2426 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *56*, *2426—2431 (1983)* [Vol. 56, No. 8

Potentiometric and Calorimetric Studies on the Formation of Ethylenediamine Complexes of Nickel(II) Ion in Water and Dioxane-Water Mixtures

Shin-ichi Ishiguro, Yoshihiro Oka, and Hitoshi Ohtaki*
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259
Nagatsuta-cho, Midori-ku, Yokohama 227

(Received December 27, 1982)

Equilibria between ethylenediamine and protons or nickel(II) ions have been investigated at 25 °C by means of potentiometric and calorimetric titrations in water and in dioxane–water mixtures (the dioxane contents are 0.1 and 0.2 mole fractions, which correspond to 35.2 and 55.0%w/w, respectively) containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium. Thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) referring to the formation of the species HL^+, H_2L^{2+}, NiL^{2+}, $NiL_2{}^{2+}$, and $NiL_3{}^{2+}$ (L denotes ethylenediamine) have been determined in the solutions. All the formation constants of the nickel(II)–ethylenediamine complexes increased with increasing dioxane content in the solvent mixtures, although the formation constants of the ethylenediammonium ions remained practically unchanged. On the other hand, enthalpies referring to the formation of the nickel(II)–ethylenediamine complexes became less negative, and thus entropies for the corresponding reactions increased remarkably with increasing dioxane content in the mixtures. The solvent effects on the thermodynamic parameters of the complex formation of nickel(II) ions with ethylenediamine are discussed in terms of enhancement of solvation of the complexes due to weakening of the hydrogen-bonded structure of the bulk water by the addition of dioxane.

We have reported solvent effects on hydrolytic reactions of metal ions in water and in dioxane–water mixtures.[1–3] The thermodynamic quantities of transfer of the hydrolyzed species from water to aqueous dioxane solutions have been discussed in terms of the change in the structures of the bulk solvent and in the second coordination sphere of metal ions of the aqua and hydroxo complexes. The Gibbs energy difference divided by P (*i.e.*, $\Delta G^{t}_{pq}/p$) for the reaction $qM^{2+}+pOH^{-}=M_q(OH)_p{}^{(2q-p)+}$ between the aqueous solution and an aqueous dioxane mixture was approximately independent of the composition (p,q) of the complex and the kind of the metal ion, where $\Delta G^{t}_{pq}=\Delta G^{\circ}_{pq}(\mathrm{mix})-\Delta G^{\circ}_{pq}(\mathrm{aq})=-RT\ln\{\beta_{pq}(\mathrm{mix})/\beta_{pq}(\mathrm{aq})\}$ and β_{pq} denotes the overall formation constant of the $M_q(OH)_p{}^{(2q-p)+}$ complex.

On the other hand, values of $\Delta H^{t}_{pq}/p$ for the enthalpy difference of the reaction between in water and in dioxane–water mixtures largely depended on the species, and thus the contribution of the enthalpy term to the formation of the hydroxo complexes was practically compensated for that of the $T\Delta S^{t}_{pq}/p$ term.

The results are summarized in the following ways:[1–3] The hydration of the hydroxo complexes is weak relative to that of the aqua complex and depends on the fractional charge on the metal ions within the complexes. The molar enthalpy of transfer of a hydroxo complex becomes less negative compared with that of the hydrated metal ion, the fractional charge of the metal ion being lower within the former complex than within the latter.

Having a much lower donor property than water, dioxane may hardly solvate primarily to metal ions in such dioxane–water mixtures as employed here (dioxane contents are 0.1 and 0.2 mole fractions, which correspond to 35.2 and 55.0%w/w, respectively), while it may destroy the hydrogen-bonded structure of the bulk water.[4] The formation of a strong solvation shell around a metal ion stabilizes the ion in water,[5] and the weakened hydrogen-bonded structure of the bulk water might cause the hydration of metal ions more favorable.[6]

The results obtained in the determination of the partial molar enthalpies of transfer of the hydroxo complexes of metal ions in the previous investigations[1–3] suggest that a complex with a larger fractional charge on the metal ion within the complex has a stronger hydration sphere than a complex in which the metal ion has a smaller fractional charge.

It is expected that the enthalpy of transfer of a complex is closely related to the solvation structure in the second coordination sphere of the complex, if the structure of the first coordination shell of the complex remains unchanged in the course of the transfer of the complex from water to a mixed solvent.

