 1/K_{\text{D}})$, ranging from 47 to 91 M^{-1} . However, these values seem to be rather overestimated, since they are subject to a considerable error, as pointed out previously.²¹ Practically negligible ion-pair formation (*i.e.*, $K_{\text{A}} < 5 \text{ M}^{-1}$ at 6–45°C) of NaDPA in “water-saturated” NB has been confirmed by conductivity measurements using the reported method.^{10,24}

Using the thus-determined K_{ex} values, the quantities of $-RT \ln K_{\text{ex}}$ (R , gas constant; T , absolute temperature) were plotted against T , and a good straight line with the correlation of 0.999 was obtained. Based on a general relation, $-RT \ln K_{\text{ex}} = \Delta G^* = \Delta H^* - T\Delta S^*$, the standard enthalpy and entropy for the extraction of NaDPA were evaluated as $\Delta H^* = -19.8 \pm 0.1 \text{ kJ mol}^{-1}$ and $\Delta S^* = -48.1 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$. These values are in fair agreement with the literature values:²¹ $\Delta H^* = -18.7 \pm 1.3 \text{ kJ mol}^{-1}$; $\Delta S^* = -45.5 \pm 4.0 \text{ J K}^{-1} \text{ mol}^{-1}$ (these are average values for some data originally reported in units of cal).

The standard entropy of transfer of Na^+ from NB to W

Fig. 1 Extraction of NaDPA into NB at different temperatures: (1) 6, (2) 15, (3) 25, (4) 35, (5) 45, (6) 55, and (7) 65°C.

Fig. 2 Temperature dependence of the n value of Na^+ .

($\Delta S_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}} = +28.8 \text{ J K}^{-1} \text{ mol}^{-1}$) has recently been reported along with the corresponding enthalpy ($\Delta H_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}} = -25.6 \text{ kJ mol}^{-1}$).²⁰ Because ΔS^* is composed of two contributions from Na^+ and DPA^- , *i.e.*, $-\Delta S^* = \Delta S_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}} + \Delta S_{\text{tr},\text{DPA}^-}^{\text{O} \rightarrow \text{W}}$, the value of $\Delta S_{\text{tr},\text{DPA}^-}^{\text{O} \rightarrow \text{W}}$ is obtained to be $+19.3 \text{ J K}^{-1} \text{ mol}^{-1}$. The enthalpy value, $\Delta H_{\text{tr},\text{DPA}^-}^{\text{O} \rightarrow \text{W}}$, is likewise evaluated to be $+45.4 \text{ kJ mol}^{-1}$.

The water concentration in NB, determined by the Karl Fischer method, increased linearly with the equilibrium concentration of Na^+ in NB at all temperatures, as previously observed at 25°C.⁸ From the slope of a linear plot at each temperature, the n value of Na^+ was determined, based on knowledge that the hydrophobic DPA^- ion has no ability to transport water to NB.⁸ As shown in Fig. 2, the n value increased from 3.1 (6°C) to 5.2 (65°C).

¹H NMR measurements

Figure 3 shows a typical NMR spectrum, which was obtained for a 2.5 mM NaDPA NB- d_5 solution containing 121 mM H_2O at 25°C. As can be seen in the figure, the water protons always appeared as a singlet, showing that the exchange of water molecules between the free and Na^+ -bound forms is very fast. Under these conditions, the chemical shift of water protons should change with the distribution of water molecules between the free and ion-bound forms. The assignments of other signals are as follows. The signal at 8.8 ppm is due to the protons of DPA^- and those around 7.5, 7.7, and 8.1 ppm are assigned, respectively, to *m*-, *p*-, and *o*-protons of the benzene ring of NB

Fig. 3 ¹H NMR spectrum of 2.5 mM NaDPA in NB- d_5 containing 121 mM H_2O at 25°C.

that remained undeuterated.

In Fig. 4, the chemical shift of water protons, δ [ppm], is plotted against the total (*i.e.*, added) water concentration, $[\text{H}_2\text{O}]_{\text{total}}$, for three different concentrations of NaDPA (*i.e.*, Na^+) at 25°C. Similar plots were also obtained at 35 and 45°C. As can be seen in Fig. 4, the chemical shift of the water protons increased with increasing ion concentration. Such a dependence is analogous to that observed for inorganic anions¹⁶ (Cl^- , Br^- , I^- , *etc.*), and could likewise be simulated by assuming successive hydration:

