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Potentiometric and Calorimetric Studies on Formation of Glycinato Complexes of Nickel(II) in Water and in an Aqueous Dioxane Solution

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Protonation equilibria of glycinate (gly$^-$) ion and complex formation equilibria between nickel(II) and glycinate ions have been studied by potentiometry and calorimetry in water and in 0.2 mole fraction (55.0%w/w) dioxane-water mixture, each containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium at 25 °C. A series of mononuclear complexes, $[NiL_n]^{(2-n)+}$ (L^-=gly$^-$ and n=1—3) were found in both solutions and their formation constants, enthalpies and entropies were determined. It elucidated that the stepwise Gibbs energies of formation of the metal complexes varied in the sequence, $\Delta G_1^\circ < \Delta G_2^\circ < \Delta G_3^\circ$, and the stepwise enthalpies, $\Delta H_1^\circ > \Delta H_2^\circ > \Delta H_3^\circ$, and thus, the stepwise entropies markedly decreased in the order, $\Delta S_1^\circ > \Delta S_2^\circ > \Delta S_3^\circ$. The result was discussed in relation to changes in the metal–water and metal–ligand bond lengths within $[NiL_n(H_2O)_{6-2n}]^{(2-n)+}$ (n=1—3) with n. As to the solvent effects, the formation constants of each metal complex increased with the addition of dioxane to water, the increase was caused by both enthalpies and entropies of formation of the complexes, the former mainly contributing to the formation of $[NiL_2]$ and the latter to $[NiL]^+$ and $[NiL_3]^-$. The Gibbs energies of transfer of single species from water to the dioxane-water mixture were also evaluated. The enthalpy and entropy of transfer of any ionic species mostly compensated each other, so that the Gibbs energies of transfer of ions were rather small.

In previous papers,[1,2] we discussed about the complex formation equilibria between ethylenediamine and bivalent metal ions, Ni(II) and Cu(II), in water and in dioxane–water mixtures.

Since ethylenediamine is a neutral ligand, charges of the ethylenediamine complexes of Ni(II) and Cu(II) are kept +2 for all the complexes formed. The stepwise formation constants of each metal complex in dioxane–water mixtures examined were appreciably larger than those in water. The corresponding enthalpies of formation became less negative by the addition of dioxane to water. Consequently, the corresponding entropies of formation markedly increased to result in more favorable formation of the complexes in the mixtures than that in water.

In the nickel(II)-glycinate system in contrast to the metal–ethylenediamine system, charges of the complexes change with the bound ligand number and a different solvent effect on the complex formation equilibria is expected.

In this work, therefore, the complexation of nickel(II) with glycinate ions has been studied by potentiometry and calorimetry in water and in 0.2 mole fraction dioxane–water mixture. The protonation equilibria of the ligand ion were separately investigated in the same solutions. On the basis of these results, the Gibbs energies of transfer of related species from water to the dioxane–water mixture were then evaluated.

Experimental

Reagents. *Nickel(II) perchlorate* was prepared as described elsewhere.[1] Bis(glycinato)nickel(II) crystals were prepared by dissolving freshly precipitated nickel(II) carbonate to an aqueous glycine solution, and then recrystallized from water. *Glycine* was recrystallized three times from an aqueous ethanol and was dried at 80—100 °C in an electric oven.

Other chemicals used were prepared and purified as described previously.[1]

Measurement. All of potentiometric and calorimetric measurements were carried out in a room thermostated at (25.0±0.2) °C. All test solutions used involved 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium throughout potentiometric and calorimetric titrations.

Potentiometric measurements were carried out in a liquid paraffin bath controlled at (25.00±0.02) °C. pH of a test solution was determined by using a glass electrode in combination with an Ag–AgCl reference electrode. The method of measurements was the same as that used in a previous work.[1]

Calorimetric measurements were carried out in a water bath thermostated at (25.000±0.007) °C. Details of measurements were described elsewhere.[1,3,4]

Solubilities of glycine and bis(glycinato)nickel(II) complex in water and in 0.2 mole fraction dioxane–water mixture were gravimetrically determined after the salts were equilibrated with the solvents without ionic medium for more than two weeks in a thermostated room at (25.0±0.2) °C.

