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Enthalpies of Transfer of Single Ions and Metal Complexes from Water to an Aqueous Dioxane Solution

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Enthalpies of solution of some 1:1 and 2:1 electrolytes were determined in water and in a dioxane–water mixture (the dioxane content; 0.2 mole fraction or 55.0% w/w) by calorimetry at 25 °C. Enthalpies of transfer (ΔH_t°) of single ions from water to the dioxane–water mixture were obtained by employing the extrathermodynamic tetraphenylarsonium tetraphenylborate (TATB) assumption. Enthalpies of transfer of nickel(II) and copper(II) complexes with glycinate (gly$^-$) and ethylenediamine (en) were also evaluated for $[\mathrm{Ni(gly)}_n]^{(2-n)+}$ (n=1—3), $[\mathrm{Ni(en)}_n]^{2+}$ (n=1—3), and $[\mathrm{Cu(en)}_n]^{2+}$ (n=1—2) by combining enthalpies of transfer of the relevant single metal ions and ligands with enthalpies of complex formation reactions $\mathrm{M}+n\mathrm{L}=\mathrm{ML}_n$ (M=$\mathrm{Ni^{2+}}$ or $\mathrm{Cu^{2+}}$ and L= gly$^-$ or en) in water and in the mixture. The enthalpies of transfer of the metal complexes examined here increased almost linearly with an increase in the number of the ligands within the complexes. The values of ΔH_t° of the ethylenediamine complexes of nickel(II) and copper(II) ions were all negative, as well as those of free $\mathrm{Ni^{2+}}$ and $\mathrm{Cu^{2+}}$ ions. On the other hand, the enthalpies of transfer of the noncharged $[\mathrm{Ni(gly)_2}]$ and anionic $[\mathrm{Ni(gly)_3}]^-$ complexes were positive, while that of the $[\mathrm{Ni(gly)}]^+$ complex was still negative. The result suggested that hydration of the ligands coordinating to the central metal ions plays an essential role in the enthalpies of transfer of the metal complexes from water to the dioxane–water mixture.

In previous papers we reported formation constants or Gibbs energies, enthalpies and entropies of formation of ethylenediamine complexes of nickel(II)[1] and copper(II)[2] ions in water and in dioxane–water mixtures containing 0.1 and 0.2 mole fractions (35.2 and 55.0% w/w, respectively) of dioxane and discussed about solvent effects on the complex formation reactions.

Although it was pointed out that the Gibbs energies of transfer of metal ions from water to the dioxane–water mixtures were negative[3–5] and thus the metal ions should be more stable in the mixtures than in water, the formation of the ethylenediamine complexes of nickel(II) and copper(II) ions was more favorable in the dioxane–water mixtures than in water. This result indicated that the ethylenediamine complexes of nickel(II) and copper(II) ions should be more stabilized than the respective free metal ions on transferring the species from water to the dioxane–water mixtures, provided that the instabilization of the neutral ligand in the mixtures was not too significant compared with that in water.

NMR studies[6,7] suggested that metal ions were preferentially solvated with water in their primary coordination sphere over a wide range of composition of dioxane–water mixtures. Thus, we concluded[1–3] that the aqua and ethylenediamine complexes of nickel(II) and copper(II) ions were hydrated even in aqueous mixture of dioxane because of weaker donor property of dioxane (the donor number (DN)=14.8) than water (DN=18.0)[8] and the hydration of the metal ions and complexes was more enhanced in the mixtures than in water.

The above conclusion was supported by evidence from calorimetric measurements. Enthalpies of solution of some 1:1 electrolytes so far reported indicated that hydration of metal ions was strengthened in dioxane–water mixtures due, probably, to breaking of the hydrogen-bonded structure of water in the bulk solvents.[9,10] The enthalpies of transfer of the $[\mathrm{Ni(en)}_n]^{2+}$ (n=1—3) complexes estimated were all negative, which showed that solvation of the complexes was enhanced in the dioxane–water mixtures.[1]

In order to expand our studies to other metal–ligand systems, we first undertook to determine enthalpies of transfer of single metal ions and ligands involved in the metal–ligand complexes from water to a dioxane–water mixture. The mixture of the dioxane content of 0.2 mole fraction (55.0% w/w) was chosen as the mixed solvent in the present study, because complex formation reactions of various metal ions were studied in this mixture in our laboratory. Moreover, various solvent properties of dioxane–water mixture show a significant variation with changing solvent composition in the water-rich region of about 0.2 mole fraction dioxane content.[11]

In the present work the extrathermodynamic tetraphenylarsonium tetraphenylborate assumption $\Delta H_t^\circ(\mathrm{Ph_4As^+})=\Delta H_t^\circ(\mathrm{BPh_4^-})$, was adopted[12] for dividing enthalpies of transfer of salts from water to the dioxane–water mixture into those of individual ions, where ΔH_t° denotes the enthalpy of transfer of a species from water to the 0.2 mole fraction dioxane–water mixture, which is given by the difference between enthalpies of solution of the species in the two solvents.