In this mechanism the observed chemical shift of water protons is given by

$$\begin{aligned} \delta &= \delta_{\text{blank}} + \frac{[\text{Na}^+(\text{H}_2\text{O})]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_1 + 2 \frac{[\text{Na}^+(\text{H}_2\text{O})_2]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_1 + \\ &3 \frac{[\text{Na}^+(\text{H}_2\text{O})_3]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_3 + \dots + m \frac{[\text{Na}^+(\text{H}_2\text{O})_m]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_m + \dots \\ &= \delta_{\text{blank}} + \frac{K_1 [\text{Na}^+][\text{H}_2\text{O}]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_1 + 2 \frac{K_1 K_2 [\text{Na}^+][\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}]_{\text{total}}} \delta_2 + \\ &\frac{3 K_1 K_2 K_3 [\text{Na}^+][\text{H}_2\text{O}]^3}{[\text{H}_2\text{O}]_{\text{total}}} \delta_3 + \dots \\ &+ m \frac{K_1 K_2 K_3 \dots K_m [\text{Na}^+][\text{H}_2\text{O}]^m}{[\text{H}_2\text{O}]_{\text{total}}} \delta_m + \dots, \end{aligned} \quad (7)$$

where δ_m ($m = 1, 2, 3, \dots$) is the intrinsic chemical shift for an m -hydrated ion, $\text{Na}^+(\text{H}_2\text{O})_m$, and K_m is the successive formation constant of the m -hydrated ion, defined by

$$K_m = \frac{[\text{Na}^+(\text{H}_2\text{O})_m]}{[\text{Na}^+(\text{H}_2\text{O})_{m-1}][\text{H}_2\text{O}]} \quad (m = 1, 2, 3, \dots). \quad (8)$$

In Eq. (7), the term δ_{blank} represents the chemical shift for a “blank” solvent, *i.e.*, NB- d_5 containing no ions. Since it was reported that water exists as a monomer or dimer in NB,²⁵ we assumed a monomer-dimer equilibrium:

Fig. 4 Plots of the chemical shift of water protons against the water concentration for 20, 10, 5.0, 2.5, and 0 mM Na⁺ in NB-d₅ at 25°C. The solid lines show the best fits to the experimental data with a successive hydration mechanism.

Accordingly, δ_{blank} is given by

$$\begin{aligned}\delta_{\text{blank}} &= \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_{\text{mono}} + 2 \frac{[\text{H}_2\text{O}]_2}{[\text{H}_2\text{O}]_{\text{total}}} \delta_{\text{di}} \\ &= \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{O}]_{\text{total}}} \delta_{\text{mono}} + 2 \frac{K_s [\text{H}_2\text{O}]^2}{[\text{H}_2\text{O}]_{\text{total}}} \delta_{\text{di}},\end{aligned}\quad (10)$$

where δ_{mono} and δ_{di} are the intrinsic chemical shifts of the monomer and dimer, respectively, and K_s is the monomer-dimer equilibrium constant for water in NB,

$$K_s = \frac{[\text{H}_2\text{O}]_2}{[\text{H}_2\text{O}]^2}.\quad (11)$$

The K_s value was reported to be 1.054 M⁻¹ at 25°C.^{25,26} Using Eq. (10) with this value, the experimental data shown by the crosses in Fig. 4 were simulated well with δ_{mono} (= 2.40 ppm) and δ_{di} (= 2.87 ppm) as fitting parameters.¹⁶ Unfortunately, however, there are no data available on the K_s values for other temperatures. Therefore, the value of 1.054 M⁻¹ was also employed for the K_s values at 35 and 45°C. Although the true values would be somewhat different, a deviation on the order of 20–30% hardly influenced the results of the theoretical analyses described below.

The terms in Eqs. (7) and (10) are interdependent of each other, because each term involves the concentration of monomeric water, [H₂O]. However, the crucial parameters (δ_m , K_m , K_s , etc.) involved in those terms are likely to be independent of each other, in the studied concentration range. Using the K_m values, the concentration of the nonhydrated ion, [Na⁺], is given by

$$[\text{Na}^+] = [\text{Na}^+]_{\text{total}} / \{1 + K_1[\text{H}_2\text{O}] + K_1K_2[\text{H}_2\text{O}]^2 + K_1K_2K_3[\text{H}_2\text{O}]^3 + \dots + (K_1K_2K_3\dots K_m)[\text{H}_2\text{O}]^m + \dots\},\quad (12)$$

where $[\text{Na}^+]_{\text{total}}$ is the total concentration of Na⁺.

Based on the above equations, the experimental data, as shown in Fig. 4, were fitted to theoretical curves by assuming $m = 1-6$. The detailed method of calculation was previously described.¹⁶ As shown in Fig. 4, a satisfactory agreement was obtained between the experimental and theoretical curves at all temperatures, giving the values of K_m , δ_m , etc. as listed in Table 1.