Analysis of Potentiometric and Calorimetric Data. The protonation constants and enthalpies of protonation of glycinate ion, which had been determined in advance by separate experiments, were kept constant in the course of determining the formation constants and enthalpies of the metal–ligand complexation. Details of the analysis of potentiometric and calorimetric data were described previously.[1]

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Results and Discussion

The formation function $\bar{n}$ plotted against $-\log([\mathrm{L}^-]/\mathrm{mol\,dm^{-3}})$($\mathrm{L}^-$=gly$^-$) for the nickel(II)-glycinate system in water and in the 0.2 mole fraction dioxane-water mixture are depicted in Fig. 1. In each solvent experimental points obtained at various metal concentrations fell on a single curve, indicating that the only mononuclear complexes were formed in the solutions. Since the $\bar{n}_{\mathrm{exp}}$ values in each solution approached 3, the potentiometric data were analyzed by assuming the formation of the $[\mathrm{NiL}_n]^{(2-n)+}$ (n=1—3) complexes in both solutions. As shown by the solid lines in Fig. 1, the theoretical formation functions well fitted the experimental ones over the whole range of $-\log([\mathrm{L}^-]/\mathrm{mol\,dm^{-3}})$ examined.

Calorimetric titration curves obtained for the nickel(II)-glycinate system in water and in the dioxane-water mixture are depicted in Figs. 2 and 3, respectively. Enthalpies $\Delta H^\circ/\mathrm{kJ\,mol^{-1}}$ calculated by $\Delta H^\circ = -q/(\delta v C_{\mathrm{H,tit}})$ were plotted against the degree of neutralization X of glycinate ion in a solution, where q and δv denote the heat evolved and the volume of the titrant added at each titration point, respectively, and $C_{\mathrm{H,tit}}$ stands for the concentration of $\mathrm{HClO_4}$ in the titrant solution. The solid lines in Figs. 2 and 3 show the curves calculated by using the formation constants and enthalpies of formation of the complexes finally obtained, which well reproduced the experimental points.

The overall formation constants β_n and overall enthalpies $\Delta H^\circ_{\beta n}$ of formation of $[\mathrm{H}_n\mathrm{L}]^{(n-1)+}$ (n=1 and 2) and $[\mathrm{NiL}_n]^{(2-n)+}$ (n=1—3) in these solutions are summarized in Tables 1 and 2, respectively.

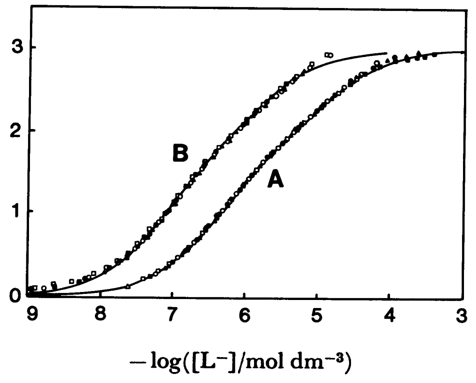

Fig. 1. Formation functions of the nickel(II) glycinate complexes in water (A) and in the 0.2 mole fraction dioxane-water mixture (B). Initial concentrations of metal and ligand ions, C_{M} and $C_{\mathrm{L}}/\mathrm{mol\,dm^{-3}}$: 0.00413, 0.02030(▲); 0.00609, 0.02014(○ and △); 0.00688, 0.03383(■); 0.01015, 0.03357 (□); 0.01522, 0.05035 (●) in water and 0.00201, 0.01108(□); 0.00335, 0.01847(○); 0.00405, 0.01405(■); 0.00503, 0.02270 (●); 0.00675, 0.02342(▲); 0.01012, 0.03512(△) in the mixture.

The solid lines show the curves calculated by using the formation constants in Tables 1 and 2.

Thermodynamic quantities, $\log(K_n/\mathrm{mol^{-1}\,dm^3})$, $\Delta G^\circ_n/\mathrm{kJ\,mol^{-1}}$, $\Delta H^\circ_n/\mathrm{kJ\,mol^{-1}}$, and $\Delta S^\circ_n/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the stepwise formation of $[\mathrm{H}_n\mathrm{L}]^{(n-1)+}$ and $[\mathrm{NiL}_n]^{(2-n)+}$ are listed in Table 3, together with the differences, $P_n(\mathrm{mix})-P_n(\mathrm{w})$ (P=log K, ΔG°, ΔH°, and ΔS°), in water (w) and in the dioxane-water mixture (mix).