Enthalpies of transfer of $\mathrm{Ni^{2+}}$, $\mathrm{Cu^{2+}}$, and glycinate (gly$^-$) ions and ethylenediamine (en) from water to the 0.2 mole fraction dioxane–water mixture thus evaluated were combined with enthalpies of formation of the $[\mathrm{Ni(gly)}_n]^{(2-n)+}$ (n=1—3), $[\mathrm{Ni(en)}_n]^{2+}$ (n=1—3), and $[\mathrm{Cu(en)}_n]^{2+}$ (n=1—2) complexes in the solvents and thus enthalpies of transfer of the metal complexes were obtained. The enthalpy of transfer of proton was calculated by using ΔH_t°'s of glycinate ion and glycine, and enthalpies of formation of glycine in water and in the dioxane–water mixture. Enthalpies of transfer of the $\mathrm{Hen^+}$, $\mathrm{H_2en^{2+}}$, and $\mathrm{H_2gly^+}$ species from water to the

0.2 mole fraction dioxane–water mixture were also estimated.

Experimental

Reagents. All chemicals used were of reagent grade. *Nickel(II) and copper(II) chlorides* were prepared by dissolving respective metal oxides into hydrochloric acid of super special grade. The metal oxides had been prepared as described elsewhere.[1] The hexahydrates of nickel(II) and copper(II) chlorides were prepared by drying the solutions in a vacuum evaporator, and then dried at 150 °C in a vacuum oven to obtain the anhydrous salts. *Bis(glycinato)nickel(II) dihydrate crystals* were prepared by dissolving freshly precipitated nickel(II) carbonate to an aqueous glycine solution, and then recrystallized from water. The dihydrate salt was dried at 150 °C in a vacuum oven to obtain the anhydrous one. *Sodium glycinate* was prepared by mixing equimolar amounts of glycine and sodium hydroxide in methanol and recrystallized three times from methanol. Purity of the sodium glycinate thus prepared was more than 99.8%. *Glycine* was recrystallized three times from water. *Sodium perchlorate* was prepared and purified as described previously.[13] *Sodium tetraphenylborate, tetraethylammonium chloride, and tetraethyl ammonium perchlorate* used were recrystallized from acetone and then washed with ester. *Tetraphenylarsonium chloride and sodium chloride* were used without further purification and dried at 180 °C. All chemicals thus prepared and purified were stored in a vacuum desiccator over P_2O_5. *Dioxane and ethylenediamine* were dried by using metallic sodium and then distilled.

Calorimetric Measurements. Enthalpies of solution were measured in a room thermostated at (25.0±0.2) °C by using an MPS-11 calorimeter (Tokyo Riko, Tokyo). A teflon vessel was placed in an aluminium block controlled at (25.000±0.003) °C in an air-bath. All parts inserted in the vessel were made of teflon. A standard heater and a thermal sensor were sandwiched between the bottom of the vessel and the aluminium block. Powder of a sample salt was placed in a glass ampoule in a dry box over P_2O_5, and the ampoule was weighed and then sealed. An ampoule containing a given amount of a sample salt was immersed in a solvent of 50 cm^3 in the teflon vessel.

The measurement of heat of solution of a sample consisted of two stages I and II. A typical chart for a heat measurement of a sample salt is shown in Fig. 1.

A vessel equipped with an ampoule in a solvent was installed in an aluminium block. At the beginning of measurement, the vessel was thermally equilibrated with the aluminium block (temperature: θ_0). Then the vessel was heated with a standard heater for a given period of time from $t=0$ to $t=t_h$. Thus temperature of the vessel rose during the heating period then spontaneously fell and became to the initial temperature (θ_0) within a few hours (stage I). Then the ampoule was mechanically broken and the temperature increased or decreased depending on the exothermic or endothermic dissolution of a salt. In Fig. 1 an example for the endothermic dissolution of a salt (NaCl in this case) is depicted (stage II). The temperature change detected by using a thermal sensor was recorded in a JEC 6 electronic computer (JEOL, Tokyo) every second through a 10-bit AD converter. Measurements were performed with the aid of the on-line system for calorimetry developed in our laboratory.