Considering that the charge of the complexes affects significantly the structure of the second solvation sphere, we employ ethylenediamine complexes of divalent metal ions keeping the total charge at +2, and the Gibbs energies and enthalpies of transfer of the complexes with different ligand numbers are compared. In the present investigation, the ethylenediamine complexes of nickel(II) ions were chosen on considering that the structures of some of the complexes were determined by means of X-ray diffraction in aqueous solutions.[7]

Experimental

Reagents. *Lithium perchlorate*, *lithium hydroxide*, and *perchloric acid* were prepared as described previously.[8] *Dioxane* was purified by an ordinary method.[8] *Ethylenediamine* of reagent grade was first dried by adding sodium hydroxide, and then further dried by using metallic sodium with refluxing overnight under a nitrogen atmosphere, and finally distilled. *Nickel(II) perchlorate* was prepared from nickel(II) oxide and perchloric acid, and the nickel(II) oxide had been prepared by decomposition of nickel(II) nitrate under an infrared lamp, followed by heating in an electric oven at 500 °C for 12 h. The nickel(II) nitrate was of reagent grade and recrystallyzed twice from water. The nickel(II) perchlorate thus prepared was filtered through a G4 glass filter and then recrystallyzed twice from water. In order to prevent hydrolysis of nickel(II) ions, a small amount of perchloric acid was added to the stock solution and pH of the solution was adjusted to be about 3. The concentration of the free acid in the stock solution was determined coulometrically. The concentration of nickel(II) ions was determined gravimetrically by using dimethylglyoxime.

Measurements. All potentiometric and calorimetric titrations were performed in a room thermostated at (25.0± 0.5) °C. Throughout the measurements, $LiClO_4$ of 3 mol dm^{-3} was employed as a constant ionic medium.

Potentiometric Measurement. Potentiometric measurements were performed in a liquid paraffin bath controlled at (25.00± 0.02) °C, and pH of a test solution was determined by using a glass electrode in combination with an Ag–AgCl electrode as a reference. The measurements were carried out under an atmosphere of nitrogen gas which was equilibrated with solvent vapor. In each series of titrations the constant appearing in the Nernst equation, E_0, was first determined by means of Gran plots[9] by titrating 10 cm^3 of a perchloric acid solution of a known concentration with a lithium hydroxide solution in the constant ionic medium, the concentration of the lithium hydroxide solution being also known. Then, 10 cm^3 of a solution containing metal and hydrogen ions and ethylenediamine of known concentrations was added to the solution and titrations were continued with the same lithium hydroxide solution as used for the Gran-plot procedure until pH of the test solution reached about 10. Potentials at each point of measurements were related to the concentration of free hydrogen ions, h, by the Nernst equation, $E=E_0+59.15 \log h$, in the pH region where the liquid junction potential was negligible ($3 \leq \mathrm{pH} \leq 10$). Concentrations of nickel(II) ions and ethylenediamine in the test solutions at the initial stage of titration ranged from 8—46 mmol dm^{-3} and 32—111 mmol dm^{-3}, respectively.

Calorimetric Measurement. In the course of calorimetric measurements, a test solution of 150 cm^3 was placed in a Dewar vessel immersed in a water bath thermostated at (25.000± 0.007) °C. Initial test solutions contained nickel(II) ions and ethylenediamine, the concentration of the latter being slightly larger than three times the concentration of the former. The concentration of hydrogen ions in the solutions was kept so low that the predominant complex species in the solutions was NiL_3^{2+} at the initial stage of the titration. Then a perchloric acid solution of *ca.* 0.4 mol dm^{-3} was used for the calorimetric titrations. At each step of the calorimetric titrations was added the perchloric acid solution of 0.6—1.6 cm^3 with the certainty of ±0.001 cm^3 to the test solution by using an automatic piston buret (Dosimat E535, Metrohm, Switzerland) The on-line calorimetric system fully automatically controlled by an electronic computer JEC-6 (JEOL, Tokyo) was employed throughout the titrations, details of the procedure having been described in previous papers.[2,3]

Analysis of Potentiometric and Calorimetric Data. At each point of titrations the total concentrations of nickel(II) (C_M) and hydrogen ions (C_H) and ethylenediamine (C_L) are related to concentrations of respective free species, m, h, and l, on the basis of the mass-balance and the mass action law:

$$C_M = \sum_p \sum_q \sum_r p\beta_{pqr} m^p h^q l^r, \tag{1}$$

$$C_H = \sum_p \sum_q \sum_r q\beta_{pqr} m^p h^q l^r - K_w h^{-1}, \tag{2}$$

$$C_L = \sum_p \sum_q \sum_r r\beta_{pqr} m^p h^q l^r, \tag{3}$$

where β_{pqr} and K_w stand for the overall formation constant of the complex $M_pH_qL_r^{(2p+q)+}$ and the autoprotolysis constant of the solvent, respectively (β_{000}, β_{100}, β_{010}, and β_{001} are defined to be unity). The formation constants were determined by the least-squares method, where the error square sum, $U = \sum \{(C_M - C_{M,\mathrm{calcd}})^2 + (C_H - C_{H,\mathrm{cacld}})^2 + (C_L - C_{L,\mathrm{calcd}})^2\}$ was minimized by using the MINIQUAD program.[10] The protonation constants of ethylenediamine had been determined in advance of the equilibrium measurements of the complexes by separate experiments, and they were kept constant in the course of the least-squares refinement of the formation constants of the nickel(II)–ethylenediamine complexes.