Formation of Glycinato Complexes of Ni(II). As seen in Table 3, the ΔG°_n values in any solution examined varied, as usual, in the sequence, $\Delta G^\circ_1 < \Delta G^\circ_2 < \Delta G^\circ_3$, the ΔH°_n values in the sequence, $\Delta H^\circ_1 > \Delta H^\circ_2 > \Delta H^\circ_3$ and the ΔS°_n values, $\Delta S^\circ_1 > \Delta S^\circ_2 > \Delta S^\circ_3$. Therefore, the decrease in ΔS°_n with n is responsible to the increase in ΔG°_n.

The decreased values of ΔH°_n and ΔS°_n with n might be expected if stronger metal-ligand bonds are

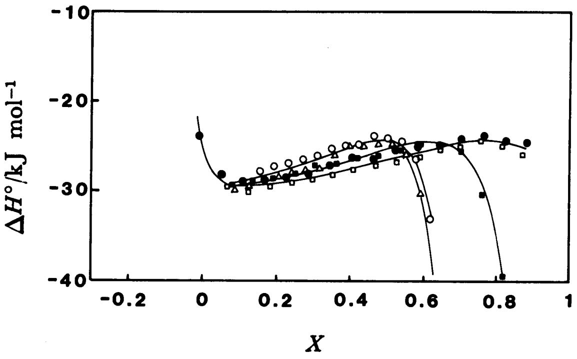

Fig. 2. Calorimetric titration curves of nickel(II) glycinate aqueous solution. Initial concentrations of metal and ligand ions, C_{M} and $C_{\mathrm{L}}/\mathrm{mol\,dm^{-3}}$: 0.01015, 0.0288(□); 0.01202, 0.0343(●); 0.01022, 0.0360 (■); 0.01085, 0.0499(△); 0.01159, 0.0520(○).

The solid lines show the curves calculated by using the formation constants in Tables 1 and 2.

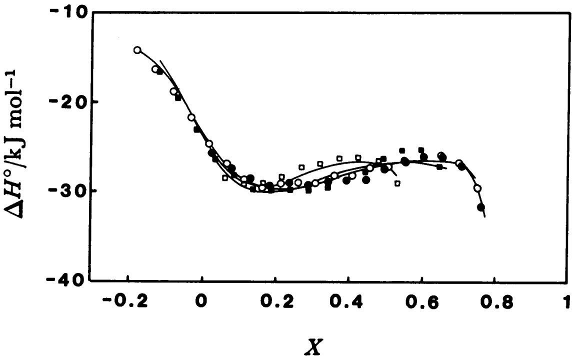

Fig. 3. Calorimetric titration curves of nickel(II) glycinate aqueous dioxane solution (0.2 mole fraction dioxane). Initial concentrations of metal and ligand ions, C_{M} and $C_{\mathrm{L}}/\mathrm{mol\,dm^{-3}}$: 0.00603, 0.02971(□); 0.00777, 0.03112(■); 0.01030, 0.03764 (○); 0.01191, 0.04405 (●).

The solid lines show the curves calculated by using the constants in Tables 1 and 2.

Table 1. The Overall Formation Constants β_n and Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, of Formation of $[H_nL]^{(n-1)+}$ (L^-=gly$^-$) in Solutions Containing 3 mol dm^{-3} $LiClO_4$ at 25 °C

$\beta_n = [H_nL^{(n-1)+}]/[H^+]^n[L^-]$

	Water	0.2 Mole Fraction Dioxane-Water Mixture
$\log \beta_1$	9.94 (0.01)	10.22 (0.01)
$\log \beta_2$	12.62 (0.01)	13.81 (0.01)
$\Delta H^\circ_{\beta 1}$	−57.9 (0.4)	−62.7 (0.5)
$\Delta H^\circ_{\beta 2}$	−63.4 (0.5)	−73.0 (0.5)

The values in parentheses refer to three standard deviations.