It should be noted that the values of K_m and δ_m were obtained

Table 1 Values of K_m (M⁻¹) and δ_m (ppm) obtained from curve fittings at three different temperatures

	<i>T</i> /C°		
	25	35	45
K_1	11	8.8	8.7
K_2	7.5	5.0	5.0
K_3	3.3	3.2	3.1
K_4	3	2	2
K_5	2	2	1
K_6	2	1	0.5
δ_1	6.8	7.1	7.1
δ_2	2.7	2.5	2.0
δ_3	5	5.5	6.0
δ_4	7	6	7
δ_5	8	8	8
δ_6	9	9	9
δ_{mono}	2.40	2.35	2.28
δ_{di}	2.87	2.83	2.78
σ^a	0.012	0.019	0.089
n^b	3.60	3.63	3.95
$\langle n \rangle^c$	4.1	4.3	4.7
$[\text{H}_2\text{O}]_{\text{blank}}^d$	168	211	270

a. Standard deviation, $\sigma = [\sum(\delta_{\text{calcd}} - \delta_{\text{obsd}})^2 / (N - 1)]^{1/2}$, where δ_{calcd} and δ_{obsd} stand for the calculated and observed chemical shifts, respectively, and N is the number of data points.

b. Hydration number of Na⁺ in NB shown in Fig. 2.

c. Average hydration number calculated from the K_m values.

d. Concentration of water saturated in the blank solvent.

as adjusting parameters, and that as many as twelve parameters were used for each temperature. Accordingly, these parameters could not be uniquely determined; a set of parameters obtained for each temperature should be regarded as one of the best parameter sets that could give us a satisfactory result of the curve fitting. Although this prevents us from examining those parameters closely, we would like to claim that there is a notable tendency of K_m to decrease with the temperature. This agrees with our expectation that hydration would generally be an entropically unfavorable process. Regarding the δ_m values, no marked dependence on the temperature was observed.

The curve-fitting analyses mentioned above have clearly shown that the selective hydration of Na⁺ in NB can be elucidated in terms of the successive reaction mechanism. A one-step reaction mechanism¹⁶ (e.g. $\text{Na}^+ + 4\text{H}_2\text{O} \rightleftharpoons \text{Na}^+(\text{H}_2\text{O})_4$) could not be used to elucidate the dependence of δ shown in Fig. 4.

The average hydration number of Na⁺ was calculated using

$$\langle n \rangle = \frac{\sum m([\text{Na}^+(\text{H}_2\text{O})_m]_{\text{sat}})}{[\text{Na}^+]_{\text{total}}},\quad (13)$$

where $[\text{Na}^+(\text{H}_2\text{O})_m]_{\text{sat}}$ represents the concentration of the m -hydrated ion in the water-saturated solvent. As can be seen in Table 1, the $\langle n \rangle$ values are in reasonable agreement with the n values determined by the Karl Fischer method, though the former are somewhat larger than the latter.

Discussion

The results of the present distribution experiments are basically in line with those reported by Rais *et al.*²¹ The negative value of ΔS^* (= -48.1 J K⁻¹ mol⁻¹) means that the extraction of NaDPA

Fig. 5 Temperature dependence of the concentration of water saturated in pure NB.

into NB is entropically unfavorable, or suppressed with increasing temperature. As shown above, the negative ΔS^* -value comes from the contributions of both Na^+ and DPA^- ; note again that $-\Delta S^* = \Delta S_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}} + \Delta S_{\text{tr},\text{DPA}^-}^{\text{O} \rightarrow \text{W}}$ with $\Delta S_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}} = +28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_{\text{tr},\text{DPA}^-}^{\text{O} \rightarrow \text{W}} = +19.3 \text{ J K}^{-1} \text{ mol}^{-1}$. Although Na^+ is known to be a water-structure making ion,^{27,28} the value of $\Delta S_{\text{tr},\text{Na}^+}^{\text{O} \rightarrow \text{W}}$ may suggest some sort of a breaking effect on the water structure. As discussed in a recent paper,²⁰ this is probably because the highly organized structure of water molecules in the first solvation shell around Na^+ would be maintained even in water-saturated NB. The water-structure making in the first solvation shell should contribute to the hydration entropy, but appears not to contribute to the transfer entropy. With regard to DPA^- , the positive entropy change for its transfer from NB to W is curious because a strongly hydrophobic ion, such as tetrabutylammonium ion, generally acts as a structure promoter in water.^{27,28} It appears likely that a structural similarity of DPA^- and NB results in a structure promotion or structure-stabilizing effect of DPA^- in NB.

