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Potentiometric and Calorimetric Studies on the Formation of Ethylenediamine Complexes of Copper(II) Ion in Water and Aqueous Dioxane Solutions

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Gibbs energies (or formation constants), enthalpies and entropies of formation of ethylenediamine complexes of copper(II) ions have been determined by means of potentiometric and calorimetric titrations at 25 °C in an aqueous solution and dioxane-water mixtures (dioxane contents are 0.1 and 0.2 mole fractions, which correspond to 35.2 and 55.0% w/w, respectively), all containing 3 mol dm^{-3} LiClO$_4$ as a constant ionic medium. The thermodynamic quantities of the reactions CuL$_{n-1}^{2+}$+L=CuL$_n^{2+}$ (L=ethylenediamine and n=1 and 2) determined in the solutions were as follows: ΔG_1°=−65.0 kJ mol^{-1} (dioxane content: 0.0 mole fraction), −66.8 kJ mol^{-1} (0.1 mole fraction), and −68.8 kJ mol^{-1} (0.2 mole fraction); ΔG_2°=−56.9 kJ mol^{-1} (0.0), −58.8 kJ mol^{-1} (0.1), and −61.1 kJ mol^{-1} (0.2); ΔH_1°=−67.7 kJ mol^{-1} (0.0), −68.6 kJ mol^{-1} (0.1), and −66.7 kJ mol^{-1} (0.2); ΔH_2°=−71.0 kJ mol^{-1} (0.0), −70.2 kJ mol^{-1} (0.1), and −68.8 kJ mol^{-1} (0.2); $T\Delta S_1^\circ$=−2.7 kJ mol^{-1} (0.0), −1.8 kJ mol^{-1} (0.1), and 2.1 kJ mol^{-1} (0.2); $T\Delta S_2^\circ$=−14.1 kJ mol^{-1} (0.0), −11.4 kJ mol^{-1} (0.1), and −7.7 kJ mol^{-1} (0.2). In any solvent examined the enthalpies contribute predominantly to the Gibbs energies. On the other hand, for a given complex with varying solvent compositions, the entropies mainly contribute to the change in the Gibbs energies of the complex formation reactions. With an increase in the dioxane content of the solvent, the Gibbs energies of the complex formation reactions become more negative, while the enthalpies of the reactions remain practically unchanged or even become less negative. Consequently, the entropies of the reactions increase with increasing dioxane content of the solvent, which is explained in terms of weakening of the hydrogen-bonded structure of water in the bulk solvent by the addition of dioxane.

In a previous paper,1) we reported the solvent effect on the formation of ethylenediamine complexes of nickel(II) ions in an aqueous solution and in aqueous dioxane mixtures. The formation constants of the NiL^{2+}, NiL$_2^{2+}$, and NiL$_3^{2+}$ complexes (L denotes ethylenediamine) increased with increasing dioxane content of the solvent, and the increment of the formation constants with varying solvent compositions was almost independent of the species. The solvent effect on the formation constants of the complexes was attributed mainly to the increase in the entropies of formation of the complexes. Enthalpies of the complex formation reactions became less negative at each stepwise reaction with the increase in the dioxane concentration in the solvents. The results have been explained in terms of the change in the hydrogen-bonded structure of water in the bulk solvent by the addition of dioxane.1−3)

In the present study, we employed copper(II) ions in order to further examine solvent effects on the complex formation reaction of metal ions with neutral ligands in which the charges of the complexes remain unchanged in the course of the complex formation reaction. Ethylenediamine was used as the neutral ligand, as was demonstrated in the previous work.1)

Experimental

Reagents. Copper(II) perchlorate was prepared from copper(II) oxide and perchloric acid of reagent grade. The copper(II) perchlorate thus prepared was recrystallized three times from water. A small amount of perchloric acid was added to the copper(II) perchlorate stock solution and pH of the stock solution was kept about 3. The concentration of free acid was determined coulometrically. The total concentration of copper(II) ions in the stock solution was determined electrogravimetrically.