Table 2. The Overall Formation Constants β_n and Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, of Formation of $[NiL_n]^{(2-n)+}$ (L^-=gly$^-$) in Solutions Constaining 3 mol dm^{-3} $LiClO_4$ at 25 °C

$\beta_n = [NiL_n{}^{(2-n)+}]/[Ni^{2+}][L^-]^n$

	Water	0.2 Mole Fraction Dioxane-Water Mixture
$\log \beta_1$	5.74 (0.02)	6.47 (0.02)
$\log \beta_2$	10.70 (0.02)	12.20 (0.03)
$\log \beta_3$	14.44 (0.03)	16.85 (0.03)
$\Delta H^\circ_{\beta 1}$	−27.3 (0.6)	−27.6 (0.9)
$\Delta H^\circ_{\beta 2}$	−59.5 (0.5)	−63.5 (0.8)
$\Delta H^\circ_{\beta 3}$	−95.0 (0.6)	−100.2 (0.9)

The values in parentheses refer to three standard deviations.

formed within higher complexes. However, according to the results from the X-ray diffraction study of the structures of the complexes in water, the Ni–N bonds as well as the Ni–OH_2 bonds within $[NiL_n(H_2O)_{6-2n}]^{(2-n)+}$ elongate with n,[5–7] due, probably, to an electron donation from the ligands to the central metal ion, so that both metal–ligand and metal–water bonds are expected to be weaker within a higher complex. The enthalpy data obtained indicate that weakening of metal-ligand bonds may be more pronounced at the formation of a higher complex, and thus, the more negative values of ΔH°_n and ΔS°_n with n may result. The same conclusion was also obtained for the nickel(II)–ethylenediamine system.[1]

As to solvent effects, all the $\log K_n$ (n=1—3) values of the glycinatonickel(II) complexes, as well as the ethylenediamine ones,[1] increased by the addition of dioxane to water. In the nickel(II)–ethylenediamine system, the increase in the $\log K_n$ (the decrease in ΔG°_n) values was fully caused by the increase in the ΔS°_n (n=1—3) values, because the ΔH°_n (n=1—3) values also increased. On the other hand, in the nickel(II)–glycinate system as seen in Table 3, the ΔH°_n (n=1—3) values decreased and the ΔS°_n (n=1—3) values increased, and thus, both values were responsible to the increase in the $\log K_n$ (n=1—3) values. However, at the formation of $[NiL_2]$ the contribution of ΔH°_2 to the increased $\log K_2$ value in the mixture was more important than that of ΔS°_2 and the reverse was the case for the $[NiL]^+$ and $[NiL_3]^-$.

Table 3. Thermodynamic Quantities, $\log(K_n/\text{mol}^{-1}\,\text{dm}^3)$, ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1} and ΔS°_n/J K^{-1} mol^{-1}, for the Stepwise Reactions, $H^+ + [H_{n-1}L]^{(n-2)+} = [H_nL]^{(n-1)+}$ (L^-=gly$^-$) and $[NiL_{n-1}]^{(3-n)+} + L^- = [NiL_n]^{(2-n)+}$, in Water and in Aqueous Dioxane of 0.2 Mole Fraction Dioxane Containing 3 mol dm^{-3} $LiClO_4$ at 25 °C, and their Differences in the Solvents

	Water	0.2 Mole Fraction Dioxane-Water Mixture	Difference
$[H_nL]^{(n-1)+}$ system			
$\log K_1$	9.94	10.22	0.28
$\log K_2$	2.68	3.59	0.91
ΔG°_1	−56.6	−58.3	−1.7
ΔG°_2	−15.3	−20.5	−5.2
ΔH°_1	−57.9	−62.7	−4.8
ΔH°_2	−5.5	−10.3	−4.8
ΔS°_1	−3	−15	−12
ΔS°_2	33	34	1
$[NiL_n]^{(2-n)+}$ system			
$\log K_1$	5.74	6.47	0.73
$\log K_2$	4.96	5.73	0.77
$\log K_3$	3.74	4.65	0.91
ΔG°_1	−32.8	−36.9	−4.1
ΔG°_2	−28.3	−32.7	−4.4
ΔG°_3	−21.3	−26.7	−5.4
ΔH°_1	−27.3	−27.6	−0.3
ΔH°_2	−32.2	−35.9	−3.7
ΔH°_3	−35.5	−36.7	−1.2
ΔS°_1	18	31	13
ΔS°_2	−13	−11	2
ΔS°_3	−48	−34	14

In a previous paper,[3] we reported the enthalpies of transfer ΔH°_t of the ethylenediamine and glycinato complexes of Ni(II) from water to the dioxane–water mixture. The ΔH°_t values of each species have significantly large absolute values. However, relatively small differences between the ΔH°_n values of the complexes in water and in the mixture was observed as seen in Table 3, because each difference involve the contributions of ΔH°_t of all species pertaining to the complex formation reaction which mostly compensate each other. The differences between the corresponding ΔG°_n values of the complexes in Table 3 were also small. The Gibbs energies of transfer of species involved in the complex formation reactions were then estimated as described in the following section.