On the basis of the formation constants of the complexes thus obtained, the calorimetric data were analyzed by using the program KALORI.[11] Concentrations of all species involved at each point of calorimetric titrations were calculated by using the formation constants determined. The total heat accompanying the formation of species involved in a solution of the volume V is given as follows:

$$Q = -V\left(\sum_p \sum_q \sum_r \beta_{pqr} \Delta H^\circ_{\beta pqr} m^p h^q l^r - K_w \Delta H^\circ_{Kw} h^{-1}\right), \tag{4}$$

where $\Delta H^\circ_{\beta pqr}$ and ΔH°_{Kw} denote the enthalpies pertaining to the reactions, $p\mathrm{Ni}^{2+} + q\mathrm{H}^+ + r\mathrm{L} = \mathrm{Ni}_p\mathrm{H}_q\mathrm{L}_r^{(2p+q)+}$ and $H^+ + OH^- = H_2O$, respectively. The values of K_w and ΔH°_{Kw} had been determined in the solvent mixtures in the previous works.[1,2] Heat evolved (q) at the i-th titration point was compared with the calculated one, $q_{i,\mathrm{calcd}} = Q_{i,\mathrm{calcd}} - Q_{i-1,\mathrm{calcd}}$, by taking into account suitable values of $\Delta H^\circ_{\beta pqr}$ for each species. The enthalpies were optimized by minimizing the error square sum, $U = \sum (q_i - q_{i,\mathrm{calcd}})^2$. Enthalpies for the protonation reactions of ethylenediamine were determined in advance by separate experiments.

All calculations were carried out by using an M-180 computer at the Tokyo Institute of Technology.

Results and Discussion

In all the solvents employed potentiometric titration curves for the nickel(II)–ethylenediamine system were well explained by assuming the formation of three mononuclear complexes NiL^{2+}, NiL_2^{2+}, and NiL_3^{2+}, and no protonated nickel(II)–ethylenediamine complex was detected in the present experiment. Typical titration curves obtained in the aqueous solution are shown in Fig. 1, where pH values measured are plotted against X, the degree of neutralization of ethylenediammonium ions in the solution.

All the experimental points fell on the lines calculated (X_{calcd}) by Eq. 5 over the whole range of pH examined.

$$X_{\mathrm{calcd}} = \left(2C_L + K_w h^{-1} - h - \sum_p \sum_q \sum_r q\beta_{pqr} m^p h^q l^r\right) / C_L \tag{5}$$

The formation constants of the complexes NiL_r^{2+} ($r=1$, 2, and 3) thus obtained are listed in Table 1, together with those of the protonated ethylenediamine species H_qL^{q+} ($q=1$ and 2).

In Fig. 2, typical results for the calorimetric titrations of the nickel(II)–ethylenediamine system in the aqueous solution are depicted, where the heat evolved q_i at the addition of the i-th portion of the titrant was plotted against the average ligand number n of the nickel(II)–ethylenediamine complexes in the solution. The solid lines are drawn by using the enthalpies of formation of each species finally obtained. The values of $\Delta H^\circ_{\beta pqr}$ thus evaluated are summarized in Table 2. At each

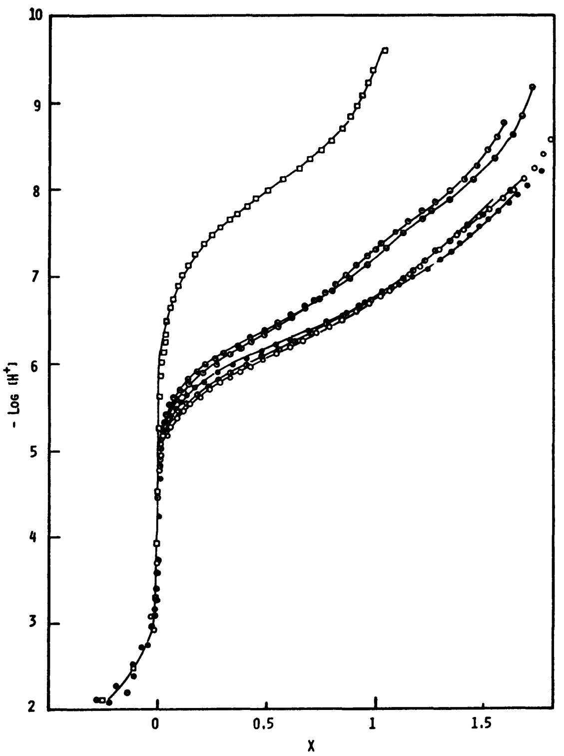

Fig. 1. Potentiometric titration curves of ethylenediamine and nickel(II)–ethylenediamine aqueous solutions.