The Karl Fischer measurements have shown that the hydration number of Na^+ in NB increases with the temperature, as shown in Fig. 2. This result is seemingly curious, because hydration or solvation would generally be an entropically unfavorable process. In fact, an analysis of the NMR chemical shifts has shown that the successive hydration constants (K_m) of Na^+ in NB tend to decrease with the temperature (Table 1). However, the concentration of water saturated in pure NB has a much stronger temperature dependence due to the mixing entropy, as shown in Fig. 5. We then employed the K_m values to calculate the distribution of Na^+ ions in several hydration states, as a function of $[\text{H}_2\text{O}]_{\text{total}}$ for three different temperatures (Fig. 6). Reflecting the temperature dependence of K_m , the fractions of more highly hydrated ions at a definite water concentration decrease with increasing temperature. Nevertheless, at the water concentrations where NB containing 5.0 mM Na^+ is saturated with water (i.e., $[\text{H}_2\text{O}]_{\text{total}} = 186, 229, \text{ and } 290 \text{ mM}$ at 25, 35, and 45°C, respectively), more highly hydrated ions appear to become more dominant with increasing temperature. Thus, the effect of the mixing entropy is so strong that it overcomes the decrease in K_m with temperature, resulting in an increase in the apparent hydration number with increasing temperature (Fig. 2).

References

1. J. Rais, M. Kyrš, and M. Pivoňková, *J. Inorg. Nucl. Chem.*,

Fig. 6 Distribution of Na^+ ions in several hydration states as a function of the water concentration at three different temperatures: (0) nonhydrated; (1) monohydrated; (2) dihydrated; (3) trihydrated; (4) tetrahydrated; (5) pentahydrated; and (6) hexahydrated. $[\text{Na}^+]_{\text{total}} = 5 \text{ mM}$.

- 1968, 30, 611.
2. S. Motomizu, K. Tōei, and T. Iwachido, *Bull. Chem. Soc. Jpn.*, **1969**, 42, 1006.
3. T. Kenjo and R. M. Diamond, *J. Phys. Chem.*, **1972**, 76, 2454.
4. T. Kenjo and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **1974**, 36, 183.
5. Y. Yamamoto, T. Tarumoto, and T. Tarui, *Bull. Chem. Soc. Jpn.*, **1973**, 46, 1466.
6. S. Kusakabe, M. Shinoda, and K. Kusafuka, *Bull. Chem. Soc. Jpn.*, **1989**, 62, 333.
7. S. Kusakabe and M. Arai, *Bull. Chem. Soc. Jpn.*, **1996**, 69, 581.
8. T. Osakai, A. Ogata, and K. Ebina, *J. Phys. Chem. B*, **1997**, 101, 8341.
9. T. Osakai, "Interfacial Catalysis", ed. A. G. Volkov, **2002**, Marcel Dekker, New York, 53.
10. A. Ogata, Y. Tsujino, and T. Osakai, *Phys. Chem. Chem. Phys.*, **2000**, 2, 247.
11. T. Osakai, S. Nakata, and H. Ogawa, *Chem. Lett.*, **2001**, 558.
12. Y. Marcus, "Ion Solvation", **1985**, Wiley, Chichester, 184.
13. I. Benjamin, *Science*, **1993**, 261, 1558.
14. I. Benjamin, "Liquid-Liquid Interfaces, Theory and Methods", ed. A. G. Volkov and D. W. Deamer, **1996**, CRC Press, Boca Raton, 179.
15. M. Lauterbach, G. Wipff, A. Mark, and W. F. van Gunsteren, *Gazz. Chim. Ital.*, **1997**, 127, 699.
16. T. Osakai, M. Hoshino, M. Izumi, M. Kawakami, and K. Akasaka, *J. Phys. Chem. B*, **2000**, 104, 12021.
17. T. Osakai and K. Ebina, *J. Phys. Chem. B*, **1998**, 102, 5691.
18. T. Osakai and K. Ebina, "Liquid Interfaces in Chemical, Biological, and Pharmaceutical Applications", ed. A. G. Volkov, **2001**, Marcel Dekker, New York, 23.
19. C. Sánchez, E. Leiva, S. A. Dassie, and A. M. Barussi, *Bull. Chem. Soc. Jpn.*, **1998**, 71, 549.
20. T. Osakai, H. Ogawa, T. Ozeki, and H. H. Girault, *J. Phys. Chem. B*, **2003**, 107, 9829.

21. J. Rais, M. Pacltová-Benešová, P. Selucký, and M. Kyrš, *J. Inorg. Nucl. Chem.*, **1973**, 35, 633.
 22. J. Rais, *Coll. Czech. Chem. Commun.*, **1971**, 36, 3253.
 23. M. Kyrš, *Coll. Czech. Chem. Commun.*, **1962**, 27, 155.
 24. M. Gérin and J. Fresco, *Anal. Chim. Acta*, **1978**, 97, 165.
 25. J. R. Johnson, S. D. Christian, and H. E. Affsprung, *J. Chem. Soc. A*, **1967**, 1924.
 26. K. Ito, E. Iwamoto, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **1983**, 56, 2290.
 27. H. S. Frank and W.-Y. Wen, *Disc. Faraday Soc.*, **1957**, 24, 133.
 28. O. Ya. Samoilov, *Disc. Faraday Soc.*, **1957**, 24, 141.
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