Gibbs Energies of Transfer of Species from Water to the Dioxane-Water Mixture. The Gibbs energies of transfer of proton $\Delta G^\circ_t(H^+)$ from water to the

0.2 mole fraction dioxane–water mixture was 1.9 kJ mol^{-1} and the corresponding value of glycinate ion $\Delta G_t^\circ(L^-)$ was approximately estimated to be 6.0 kJ mol^{-1}.[8]

The Gibbs energies of transfer of $[H_nL]^{(n-1)+}$, $\Delta G_t^\circ(H_nL)$ (L^-=gly$^-$ and n=1 and 2), were then calculated by knowing the $\Delta G_t^\circ(H^+)$ and $\Delta G_t^\circ(L^-)$ values together with the overall Gibbs energies of formation of $[H_nL]^{(n-1)+}$, $\Delta G_{\beta_n}^\circ$ (H_nL) $(=-RT\ln\beta_n)$, in water and in the mixture given in Table 1:

$$\Delta G_t^\circ(H_nL) = \Delta G_{\beta n}^\circ(H_nL, \text{mix}) - \Delta G_{\beta n}^\circ(H_nL, \text{w}) + n\Delta H_t^\circ(H^+) + \Delta H_t^\circ(L^-). \tag{1}$$

Since the enthalpies of transfer ΔH_t° of the relevant species from water to the mixture have been reported,[3] the corresponding entropies of transfer ΔS_t° were calculated. The thermodynamic quantities of transfer of proton, glycinate ion and $[H_nL]^{(n-1)+}$ (n=1 and 2) thus obtained are summarized in Table 4.

The $\Delta G_t^\circ(HL)$ value for glycine zwitterion thus obtained was 6.3 kJ mol^{-1}. The solubilities (α/mol dm^{-3}) of glycine zwitterion in water (α_w) and in the mixture (α_{mix}) were 3.23 and 0.154 mol dm^{-3}, respectively, which gave the $-RT\ln(\alpha_{mix}/\alpha_w)$ value to be 7.5 kJ mol^{-1}. The $-RT\ln(\alpha_{mix}/\alpha_w)$ value may be compared with the calculated $\Delta G_t^\circ(HL)$ of glycine zwitterion as the first approximation.

Table 4. Thermodynamic Quantities of Transfer, ΔG_t°/kJ mol^{-1}, ΔH_t°/kJ mol^{-1}, and ΔS_t°/J K^{-1} mol^{-1}, of Single Species from Water to the 0.2 Mole Fraction Dioxane Mixture at 25 °C

Species	ΔG_t°	ΔH_t° a)	ΔS_t°
H^+	1.9b)	−22.7	−83
L^-	6.0b)	28.7	76
[HL]	6.3	1.2	−17
$[H_2L]^+$	4.1	−26.3	−100
Ni^{2+}	2.7	−41.1	−147
$[NiL]^+$	4.6	−12.7	−58
$[NiL_2]$	6.2c)	12.3	21
$[NiL_3]^-$	6.8	39.8	111

L^-: $NH_2CH_2COO^-$ (gly$^-$), [HL]: $NH_3^+CH_2COO^-$ (Hgly), $[H_2L]^+$: $NH_3^+CH_2COOH$ (H_2gly^+).
a) Ref. 4. b) Ref. 7. c) From solubility measurements.

Table 5. The Solubilities, α/mmol dm^{-3}, of the Bis(glycinato)nickel(II) Complex in Water and in an Aqueous Dioxane of 0.2 Mole Fraction Dioxane at 25 °C

Solvent	α_{tot}	$\alpha([NiL]^+)$	$\alpha([NiL_2])$	$\alpha([NiL_3]^-)$
Water	110.1	17.4	73.4	18.7
0.2 Mole Fraction Dioxane–Water Mixture	9.8	1.7	6.1	1.8

The distribution of species was calculated by using the formation constants in Tables 1 and 2.