Curve □: C_{Ni}/mmol dm^{-3}=0.0, C_L/mmol dm^{-3}=39.47; ○: 7.78, 27.61; ⊙: 10.66, 32.13; ⊖: 18.79, 72.20; ◑: 19.45, 74.76; ◐: 8.21, 29.06; ●: 35.20, 111.13; ⦶: 45.75, 32.30. The concentrations of the metal ion and the ligand were changed by dilution during the titrations. The solid lines show calculated curves by using the constants in Table 1.

point of the titrations, heat of 9—22 J was evolved, and the calculated heat $q_{i,\text{ calcd}}$ agreed with the experimental one q_i within 0.3 J.

Thermodynamic parameters for the successive reactions are defined as follows:

$$H^+ + H_{q-1}L^{(q-1)+} = H_qL^+;\ \Delta G^\circ_{0q1},\ \Delta H^\circ_{0q1}, \text{and } \Delta S^\circ_{0q1}, \quad (6)$$

$$NiL^{2+}_{r-1} + L = NiL^{2+}_r;\quad \Delta G^\circ_{10r},\ \Delta H^\circ_{10r}, \text{and } \Delta S^\circ_{10r}. \quad (7)$$

These quantities are tabulated in Table 3.

Solvent Effects on the Formation Constants. The formation constants of the nickel(II)–ethylenediamine complexes slightly increased with the dioxane content in the solvents, although the β_{0q1} values of ethylenediammonium ions were practically independent of the solvent composition (Table 1). The stepwise formation constants or the stepwise Gibbs energies of formation of each complex ($-\Delta G^\circ_{10r}$) linearly increased with the mole fraction of dioxane in the solvent and the increment of the $-\Delta G^\circ_{10r}$ values was practically independent of the number of ethylenediamine molecules within the complexes (see Table 3). As we will discuss in later sections, the increase in $-\Delta G^\circ_{10r}$ with the dioxane content in the solvents was attributed to the contribution of the entropy term, and the enthalpy for the complex formation played a role unfavorable for stabilizing the complexes in the mixed solvents.

The $-\Delta G^\circ_{102}$ value was smaller than $-\Delta G^\circ_{101}$ by about 6.9 kJ mol^{-1} in all the solvents examined here, and $-\Delta G^\circ_{103}$ was still smaller than $-\Delta G^\circ_{102}$ by *ca.* 11.4

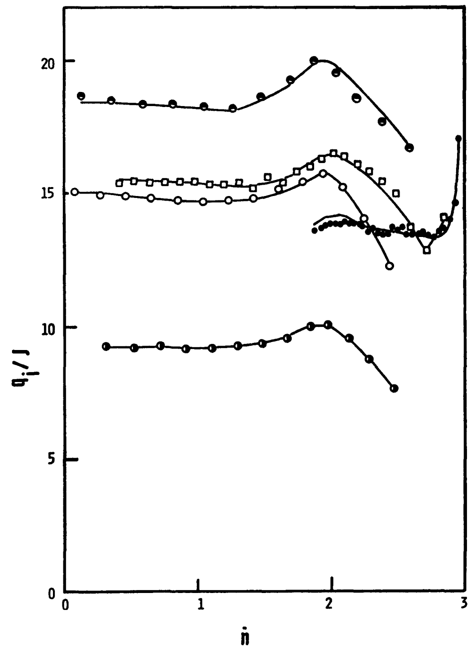

Fig. 2. Calorimetric titration curves of nickel(II)–ethylenediamine aqueous solution.

Curve ◓: C_{Ni}/mmol dm^{-3}=6.6, C_L/mmol dm^{-3}=24.4, $C_{H,tit}$/mmol dm^{-3}=288.6; ○: 6.3, 20.4, 288.6; ◑: 3.7, 13.0, 288.6; □: 11.3, 38.9, 328.2; ●: 25.0, 92.3, 310.0. $C_{H,tit}$ denotes the total concentration of hydrogen ions in the titrant used. The solid lines show calculated curve by using the constants in Table 2.