Determination of Heat of Solution. Under nonadiabatic conditions, the change in temperature $\theta(t)$ of a vessel in which heat is evolved or absorbed by dissolution of a sample salt is followed by the equation 1:

$$C_p\{d\theta(t)/dt\} = q(t) - \lambda\{\theta(t)-\theta_0\}, \qquad (1)$$

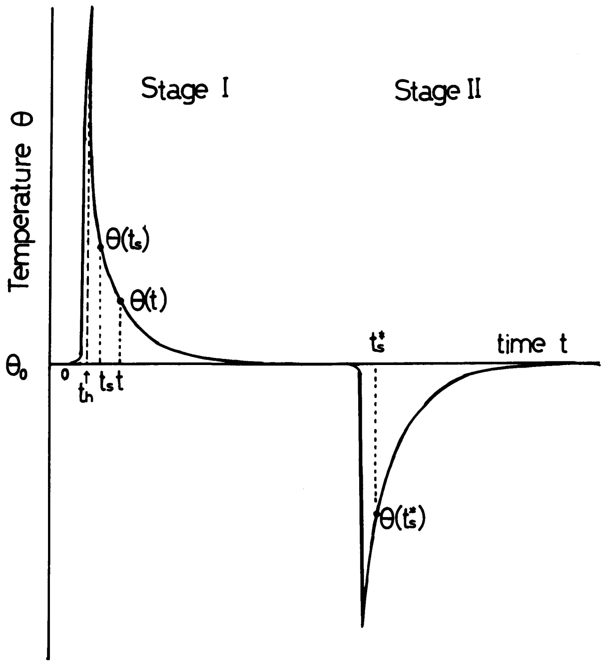

Fig. 1. A typical example for the calorimetric determination of heat of solution of a salt.

where C_p and λ stand for heat capacity and heat transfer coefficient of the vessel, respectively. $q(t)$ denotes heat evolved (or absorbed) per unit time at time t. Since $\theta(t)=\theta_0$ at $t=0$ and ∞, the total heat Q evolved (or absorbed) in the vessel is thus obtained by integrating measured temperatures from $t=0$ to $t=\infty$ as follows:

$$Q = \int_0^\infty q(t)dt = \lambda\int_0^\infty\{\theta(t)-\theta_0\}dt. \qquad (2)$$

Therefore, in order to relate measured temperature changes to the total heat it is needed to know the values of C_p and λ. The values of C_p and λ were determined by heating the vessel with a standard heater at stage I in advance of dissolution of a salt at stage II.

At stage I, a standard heater was operated for a given period of time from $t=0$ to $t=t_h$ and a given amount of heat Q_{ev} was evolved. At $t>t_h$ where no more heat is evolved, temperature of the vessel spontaneously decreased. At a region of the spontaneous cooling of the vessel, a temperature at $t=t_s$, $\theta(t_s)$, ($t_s>t_h$) decreases according to Eq. 3:

$$\theta(t) - \theta_0 = \{\theta(t_s)-\theta_0\}\exp\{-\mu(t-t_s)\}, \qquad (3)$$

where $\mu=\lambda/C_p$. The value of μ is obtained by plotting ln-$\{\theta(t)-\theta_0\}$ as a function of $(t-t_s)$, since ln $\{\theta(t)-\theta_0\}=\ln\{\theta(t_s)-\theta_0\}-\mu(t-t_s)$.

The right hand side of Eq. 2 can be separated into two terms as follows:

$$\begin{aligned} Q_{ev} &= \lambda[\int_0^{t_s}\{\theta(t)-\theta_0\}dt + \int_{t_s}^\infty\{\theta(t)-\theta_0\}dt] \\ &= \lambda[\int_0^{t_s}\{\theta(t)-\theta_0\}dt \\ &\quad + \int_{t_s}^\infty\{\theta(t_s)-\theta_0\}\exp\{-\mu(t-t_s)\}dt]. \end{aligned} \qquad (4)$$

At a given time t_s, $\theta(t_s)$ is a constant and thus the second term of Eq. 4 is given as $\{\theta(t_s)-\theta_0\}/\mu$.

Since Q_{ev} and μ are known and the first term of Eq. 4 is approximated by using the relation

$$\int_0^{t_s}\{\theta(t)-\theta_0\}\mathrm{d}t = \sum_0^{t_s}\{\theta(t)-\theta_0\}\Delta t, \tag{5}$$

the constant λ and C_p are obtained as follows:

$$\lambda = Q_{ev}/[\sum_0^{t_s}\{\theta(t)-\theta_0\}\Delta t+\{\theta(t_s)-\theta\}/\mu], \tag{6}$$

$$C_p = \lambda/\mu. \tag{7}$$

In the course of the determination of μ, a certain time after 900 seconds beyond t_h (t_h=300 seconds) was taken as t_s and successive 70 points of $\theta(t)$ measured at every 30 seconds after t_s was subjected to the least-squares calculation for the ln-$\{\theta(t)-\theta_0\}$ plots *vs.* $(t-t_s)$. The value of Δt in Eq. 6 was one second, and all the t values employed in the course of the calculation of μ were used as t_s in the evaluation of λ by using Eq. 6. Thus the final λ value was obtained by averaging 70 λ's in each set of data with different t_s's.