Other chemicals used were prepared by the same methods as described previously.1,4)

Method of Measurements and Analysis of Data. All potentiometric and calorimetric titrations were performed at 25 °C in a constant ionic medium of 3 mol dm^{-3} LiClO$_4$. The experimental method and the procedure of data analysis were described previously.1)

Results and Discussion

Over the range of −log ([H$^+$]/mol dm^{-3}) from 3 to 10 in all the solvents examined, potentiometric titration curves of the copper(II)-ethylenediamine system could be well explained by assuming the formation of two mononuclear CuL^{2+} and CuL$_2^{2+}$ complexes. The tris(ethylenediamine)copper(II) complex was not appreciably formed under the present experimental conditions. Typical titration curves obtained in the aqueous solution are shown in Fig. 1, where −log([H$^+$]/mol dm^{-3}) values measured are plotted against X, the degree of neutralization of ethylenediammonium ions in the solution. The experimental points fitted well curves calculated (X_{calcd}) by using Eq. 1 over the whole range of the −log([H$^+$]/mol dm^{-3}) values examined.

$$X_{\text{calcd}} = (2C_\text{L} - [\text{H}^+] + K_\text{W}[\text{H}^+]^{-1} - K_2{}^{-1}[\text{H}^+][\text{L}] - 2K_1{}^{-1}K_2{}^{-1}[\text{H}^+]^2[\text{L}])/C_\text{L}, \quad (1)$$

where K_1 and K_2 denote the dissociation constants of H$_2$L^{2+} and HL$^+$ ions, respectively. K_W represents the autoprotolysis constant of the solvent. Concentrations of free hydrogen ions and ethylenediamine molecules were calculated by using Eqs. 2 to 4.

$$C_\text{M} = [\text{Cu}^{2+}] + \beta_1[\text{Cu}^{2+}][\text{L}] + \beta_2[\text{Cu}^{2+}][\text{L}]^2, \quad (2)$$

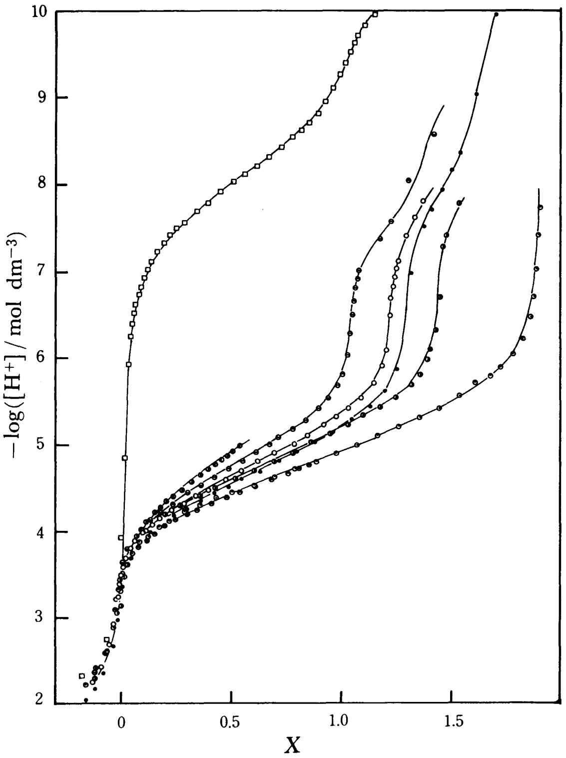

Fig. 1. Potentiometric titration curve of ethylenediamine and copper(II)-ethylenediamine aqueous solutions.

Curve □: C_M(mmol dm^{-3})=0.0, C_L(mmol dm^{-3})= 58.47; ○: 14.10, 45.75; ⊙: 16.53, 35.11; ⊖: 9.853, 37.46; ⊕: 22.96, 49.57; ●: 19.69, 61.06; ◑: 14.09, 38.57: ⦶: 12.49, 59.60.

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.

$$C_L = [L] + K_2^{-1}[H^+][L] + K_1^{-1}K_2^{-1}[H^+]^2[L] + \beta_1[Cu^{2+}][L] + 2\beta_2[Cu^{2+}][L]^2, \tag{3}$$

$$C_H = [H^+] - K_W[H^+]^{-1} + K_2^{-1}[H^+][L] + 2K_1^{-1}K_2^{-1}[H^+]^2[L]. \tag{4}$$

Here C_i denotes the total concentration of species i. β_1 and β_2 represent the overall formation constants of CuL^{2+} and $CuL_2{}^{2+}$, respectively. The values were optimized by using the least-squares method for searching the minimum error-square sum $U=\sum\{(C_M-C_{M,calcd})^2+(C_L-C_{L,calcd})^2+(C_H-C_{H,calcd})^2\}$, the program MINIQUAD[5] being employed for the calculation. The final values for the overall formation constants of the complexes are listed in Table 1.