TABLE 1. THE FORMATION CONSTANTS, β_{pqr}, PERTAINING TO THE REACTIONS, $p\text{Ni}^{2+}+q\text{H}^+ + r\text{L}=\text{Ni}_p\text{H}_q\text{L}_r^{(2p+q)+}$; $\beta_{pqr}=[\text{Ni}_p\text{H}_q\text{L}_r^{(2p+q)+}]/[\text{Ni}^{2+}]^p[\text{H}^+]^q[\text{L}]^r$ (L=ETHYLENEDIAMINE), IN SOLUTIONS CONTAINING 3 mol dm^{-3} LiClO$_4$ AT 25 °C

	Complex	Concentration of dioxane/mole fraction		
		0.0 (0.0%w/w)	0.1 (35.2%w/w)	0.2 (55.0%w/w)
log β_{011}	HL$^+$	10.56(0.01)	10.57(0.01)	10.66(0.01)
log β_{021}	H$_2$L$^+$	18.54(0.01)	18.51(0.01)	18.63(0.01)
log β_{101}	NiL$^+$	7.87(0.05)	8.18(0.05)	8.54(0.01)
log β_{102}	NiL$_2$$^{2+}$	14.53(0.07)	15.18(0.05)	15.89(0.07)
log β_{103}	NiL$_3$$^{2+}$	19.18(0.13)	20.18(0.09)	21.27(0.13)

The values in parentheses refer to the three standard deviations.

TABLE 2. THE ENTHALPIES, $\Delta H^\circ_{\beta pqr}$/kJ mol^{-1}, PERTAINING TO THE REACTIONS, $p\mathrm{Ni}^{2+}+q\mathrm{H}^{+}+r\mathrm{L} = [\mathrm{Ni}_p\mathrm{H}_q\mathrm{L}_r]^{(2p+q)+}$ (L=en), IN SOLUTION CONTAINING 3 mol dm^{-3} $\mathrm{LiClO_4}$ AT 25 °C.

	Complex	Concentration of dioxane/mole fraction		
		0.0 (0.0%w/w)	0.1 (35.2%w/w)	0.2 (55.0%w/w)
$\Delta H^\circ_{\beta 011}$	$\mathrm{HL^+}$	−65.2(0.3)	−64.0(0.3)	−62.2(0.3)
$\Delta H^\circ_{\beta 021}$	$\mathrm{H_2L^+}$	−123.7(0.4)	−122.4(0.3)	−119.7(0.3)
$\Delta H^\circ_{\beta 101}$	$\mathrm{NiL^{2+}}$	−45.4(0.9)	−44.4(0.8)	−42.9(0.8)
$\Delta H^\circ_{\beta 102}$	$\mathrm{NiL_2{}^{2+}}$	−95.6(0.9)	−92.0(0.8)	−89.1(0.9)
$\Delta H^\circ_{\beta 103}$	$\mathrm{NiL_3{}^{2+}}$	−149.1(1.0)	−142.1(0.9)	−137.4(1.0)

The values in parentheses refer to three standard deviations.

TABLE 3. THE THERMODYNAMIC PARAMETERS, ΔG°_{pqr}, ΔH°_{pqr}/kJ mol^{-1} AND ΔS°_{pqr}/J K^{-1} mol^{-1}, FOR THE SUCCESSIVE FORMATION OF $\mathrm{H}_q\mathrm{L}^{q+}$ AND $\mathrm{NiL}_r{}^{2+}$

	Concentration of dioxane mole fraction		
	0.0	0.1	0.2
H⁺–en system			
$-\Delta G^\circ_{011}$	60.3	60.3	60.9
$-\Delta G^\circ_{021}$	45.5	45.4	45.5
$-\Delta H^\circ_{011}$	65.2	64.0	62.2
$-\Delta H^\circ_{021}$	58.5	58.4	57.5
ΔS°_{011}	−16.5	−12.3	−4.5
ΔS°_{021}	−43.6	−43.7	−40.4
Ni²⁺–en system			
$-\Delta G^\circ_{101}$	44.9	46.7	48.7
$-\Delta G^\circ_{102}$	38.0	39.9	41.9
$-\Delta G^\circ_{103}$	26.5	28.5	30.7
$-\Delta H^\circ_{101}$	45.4	44.6	42.9
$-\Delta H^\circ_{102}$	50.2	47.4	46.2
$-\Delta H^\circ_{103}$	53.6	50.1	48.3
ΔS°_{101}	−1.7	7.1	19.5
ΔS°_{102}	−40.9	−25.2	−14.3
ΔS°_{103}	−90.9	−72.5	−59.1

kJ mol^{-1}. The differences between $-\Delta G^\circ_{101}$ and $-\Delta G^\circ_{102}$ and between $-\Delta G^\circ_{102}$ and $-\Delta G^\circ_{103}$ were independent of the composition of the solvents. This fact indicated that replacement of two water molecules with one ethylenediamine within the coordination sphere of nickel(II) ion became more and more difficult with successive steps, although the replacement became more and more exothermic as will be described later.