Once we know the constants λ and C_p of the vessel, we can determine unknown heat evolved or absorbed by dissolution of a sample salt. An ampoule immersed in a solvent was mechanically broken and a salt in the ampoule dissolves exothermically or endothermically to yield a temperature change as is shown in Fig. 1, stage II, as an example (in the present example an endothermic dissolution process is given). The heat Q evolved or absorbed at dissolution of m moles of a salt is given, by using the constant λ and C_p obtained at stage I, as follows:

$$Q = \lambda[\sum_0^{t_s}\{\theta(t)-\theta_0\}\Delta t+(C_p/\lambda)\{\theta(t_s^*)-\theta_0\}]. \tag{8}$$

Q values were estimated at various t_s^* and the final Q value was determined by averaging the Q values estimated at various t_s^*. The uncertainty of the Q value was within ±0.5%. The enthalpy of solution of the salt (ΔH_s°) was thus given as $\Delta H_s^\circ=-Q/m$.

Results and Discussion

Enthalpies of Transfer of Single Ions. Enthalpies of solution of six salts were measured in water and in the 0.2 mole fraction dioxane-water mixture and the results are summarized in Table 1. Enthalpies of solution of the salts showed no appreciable dependence on the concentration except for NaCl and $(C_2H_5)_4NCl$ in the dioxane-water mixture. The values in Table 1 for NaCl and $(C_2H_5)_4NCl$ were obtained by extrapolating enthalpies of solution measured in the mixture with various concentrations of the salts to those at infinite dilution. The enthalpies of solution obtained in water for all the salts examined here agree with those in the literature within±1.2 kJ mol^{-1}.[14)]

At infinite dilution all the salts in Table 1 were assumed to be fully dissociated both in water and in the dioxane-water mixture, and thus, the enthalpy of transfer of a salt i of 1 : 1 electrolyte (consisting of A^+ and B^-) from water to the mixture was represented as the sum of the enthalpies of transfer of each ionic component as follows:

$$\Delta H_t^\circ(A^+B^-) = \Delta H_t^\circ(A^+) + \Delta H_t^\circ(B^-). \tag{9}$$

Enthalpies of transfer of six single ions were thus evaluated from those of the salts in Table 1 by applying the extrathermodynamic TATB assumption $\Delta H_t^\circ(Ph_4As^+)=\Delta H_t^\circ(BPh_4^-)$ to the calculation and by minimizing the error-square sum $U=\sum\{\Delta H_{t,obsd}^\circ(i)-\Delta H_{t,calcd}^\circ(i)\}^2$.

TABLE 1. ENTHALPIES OF SOLUTION (ΔH_s°) OF SOME 1 : 1 ELECTROLYTES IN WATER AND IN DIOXANE-WATER MIXTURE (0.2 mole FRACTION OF DIOXANE), AND ENTHALPIES OF TRANSFER (ΔH_t°) OF THE ELECTROLYTES FROM WATER TO THE MIXTURE AT 25 °C

Species	ΔH_s°(w) / kJ mol^{-1}	ΔH_s°(mix) / kJ mol^{-1}	ΔH_t° / kJ mol^{-1}
$NaBPh_4$	−20.0(−20.0)$^{a)}$	−39.4	−19.4
Ph_4AsCl	−10.2(−10.9)$^{a)}$	5.7	15.9
NaCl	4.4(3.8)$^{a)}$	0.2	−4.2
$NaClO_4$	15.0(13.8)$^{a)}$	−9.4	−24.4
$(C_2H_5)_4NClO_4$	32.2(31.0)$^{a)}$	23.2	−9.0
$(C_2H_5)_4NCl$	−12.4(−13.6)$^{a)}$	−1.4	−11.0

a) Values in parentheses are those quoted from Ref. 14.

TABLE 2. ENTHALPIES OF TRANSFER (ΔH_t°) OF SINGLE IONS FROM WATER TO THE DIOXANE-WATER (0.2 mole FRACTION OF DIOXANE) AT 25 °C.

Ion	ΔH_t°/kJ mol^{-1}
Ph_4As^+	0.4
BPh_4^-	0.4
Na^+	−19.8
Cl^-	15.5
$(C_2H_5)_4N^+$	−4.5
ClO_4^-	−4.6

The enthalpies of transfer of the single ions thus obtained are tabulated in Table 2. The enthalpies of transfer of all the salts in Table 1 were satisfactorily reproduced by those of the single ions in Table 2 within ±0.1 KJ mol^{-1}. The enthalpies of transfer of single ions in Table 2 are consistent with those calculated by interpolating the enthalpies of transfer from water to dioxane-water mixtures of different composition, which were obtained by employing the tetraphenylphosphonium tetraphenylborate assumption $\Delta H_t^\circ(Ph_4P^+)=\Delta H_t^\circ(BPh_4^-)$.[10)]