The solubilities of the bis(glycinato)nickel(II) complex determined in water and in the dioxane–water mixture are given in Table 5. Since several glycinatonickel(II) complexes coexisted in the solutions, the distribution of species was calculated by using the formation constants of the complexes in each solution. The Gibbs energy of transfer of the neutral $[NiL_2]$ complex ΔG_t° (NiL_2) from water to the mixture was then calculated according to $\Delta G_t^\circ(NiL_2) = -RT\ln\{\alpha_{mix}(NiL_2)/\alpha_w(NiL_2)\}$, which, although being an approximate value, may be sufficient for the discussion given in a later section. By using the $\Delta G_t^\circ(NiL_2)$ and $\Delta G_t^\circ(L^-)$ values together with the Gibbs energies of formation $\Delta G_{\beta 2}^\circ$ of $[NiL_2]$ in water and in the mixture given in Table 2, the Gibbs energy of transfer of nickel(II) ion $\Delta G_t^\circ(Ni^{2+})$ from water to the mixture was calculated:

$$\Delta G_t^\circ(Ni^{2+}) = \Delta G_{\beta 2}^\circ(NiL_2, \text{w}) - \Delta G_{\beta 2}^\circ(NiL_2, \text{mix}) + \Delta G_t^\circ(NiL_2) - 2\Delta G_t^\circ(L^-). \tag{2}$$

The corresponding ΔG_t° values for $[NiL]^+$ and $[NiL_3]^-$ were then calculated by the similar procedure to that employed above. The ΔG_t° values of the glycinatonickel(II) complexes from water to the mixture thus obtained are summarized in Table 4, together with the corresponding enthalpies and entropies of transfer of the complexes.

As seen in Table 4, both enthalpy and entropy of transfer of proton from water to the mixture are significantly negative but compensate each other to result in a positive $\Delta G_t^\circ(H^+)$ value. The same trend is oserved for the corresponding ΔG_t°, ΔH_t°, and ΔS_t° values of $[H_2L]^+$. On the contary, both ΔH_t° and ΔS_t° values of glycinate ion are significantly positive but almost compensate each other to yield a relatively small positive $\Delta G_t^\circ(L^-)$ value. As to glycine zwitterion, the ΔH_t° value is positive and the ΔS_t° value negative, so that both values contribute to the positive $\Delta G_t^\circ(HL)$ value.

Both ΔH_t° and ΔS_t° values for nickel(II) ion are especially largely negative, which also compensate each other to lead to a relatively small positive ΔG_t° value. Although the ΔH_t° values for $[NiL_n]^{(2-n)+}$ (n=1—3) vary from negative to positive with n, each ΔH_t° value is compensated with the corresponding ΔS_t° value and the resultant ΔG_t° values of the complexes are all positive.

As noted in a previous paper,[3] a negative or positive ΔH_t° value of an ion from water to the dioxane–water mixture may reflect the enhanced or weakened solvation structure around the ion in the secondary solvation shell in the mixture compared to that in water. It was then suggested that the solvation structures were enhanced around cations but weakened around anions. If this consideration is applied to the entropies of transfer of ions, it is also indicated that the negative or positive values of ΔS_t° for cations or anions from water to the mixture should result. As seen in Table 4, the ΔS_t° values obtained were significantly negative for H^+, $[H_2L]^+$ and $[NiL]^+$ but positive for L^- and $[NiL_3]^-$, the result being consistent with those expected from the consideration above.

To conclude, it was also suggested by the entropies of transfer of ions from water to the dioxane–water mixture that the solvation structure around cations is enhanced but that around anions is weakened by the addition of dioxane to water. The change in the solvation structures around the ions with varying solvent compositions in dioxane–water mixtures may be related to the partially destroyed hydrogen-bonding structure of water in the bulk solvent mixtures. A dioxane molecule has oxygen atoms which can act as an electron donor and through which the hydrogen-bonds can be formed with water molecules, but it has a very poor electron acceptor ability. By forming the dioxane–water bonds, oxygen atoms of water which can not form sufficient hydrogen-bonds are generated in the mixture. The amount of the non-hydrogen-bonding oxygen atoms of water may increase with an increase in the dioxane content in the mixtures, so that the non-hydrogen-bonding oxygen atoms of water can favorably solvate to cations in the dioxane–water mixture, but solvation of anions may become less favorable due to the decreased acceptor ability of the solvent.

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