Solvent Effects on the Enthalpies. According to the X-ray diffraction measurements of the hexaaquanickel(II) ions[12] and the nickel(II)–ethylenediamine complexes[7] in aqueous solutions, the Ni–O bond length increased from 2.04 Å within the $[\mathrm{Ni(H_2O)_6}]^{2+}$ ion to 2.10 Å within the $[\mathrm{Ni(H_2O)_2L_2}]^{2+}$ complex with the increase in the number of ethylenediamine molecules coordinated. The lengthening of the Ni–O bond indicated weakening of the bond due, perhaps, to the electron donation from the nitrogen atoms within the ethylenediamine molecules to the central metal ion by which the fractional charge on the nickel(II) atom might decrease. Although no structural data have been reported for the $\mathrm{Ni(H_2O)_4L^{2+}}$ complex, we can expect such an elongation of the Ni–O bond within the $\mathrm{Ni(H_2O)_4L^{2+}}$ complex when an ethylenediamine molecule coordinates to an aquanickel(II) ion. Therefore, the replacement of water molecules within the $[\mathrm{Ni(H_2O)}_{6-2r}\mathrm{L}_r]^{2+}$ complex ($0 \leq r \leq 3$) needs less and less energies with the increase in the number of ethylenediamine molecules r within the complex.

The Ni–N bond lengths are 2.10 Å and 2.20 Å within the $[\mathrm{Ni(H_2O)_2L_2}]^{2+}$ and $[\mathrm{NiL_3}]^{2+}$ complexes, respectively,[7] and therefore, the Ni–N bond may be weaker in the latter than in the former. Thus, we can expect that both Ni–O and Ni–N bonds more and more weaken with the introduction of ethylenediamine molecules to the coordination sphere of nickel(II) ion.

In spite of the weakening of the Ni–N bond in the $[\mathrm{Ni(H_2O)}_{6-2r}\mathrm{L}_r]^{2+}$ complex with increasing r, ΔH°_{10r} in the aqueous solution became more negative. This suggests that the decrease of the Ni–O bond energy within the $[\mathrm{Ni(H_2O)}_{6-2r}\mathrm{L}_r]^{2+}$ complex may be more enhanced than that of the Ni–N bond by the ligand substitution of two moles of $\mathrm{H_2O}$ with one mole of ethylenediamine.

From the enthalpic point of view, the formation of nickel(II)–ethylenediamine complexes became less favorable in a dioxane–water mixture than in water, although the decrease in the Gibbs energies at each successive complexation reaction was more pronounced in mixed solvents than in water.

We can assume that the bond lengths within the complexes are not appreciably changed when the complexes are transferred from water to a dioxane–water mixture, because no change has been observed in the UV and visible absorption spectra of the complexes in solutions with different dioxane contents. Invariable $\Delta\Delta G^\circ_{10r}$ and $\Delta\Delta H^\circ_{10r}$ values between the successive stages of formation of a given pair of complexes in two different solutions may give an indirect support for the invariable structures of the complexes concerned. Therefore, the changes in the enthalpy of the complex formation reactions in different solvents, as well as entropy changes, should be attributed to the structural changes in the second coordination sphere of the complexes, in which solvent molecules interact with the ligand molecules coordinated to the central nickel(II) ion.

It is well accepted that water molecules interact each other through hydrogen bonds in the bulk water and that the hydrogen-bonded water structure is broken by the addition of dioxane. In the ionic medium employed here, many water molecules are hydrated to the medium salt, but still there are some water molecules having a bulk-like structure in the solution.

When nickel(II) ions are brought into the aqueous solution, the nickel(II) ions form the hexaaquanickel(II) complex which can still be solvated with water molecules in their second coordination sphere. Nickel(II)–ethylenediamine complexes, the first coordination shell of which are filled with ethylenediamine and water molecules (except for the NiL_3^{2+} complex), can be also solvated with water molecules in the aqueous solution. The second-sphere hydration of the complexes may be weak and not highly ordered, and therefore, the interaction between the ligand molecules in the first coordination sphere and water molecules in the second solvation shell may be affected rather sensitively by the change in the hydrogen-bonded structure of the bulk water. The more the hydrogen-bonded structure of the bulk water is broken by the addition of dioxane, the easier the construction of the second hydration shell is, and thus, the more negative the enthalpy of hydration in the second sphere of the complex should be, provided that the structure of the first coordination shell of the complex is not practically affected by the change in the bulk structure of water.

The enthalpies of each successive formation of the complexes became less negative with increasing dioxane content in the solvent (see Table 3). This fact suggests that the enthalpy difference of a complex $[Ni(H_2O)_{6-2r}L_r]^{2+}$ in two different solvents is larger than that of a complex $[Ni(H_2O)_{6-2(r+1)}L_{r+1}]^{2+}$.