Enthalpies of solution of $NiCl_2$, $CuCl_2$, sodium glycinate, glycine, and ethylenediamine were also measured in these solvents and the values are listed in Table 3. Sodium glycinate and ethylenediamine were dissolved in an alkaline solution to prevent protonation of the species. Glycine was dissolved in neutral solvents in which glycine form the zwitterion, Hgly. For all the species in Table 3, no appreciable change was found for the enthalpies of solution with the concentration of the salts over a range of 10^{-3} to 10^{-2} mol dm^{-3}. The enthalpy of solution of ethylenediamine obtained in water agreed well with the value reported by Nochols *et al.*[15)]

It was also assumed that $NiCl_2$, $CuCl_2$, and sodium glycinate are completely dissociated in the solvents examined, and the enthalpies of transfer of nickel(II), copper(II) and glycinate ions from water to the dioxane-water mixture are thus estimated by subtracting the contribution of their counter ions which had been obtained in advance.

TABLE 3. ENTHALPIES OF SOLUTION (ΔH°_s) OF SOME COMPOUNDS IN WATER AND IN THE DIOXANE-WATER MIXTURE (0.2 mole FRACTION OF DIOXANE), AND THEIR ENTHALPIES OF TRANSFER (ΔH°_t) FROM WATER TO THE MIXTURE AT 25 °C

Species	ΔH°_s(w) / kJ mol^{-1}	ΔH°_s(mix) / kJ mol^{-1}	ΔH°_t / kJ mol^{-1}
$NiCl_2$	−79.9	−90.0	−10.1
$CuCl_2$	−56.3	−61.0	−4.7
Nagly[a)]	−11.3	−2.4	8.9
Hgly	15.0	16.2	1.2
en[b)]	−34.5(−32.0)	−34.8	−0.3

a) Dissolved in solutions containing 0.01 mol dm^{-3} NaOH. b) Dissolved in solutions containing 0.1 mol dm^{-3} LiOH and 3 mol dm^{-3} $LiClO_4$. The value in parentheses was obtained in the same alkaline solution without $LiClO_4$.

Enthalpies of Transfer of Proton, Protonated Glycine and Protonated Ethylenediamine. Glycinate ion (gly$^-$) reacts with proton to form the zwitterionic glycine (Hgly or $NH_3^+CH_2COO^-$) in solution. The enthalpy of the reaction, $H^+ + gly^- = Hgly$, was −57.9 and −62.7 kJ mol^{-1} in water ($\Delta H^\circ_{\mathrm{Hgly}}$(w)) and in the dioxane-water mixture ($\Delta H^\circ_{\mathrm{Hgly}}$(mix)), respectively.[16)] The difference between the enthalpies of formation of Hgly in these solvents is related to the enthalpies of transfer of the species participating in the formation reaction as follows:

$$\Delta H^\circ_{\mathrm{Hgly}}(\mathrm{mix}) - \Delta H^\circ_{\mathrm{Hgly}}(\mathrm{w}) = \Delta H^\circ_t(\mathrm{Hgly}) - \Delta H^\circ_t(\mathrm{H^+}) - \Delta H^\circ_t(\mathrm{gly^-}). \tag{10}$$

Since the ΔH°_t values of gly$^-$ and Hgly were already determined as described in the previous section, the enthalpy of transfer of proton $\Delta H^\circ_t(H^+)$ from water to the mixture could be evaluated. By knowing ΔH°_t(en) and $\Delta H^\circ_t(H^+)$ thus obtained and the enthalpies of formation of Hen$^+$ in the two solvents,[1)] the enthalpy of transfer of Hen$^+$ could also be estimated.

By the same procedure as described above the enthalpies of transfer of H_2gly^+ and H_2en^{2+} from water to the 0.2 mole fraction dioxane-water mixture were calculated, since the enthalpies of formation of these species in both solvents were known:

$$\Delta H^\circ_t(\mathrm{H_2L^{(q+2)+}}) = \Delta H^\circ_t(\mathrm{HL^{(q+1)+}}) + \Delta H^\circ_t(\mathrm{H^+}) + \Delta H^\circ_{\mathrm{H_2L}}(\mathrm{mix}) - \Delta H^\circ_{\mathrm{H_2L}}(\mathrm{w}), \tag{11}$$

where L denotes gly ($q=-1$) or en ($q=0$), and $\Delta H^\circ_{\mathrm{H_2L}}$(s) stands for the enthalpy of the second stepwise formation reaction, $H^+ + HL^{(q+1)+} = H_2L^{(q+2)+}$, in solvents. The value of $\Delta H^\circ_{\mathrm{H_2L}}$ for glycine was determined to be −5.5 and −10.3 kJ mol^{-1} in water and in the dioxane-water mixture, respectively.[16)] The values for ethylenediamine were reported previously.[1)] The enthalpies of transfer of glycinate ion and ethylenediamine and their protonated species, as well as the value for proton, from water to the dioxane-water mixture thus evaluated are summarized in Table 4.