In Fig. 2 typical results for the calorimetric titrations of aqueous copper(II)-ethylenediamine solutions are depicted, where heats evolved q_i at the addition of the i-th portion of a titrant are plotted against the average number $\bar{n}$ of ethylenediamine molecules bound per copper(II) ion in the solution. The solid lines are drawn by using the enthalpy values finally obtained with the aid of the least-squares program KALORI.[6] The results obtained are tabulated in Table 2.

Table 1. The formation constants, β_n, for the reactions, $Cu^{2+}+nL=CuL_n{}^{2+}$; $\beta_n=[CuL^{2+}]/[Cu^{2+}][L]^n$ (L=en) in aqueous dioxane 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_1	CuL^{2+}	11.38(0.04)	11.70(0.04)	12.05(0.04)
log β_2	$CuL_2{}^{2+}$	21.35(0.09)	22.00(0.09)	22.76(0.09)

Values in parentheses refer to 3σ where σ denotes the standard deviation.

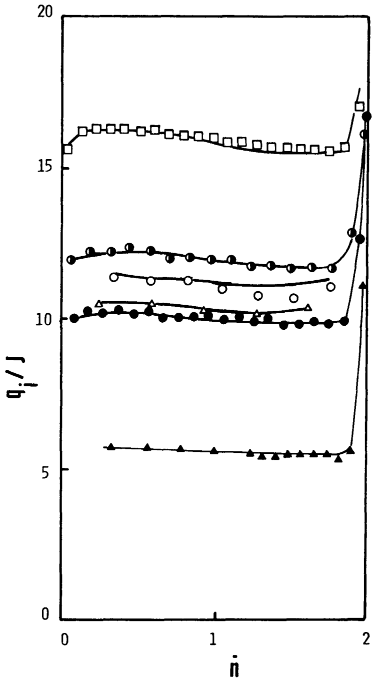

Fig. 2. Calorimetric titration curves of copper(II)-ethylenediamine aqueous solution.

Curve ▲: C_M(mmol dm^{-3})=8.0, C_L(mmol dm^{-3})=24.2; △: 3.6, 15.4; ○: 5.8, 18.6; ●: 9.6, 29.8; ◑: 10.9, 31.2; □: 19.6, 48.6.

The solid lines show calculated curve by using the constants in Table 2.

Table 2. The enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, for the reactions, $Cu^{2+}+nL=CuL_n{}^{2+}$ (L=en) in aqueous dioxane 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)
ΔH_{β_1}	CuL^{2+}	−67.7(0.4)	−68.6(0.4)	−66.7(0.5)
ΔH_{β_2}	$CuL_2{}^{2+}$	−138.7(0.4)	−138.8(0.5)	−135.5(0.6)

Values in parentheses refer to 3σ where σ denotes the standard deviation.

The thermodynamic quantities, ΔG°_n, ΔH°_n, and ΔS°_n for each successive complex formation reaction, $CuL_{n-1}{}^{2+}+L=CuL_n{}^{2+}$ (n=1 and 2) are summarized in Table 3.

TABLE 3. THE THERMODYNAMIC PARAMETERS, ΔG_n°, ΔH_n°/kJ mol^{-1} AND ΔS_n°/J K^{-1} mol^{-1}, FOR THE SUCCESSIVE REACTIONS, $CuL_{n-1}^{2+}+L=CuL_n^{2+}$, IN AQUEOUS DIOXANE CONTAINING 3 mol dm^{-3} $LiClO_4$ AT 25 °C

	Concentration of dioxane/mole fraction		
	0.0 (0.0%w/w)	0.1 (35.2%w/w)	0.2 (55.0%w/w)
$-\Delta G_1^\circ$	65.0	66.8	68.8
$-\Delta G_2^\circ$	56.9	58.8	61.1
$-\Delta H_1^\circ$	67.7	68.6	66.7
$-\Delta H_2^\circ$	71.0	70.2	68.8
ΔS_1°	−9.1	−6.0	7.1
ΔS_2°	−47.3	−38.3	−25.8

Aqueous Solution. Since the stepwise formation constants of the mono- and bis(ethylenediamine)copper(II) complexes decrease with the ligand number within the complexes, the Gibbs energies of the first complex is more negative than the second one. However, the stepwise enthalpy of formation of the mono(ethylenediamine)copper(II) complex is less negative than that of the bis-complex. Therefore, the stepwise entropy of formation of the former complex is larger than that of the latter, although the values are both negative (see Table 3). Thus, $\Delta G_1^\circ<\Delta G_2^\circ$, $\Delta H_1^\circ>\Delta H_2^\circ$ and $\Delta S_1^\circ>\Delta S_2^\circ$. Similar trends in the variations of ΔG_n°, ΔH_n° and ΔS_n° have been observed in the formation of nickel(II)-ethylenediamine complexes.[1)]