In order to discuss the enthalpy changes of the complex formation reactions in different solvents, we estimated enthalpies of transfer of each complex ion from water to the dioxane–water mixtures employed in the present work.

Underdown *et al.*[13] have reported that the enthalpy of transfer of nickel(II) ion from water to a dioxane–water mixture was positive (endothermic) when the dioxane content in the mixture was lower than 0.04 mole fraction, but decreased to tend to be negative (exothermic) with an increase in the dioxane concentration. In an aqueous mixture with the dioxane content larger than 0.06 mole fraction, the enthalpy of transfer of nickel(II) ion from water to the mixture became negative. This fact indicates that the solvation of nickel(II) ion is enhanced in the aqueous dioxane mixtures with the dioxane content higher than 0.06 mole fraction.

The solvation of ethylenediamine does not seem to change significantly when dioxane is added to water. The heats of solution of ethylenediamine in water and in a dioxane–water mixture containing 0.2 mole fraction dioxane, both solutions having 3 mol dm^{-3} $LiClO_4$, were 34.5 kJ mol^{-1} and 34.8 kJ mol^{-1}, respectively.[14] Therefore, the enthalpy of transfer of ethylenediamine from water to the dioxane–water mixture was practically zero.

The difference $\Delta H^\circ_{\beta 10r}(\mathrm{mix})-\Delta H^\circ_{\beta 10r}(\mathrm{aq})$ can be separated into contributions of each species concerned as follows:

$$\begin{aligned}
&\Delta H^\circ_{\beta 10r}(\mathrm{mix}) - \Delta H^\circ_{\beta 10r}(\mathrm{aq}) \\
&\quad = \{\Delta H^\circ_{\mathrm{sv.mix}}(\mathrm{NiL}_r{}^{2+}) - \Delta H^\circ_{\mathrm{sv.aq}}(\mathrm{NiL}_r{}^{2+})\} \\
&\qquad - \{\Delta H^\circ_{\mathrm{sv.mix}}(\mathrm{Ni}^{2+}) - \Delta H^\circ_{\mathrm{sv.aq}}(\mathrm{Ni}^{2+})\} \\
&\qquad - r\{\Delta H^\circ_{\mathrm{sv.mix}}(\mathrm{L}) - \Delta H^\circ_{\mathrm{sv.aq}}(\mathrm{L})\} \\
&\quad = \Delta H^\circ_{\mathrm{tr}}(\mathrm{NiL}_r{}^{2+}) - \Delta H^\circ_{\mathrm{tr}}(\mathrm{Ni}^{2+}) - r\Delta H^\circ_{\mathrm{tr}}(\mathrm{L}), \qquad (8)
\end{aligned}$$

where $\Delta H^\circ_{\mathrm{sv}}(j)$ and $\Delta H^\circ_{\mathrm{tr}}(j)$ stand for the enthalpies of solvation and of transfer of species j, respectively. Here we can reasonably assume that $\Delta H^\circ_{\mathrm{tr}}(\mathrm{L})$ is zero. $\Delta H^\circ_{\mathrm{tr}}(\mathrm{Ni}^{2+})$ can be estimated by inter- and extrapolating the values reported by Underdown *et al.*[13] to 0.1 and 0.2 mole fraction dioxane–water mixtures, respectively. Therefore, by using experimental values given in Table 2 for $\Delta H^\circ_{\beta 10r}$ of each complex formation reaction, we can evaluate the values of $\Delta H^\circ_{\mathrm{tr}}(\mathrm{NiL}_r{}^{2+})$ for the various complexes. The values thus estimated are tabulated in Table 4. The enthalpies of transfer of all the species from water to the aqueous dioxane mixtures are negative, and the values are more negative in the mixtures with the higher dioxane content. The result implies that the second-sphere solvation of the nickel(II)–ethylenediamine complexes, as well as the aquanickel(II) ion, is enhanced in the dioxane–water mixtures, but the degree of the enhancement of the second-sphere solvation is less in the complexes than in the aquanickel(II) ion.

This result indicates that the enhancement of the second-sphere solvation of the complexes and the aquanickel(II) ion may be due to a less energy needed for breaking the water structure to produce non-hydrogen-bonded water molecules which solvate the complexes, and the hydrogen-bonding of water molecules in the second-coordination sphere may be stronger in the hexaaquanickel(II) ion than in the nickel(II)–ethylenediamine complexes.

The enthalpies for the formation of ethylenediammonium ions (HL^+ and H_2L^{2+}) slightly increased with an increase in the dioxane content of the solvents, and the increment of the ΔH°_{0q1} values was practically compensated for an increase in the ΔS°_{0q1} values, which led to the ΔG°_{0q1} values practically independent of the solvent composition (see Table 3).