The enthalpy of transfer of proton was −22.7 kJ mol^{-1}, which was close to that of sodium ion (−19.8 kJ mol^{-1}).

TABLE 4. ENTHALPIES OF TRANSFER (ΔH°_t) OF SINGLE SPECIES FROM WATER TO THE 0.2 mole FRACTION DIOXANE-WATER MIXTURE AT 25 °C

Species	ΔH°_t/kJ mol^{-1}	Species	ΔH°_t/kJ mol^{-1}
H^+	−22.7	$[Ni(gly)]^+$	−12.7
Ni^{2+}	−41.1	$[Ni(gly)_2]$	12.3
Cu^{2+}	−35.7	$[Ni(gly)_3]^-$	39.8
gly$^-$	28.7	$[Ni(en)]^{2+}$	−38.9
en	−0.3	$[Ni(en)_2]^{2+}$	−35.2
Hgly[a)]	1.2	$[Ni(en)_3]^{2+}$	−30.2
H_2gly^+	−26.3	$[Cu(en)]^{2+}$	−35.0
Hen$^+$	−20.0	$[Cu(en)_2]^{2+}$	−33.1
H_2en^{2+}	−41.7		

a) Zwitterion, $NH_3^+CH_2COO^-$.

The ΔH°_t value of ethylenediamine was practically zero. The ΔH°_t values of Hen$^+$ and H_2en^{2+} were −20.0 and −41.7 kJ mol^{-1}, respectively, the latter value being almost double of the former. These results suggest that the enthalpies of transfer of the protonated ethylenediamine species are mostly influenced by the change in the enthalpies of solvation of charged ammonio groups within the species.

The enthalpy of transfer of protonated glycine H_2gly^+, which has a charged ammonio group and a noncharged carboxyl group, was −26.3 kJ mol^{-1}, the value being slightly more negative than that of Hen$^+$. Glycinate ion involving an anionic carboxylato group and a neutral amino group gave a positive ΔH°_t value (28.7 kJ mol^{-1}).

The enthalpy of transfer of zwitterionic glycine was small (1.2 kJ mol^{-1}), which might be compared with that of ethylenediamine (−0.3 kJ mol^{-1}). In fact, the enthalpy of hydration of glycine zwitterion in water was estimated to be −243 kJ mol^{-1},[17)] which was considerably negative compared with those of noncharged molecules such as methylamine (−45.2 kJ mol^{-1}) and neutral acetic acid (−52.7 kJ mol^{-1}), although the value for the glycine zwitterion was less negative than those of H_2gly^+ (−365.4 kJ mol^{-1}) and gly$^-$ (−379.5 kJ mol^{-1}).[17)] The result suggests that the glycine zwitterion is strongly hydrated in water through both the ammonio and carboxylato groups. Two plausible interpretations for the small enthalpy of transfer of glycine from water to the dioxane-water mixture may be given: 1) hydration of a zwitterion is restricted to the vicinity of charged groups and is not appreciably changed when a part of water of the solvent is replaced with dioxane, 2) a large, negative enthalpy of transfer of an ammonio group is cancelled by a large, positive enthalpy of transfer of a carboxylato group within a zwitterionic glycine. Since the entropy of transfer of glycine between the two solvents is estimated to be −21 JK^{-1} mol^{-1},[16)] which is rather largely negative, the latter interpretation is more acceptable.

Neutral Bis(glycinato)nickel(II) Complex. Enthalpy of transfer of the neutral bis(glycinato)nickel(II) complex can be determined without the extrathermodynamic assumption. However, the solubility of the complex was too low in both water and the dioxane–water mixture to directly measure the heat of solution of the complex with a sufficient accuracy. Therefore, the complex salt was dissolved in each of the solvents containing sodium or lithium glycinate in which the neutral species was expected to be fully converted to the tris(glycinato)nickel(II) complex, and thus, the measured enthalpy at dissolution of the bis(glycinato)nickel(II) complex in the solvents was given as the sum of the enthalpy of solution (ΔH°_{s1}) of the complex and the enthalpy (ΔH°_3) of the reaction, $Ni(gly)_2+gly^-=Ni(gly)_3^-$, in the solvents. Since the latter was already known,[16] the former value was determinable.

The enthalpy of solution (ΔH°_{s2}) of the dihydrate salt $[Ni(gly)_2(H_2O)_2]$ was also determined by the same procedure as mentioned above in the two solvents. In a given solvent used, as is shown in Fig. 2, enthalpies of solution of the bis(glycinato)nickel(II) (ΔH°_{s1}) and diaquabis(glycinato)nickel(II) (ΔH°_{s2}) complexes are related to the enthalpy of reaction 12, ΔH°_h:

$$Ni(gly)_2(c) + 2H_2O(s) = Ni(gly)_2(H_2O)_2(c), \qquad (12)$$

where (c) and (s) denote the crystalline and solution states, respectively. The enthalpy values of ΔH°_{s1}, ΔH°_{s2}, and ΔH°_h thus obtained in water and in 0.2 mole fraction dioxane-water mixture are summarized in Table 5, together with the values of ΔH°_3 in the solvents.