It may be generally accepted that metal-water bonds within an aquametal ion weaken when a part of water molecules within the aquametal ion are replaced with a ligand which has an atom or atoms with a stronger donor property than water.[7)] Thus, we can expect that the Cu-OH_2 bonds within the mono(ethylenediamine)copper(II) complex is weaker than those within the aquacopper(II) ion. Therefore, when we introduce the second ethylenediamine molecule to the mono(ethylenediamine)copper(II) complex, an energy (enthalpy) to expell two water molecules from the coordination sphere of the mono-complex may be less than that of the aquacopper(II) ion. Consequently, the stepwise enthalpy of formation of the CuL_2^{2+} complex becomes more negative than that of the CuL^{2+} complex. On the contrary, when water molecules within the mono(ethylenediamine)copper(II) complex in which the water molecules combine relatively weakly with the metal ion are removed from the coordination sphere, a less entropy gain may be resulted compared with that for releasing water molecules from the aquacopper(II) ion. The negative values of the entropies of formation of the CuL^{2+} and CuL_2^{2+} complexes indicate that the complex formation is accompanied by the loss of entropy due to the combination of ethylenediamine molecules with the copper(II) ion and also to the recombination of dehydrating water molecules from the metal ion with those in the bulk solvent by the formation of hydrogen bonds.

The Solvent Effect on the Complex Formation. The Gibbs energies of formation of each complex became more negative with increasing dioxane content of the solvent. The decrease in the Gibbs energy of a given complex with varying solvent compositions is attributable to the increase in the entropy of formation of the complex, the enthalpy contributing to the Gibbs energy less favorably with the solvent effect.

As has been pointed out in the previous paper,[1)] the secondary solvation of the both aquametal ion and metal-ethylenediamine complexes is enhanced in dioxane-water mixture and the degree of enhancement of the solvation is larger in the aquametal ion than in the metal-ethylenediamine complexes. Moreover, the enhancement become less significant within a complex with a larger number of the ethylenediamine molecules coordinated to the metal ion.

Although we have no experimental data for the enthalpy of transfer of copper(II) ions from water to a dioxane-water mixture and, therefore, we cannot calculate the enthalpies of transfer of each complex between the two solvents, we can expect that the secondary solvation of the aquacopper(II) ion is enhanced more strongly than that of a copper(II)-ethylenediamine complex in a given solvent mixture. Consequently, the formation of the copper(II)-ethylenediamine complexes becomes less favorable in the enthalpic point of view in a solvent with a larger dioxane content.

On the other hand, water molecules liberated from the coordination sphere of a complex can behave more freely in a dioxane-water mixture in which the hydrogen-bonded structure of water is partially destroyed. Therefore, the increase in the entropy of any copper(II)-ethylenediamine complex in a dioxane-water mixture is attributable mainly to an entropy gain of water liberated.

Such trends in the changes of the Gibbs energies, enthalpies and entropies of formation of complexes have also been observed in the nickel(II)-ethylenediamine system.[1)]

The decrements of the Gibbs energies of formation of the copper(II)-ethylenediamine complexes with varying dioxane contents in the solvent are practically the same as those of the nickel(II)-ethylenediamine ones. Moreover, the changes are essentially independent of the number of ethylenediamine molecules coordinated. Such results are predictable from a simple Born equation by assuming the same ionic radii of the CuL_n^{2+} and NiL_n^{2+} ions. However, it should be noted that the increments of the both enthalpy and entropy of formation of each copper(II)-ethylenediamine complex are smaller than those of the corresponding nickel(II)-ethylenediamine ones (2.5 kJ mol^{-1} and 4.0 kJ mol^{-1} for the enthalpies of NiL^{2+} and NiL_2^{2+} complexes, respectively, at the transfer from water to the aqueous dioxane of 0.2 mole fraction dioxane content and 21.1 J K^{-1} mol $^{-1}$ and 26.6 J K^{-1} mol^{-1} for the corresponding entropies of the respective species). The reason why the solvent effects on the enthalpies and entropies of formation of the CuL_n^{2+} complexes are smaller than those of the NiL_n^{2+} ones is not clear at the present stage.

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