Solvent Effects on the Entropies. Entropies of the reaction, $[Ni(H_2O)_{6-2r}L_r]^{2+}+L=[Ni(H_2O)_{6-2(r+1)}L_{r+1}]^{2+}+2H_2O$, decreased with an increase in the number of ethylenediamine molecules r within the complex, as reported previously by many authors. On the other hand, in the formation of a given complex, the entropies increased remarkably with increasing dioxane content

TABLE 4. ENTHALPIES OF TRANSFER, $\Delta H^\circ_{\mathrm{tr}}$/kJ mol^{-1}, OF THE AQUANICKEL(II) ION AND NICKEL(II) –ETHYLENEDIAMINE COMPLEXES FROM WATER TO DIOXANE–WATER MIXTURES[a)]

Dioxane content	$-\Delta H^\circ_{\mathrm{tr}}$			
mole fraction	Ni^{2+}	NiL^{2+}	NiL_2^{2+}	NiL_3^{2+}
0.1	8.0[b)]	7.0	4.4	1.0
0.2	24.0[c)]	21.5	17.5	12.3

a) Values for NiL_r^{2+} complexes were calculated by assuming $\Delta H^\circ_{\mathrm{tr}}(\mathrm{L})=0$. b) Interporated from the values in Ref. 13. c) Extraporated from the values in Ref. 13.

in the solutions (Table 3). The increase in the entropies for the stepwise complex formations with an increase in the dioxane content in the solution is most remarkable in the formation of the highest complex NiL_3^{2+}.

The formation of the $[Ni(H_2O)_{6-2(r+1)}L_{r+1}]^{2+}$ complex is accompanied by the dehydration of two moles of water in the first coodination sphere of the $[Ni(H_2O)_{6-2r}L_r]^{2+}$ complex. The number of water molecules expelled from the whole coordination shell of the complex at the introduction of one ethylenediamine molecule may be larger than 2, because dehydration of the ethylenediamine molecule and from the second coordination sphere of the complex may also be expected in the complex formation reaction. The dehydration will cause the increase in entropy, although a part of the entropy increase in the dehydration process may be cancelled out by a decrease in entropy due to combination of an ethylenediamine molecule with the metal ion.

As we have discussed in the previous section, the hydrogen-bonded structure of water is broken by the addition of dioxane, and therefore, in the dioxane–water mixture water molecules can behave more freely compared with those in the aqueous solution.

When water molecules are liberated from the coordination sphere of a nickel(II) ion by the chelate formation with ethylenediamine molecules, the water molecules can behave more freely in the bulk phase of a dioxane–water mixed solvent than in an aqueous solution. Therefore, in the dehydration process accompanying the chelate formation with ethylenediamine, the entropy of the reaction becomes more positive in a dioxane–water mixture than in water.

The entropies for the protonation of ethylenediamine increased with increasing dioxane content in the mixture, although the increase was not remarkable compared with that for the formation of any of the nickel(II)–ethylenediamine complexes in the same solvents. In the course of the protonation reaction of ethylenediamine, $L+qH_3O^+=LH_q^{q+}+qH_2O$, the liberated water molecules might solvate the protons at the amino groups within the ethylenediammonium ion formed, so that the entropy gain by the liberation of water molecules from H_3O^+ may be cancelled out by the combination of the water molecules with the NH_3^+ groups formed.

The work has partially been supported by the Grant-in-Aid for Scientific Research No. 57470054 from the Ministry of Education, Science and Culture and by the Asahi Glass Foundation for Industrial Technology.

References

1) T. Kawai, S. Ishiguro, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **53**, 2221 (1980).

2) S. Ishiguro and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **52**, 3198 (1979).

3) S. Ishiguro and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **54**, 335 (1981).

4) D. N. Glew, H. D. Mak, and N. H. Rath, "Hydrogen-bonded Solvent Systems," Taylor and Francis Ltd., London (1968), p. 195.

5) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

6) D. Feakins and C. T. Allan, *J. Chem. Soc., Faraday Trans. 1*, **1976**, 314.

7) T. Fujita and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **55**, 455 (1982).

8) H. Ohtaki, *Inorg. Chem.*, **6**, 808 (1967).

9) G. Gran, *Analyst*, **77**, 661 (1952).

10) S. Sabatini, A. Vacca, and P. Gans, *Talanta*, **21**, 53 (1974).

11) R. Karlsson and L. Kullberg, *Chem. Scr.*, **9**, 54 (1976).

12) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976); "Analytical Chemistry: Essays in Memory of Anders Ringbom," ed by E. Wänninen, Pergamon Press, New York (1977), p. 163.

13) D. R. Underdown, S. S. Yun, and J. L. Bear, *J. Inorg. Nucl. Chem.*, **36**, 2043 (1974).

14) S. Ishiguro and H. Ohtaki, unpublished data.