The difference between the enthalpies of reaction 12 in water ($\Delta H^\circ_h(w)$) and in the 0.2 mole fraction dioxane-water mixture ($\Delta H^\circ_h(mix)$) is attributed to the enthalpy of transfer of two moles of water from water to the dioxane-water mixture:

$$\Delta H^\circ_h(w) - \Delta H^\circ_h(mix) = 2\Delta H^\circ_t(H_2O). \qquad (13)$$

The values of ΔH°_h were −60.0 and −58.8 kJ mol^{-1} in water and in the dioxane-water mixture, respectively,

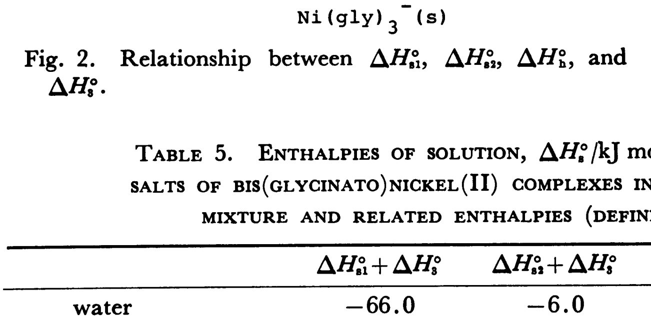

Fig. 2. Relationship between ΔH°_{s1}, ΔH°_{s2}, ΔH°_h, and ΔH°_3.

and thus, the $\Delta H^\circ_t(H_2O)$ value was estimated to be −0.6 kJ mol^{-1}. This result is consistent with the fact that the heat of mixing of water with dioxane is only slightly exothermic in a composition of water-rich.[18] The relatively small $\Delta H^\circ_t(H_2O)$ value suggested that the interaction energy between water molecues or between water and dioxane molecules in the dioxane-water mixture was not appreciably different from that between water molecules in water.

Since the interaction energies between solvent molecules in the two solvents are thus concluded to be similar, the difference in the enthalpies of transfer of ions and complexes in the two solvents should be ascribed to the different solvation energies of the species in the solvents.

Enthalpies of Transfer of Metal Complexes. By a similar way of evaluation of enthalpies of transfer of protonated glycine and ethylenediamine as described in the previous section, the enthalpies of transfer of glycinato and ethylenediamine complexes of nickel(II) ions and ethylenediamine complexes of copper(II) ions were determined. The enthalpies of formation of a complex ML_n (charge is omitted) pertaining to the reaction, $M+nL=ML_n$, in water ($\Delta H^\circ_{\beta n}(w)$) and in the 0.2 mole fraction dioxane-water mixture ($\Delta H^\circ_{\beta n}(mix)$) are related to the enthalpies of transfer of the free metal ion M, ligand L and the complex ML_n as follows:

$$\Delta H^\circ_{\beta n}(mix) - \Delta H^\circ_{\beta n}(w) = \Delta H^\circ_t(ML_n) - \Delta H^\circ_t(M) - n\Delta H^\circ_t(L). \qquad (14)$$

The enthalpies of formation of the (glycinato)nickel(II) complexes[16] and ethylenediamine complexes of nickel(II) and copper(II) ions[1,2] have been measured in both solvents. Since the enthalpies of transfer of free nickel(II), copper(II), and glycinate ions and ethylenediamine have been determined in the previous sections, the enthalpies of transfer of the relevant metal complexes can be evaluated by using Eq. 14. The ΔH°_t value for the $[Ni(gly)_2]$ complex thus evaluated was in accord with that obtained by the difference $\Delta H^\circ_{s1}(mix)-\Delta H^\circ_{s1}(w)$ in enthalpies of solution of the anhydrous bis(glycinato)nickel(II) complex salt in water and in the dioxane-water mixture. Enthalpies of transfer of the metal complexes thus obtained are summarized in Table 4, together with the enthalpies of transfer of the free metal ions and ligands.

It has been known that metal ions are preferentially solvated by water molecules in the first coordination sphere in dioxane-water mixtures of water-rich,[6,7] and thus the difference in the enthalpies of solvation of ions, as well as complexes whose first coordination shells are

TABLE 5. ENTHALPIES OF SOLUTION, ΔH°_s/kJ mol^{-1}, OF ANHYDROUS (ΔH°_{s1}) AND DIHYDRATE (ΔH°_{s2}) SALTS OF BIS(GLYCINATO)NICKEL(II) COMPLEXES IN WATER AND IN 0.2 mole FRACTION DIOXANE-WATER MIXTURE AND RELATED ENTHALPIES (DEFINITION OF WHICH IS GIVEN IN FIG. 2) AT 25 °C

	$\Delta H^\circ_{s1}+\Delta H^\circ_3$	$\Delta H^\circ_{s2}+\Delta H^\circ_3$	ΔH°_3 a)	ΔH°_{s1}	ΔH°_{s2}	ΔH°_h
water	−66.0	−6.0	−35.5	−30.5	29.5	−60.0
mixture	−55.4	3.4	−36.7	−18.7	40.1	−58.8
ΔH°_t(w→mix)	10.6	9.4	−1.2	11.8	10.6	1.2

a) Ref. 16.

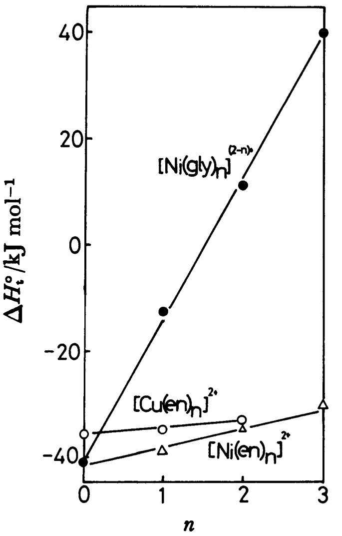

Fig. 3. Enthalpies of transfer of the (glycinato)nickel (II), (ethylenediamine)nickel(II) and (ethylenediamine)copper(II) complexes plotted against n, the number of ligands within the complexes.

filled with ligands, in water and the dioxane–water mixture should be caused by the change in solvation in the second and further solvation shells.

Plots of the ΔH°_t values of the [Ni(gly)$_n$]$^{(2-n)+}$, [Ni(en)$_n$]$^{2+}$, and [Cu(en)$_n$]$^{2+}$ complexes against n are shown in Fig. 3. They linearly increased with n for all the complexes, although the changes in ΔH°_t of the latter two were rather insensitive to n.

The ethylenediamine complexes of nickel(II) and copper(II) ions gave relatively large negative values of ΔH°_t. Since the first coordination shell of the metal ions within the complexes were occupied by ethylenediamine and/or water molecules, the result showed that solvation of the second coordination shell of the species was enhanced in the mixture than in water, although the enhancement may be less pronounced in a complex with a larger number of ethylenediamine coordinated to the metal ion.

In the case of the glycinato complexes of nickel(II) ions in which the charge of the complexes change from +2 (for Ni^{2+}) to −1 (for [Ni(gly)$_3$]$^-$), the ΔH°_t values of the complexes much more steeply increased with n than those of [Ni(en)$_n$]$^{2+}$ and [Cu(en)$_n$]$^{2+}$ did, the charge of these complexes being independent of n. Although the ΔH°_t value of the [Ni(gly)]$^+$ complex was still negative, the value was much less negative than the values of H$^+$ and Na$^+$. The ΔH°_t values for [Ni(gly)$_2$] and [Ni(gly)$_3$]$^-$ were positive, the latter being much larger than that of glycinate ion. The result indicated that the solvation structure of the second coordination shell of the [Ni(gly)$_2$] and [Ni(gly)$_3$]$^-$ complexes was partly destroyd in the dioxane–water mixture compared with that in water.

The linear relationship between ΔH°_t and n for the [Ni(gly)$_n$]$^{(2-n)+}$ complexes suggests that solvation of glycinate ions coordinated to the central nickel(II) ion is most responsible for the stabilization of the solvation structure of the second coordination shell of the complexes. In the [Ni(gly)$_n$]$^{(2-n)+}$ complexes, one of oxygen atoms within each carboxylato group of glycinate ions combines with the central metal ions, while the other oxygen atom of the carboxylato group faces to solvent molecules in the second coordination shell to interact each other. Since free glycinate ion has a positive value of ΔH°_t, the interaction between the latter glycinato-oxygen atom and solvent molecules in the second coordination shell may have a contribution to the ΔH°_t values of the complexes to make them more positive. The linear change in the ΔH°_t of the [Ni(gly)$_n$]$^{(2-n)+}$ complexes with n suggests that the interaction between the glycinato-oxygen atom and solvent molecules in the second coordination shell may proportionally change with the number of the oxygen atoms. The same trend can be seen for the ΔH°_t values of [Ni(en)$_n$]$^{2+}$ and [Cu(en)$_n$]$^{2+}$, although the change in the ΔH°_t values with n is much less pronounced compared with those of [Ni(gly)$_n$]$^{(2-n)+}$, probably due to the invariable charge of the former complexes and a relatively small ΔH°_t value of ethylenediamine.

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