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Thermodynamic Quantities of Transfer of Glycinato and β-Alaninato Complexes of Silver(I) and Related Species from Water to an Aqueous Dioxane Solution

Shin-ichi Ishiguro, Honoh Suzuki, Masayuki Zama, Arup K. Basak,† and Hitoshi Ohtaki*
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, 4259,
Nagatsuta-cho, Midori-ku, Yokohama 227

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Complexation of silver(I) with glycinate (gly$^-$) and β-alaninate (β-ala$^-$) ions have been studied by potentiometry and calorimetry in 0.2 mole fraction (55.0 %w/w) dioxane-water mixture containing 3 mol dm^{-3} LiClO$_4$ as a constant ionic medium at 25 °C. Potentiometric titration curves obtained were well-explained in terms of formation of [AgL], [AgL$_2$]$^-$, and [AgHL]$^+$ (L$^-$=gly$^-$ or β-ala$^-$) in both systems, together with [Ag(OH)L]$^-$ in the Ag(I)-β-alanine system, and their formation constants were determined. Enthalpies of formation of the complexes in the mixed solvent, as well as in water containing the same ionic medium, were calorimetrically determined on the basis of the formation constants potentiometrically determined. Solubilities and enthalpies of solution of the neutral [AgL] (L$^-$=gly$^-$ and β-ala$^-$) complexes and some related compounds were determined in water and the mixture, the Gibbs energies of transfer, ΔG°_t, of silver(I) ion and proton from water to the mixture being also determined by potentiometry. By combining the thermodynamic quantities thus obtained, thermodynamic quantities of transfer of single species from water to the mixture were evaluated. Compared to the enthalpy, ΔH°_t, and entropy, ΔS°_t, of transfer of a neutral species, the ΔH°_t and ΔS°_t values of any charged species were significantly large with the negative sign for cations and positive one for anions. As to neutral species, [HL] and [AgL], the relation, $\Delta G^\circ_t > \Delta H^\circ_t \cong 0$ and $\Delta S^\circ_t < 0$, was found, suggesting that the [AgL] complexes have a similar zwitterionic structure to that of glycine and β-alanine zwitterions.

Complex formation equilibria between silver(I) ion and amino acids have so far been studied in water.[1] In a previous paper,[2] we also reported the formation of glycinato (gly$^-$) and β-alaninato (β-ala$^-$) complexes of Ag(I) in water, and suggested that the metal ion was coordinated with the amino nitrogen atom within [AgL] and [AgL$_2$]$^-$ (L$^-$=gly$^-$ and β-ala$^-$) but with the carboxylato oxygen atom within [AgHL]$^+$.

In water-rich dioxane-water mixtures, although metal ions and ligands are expected to be preferentially solvated with water, complexation in some metal-ligand systems, such as nickel(II)-ethylenediamine,[3] nickel(II)-glycinate[4] and copper(II)-ethylenediamine systems,[5] are appreciably different from those in water, due perhaps to a partially destroyed hydrogen-bonding structure of bulk water in the mixture compared to that in water.

Silver(I) ion which tends to have a linear coordination structure with ligands may show a different solvent effect on complexation from that of the bivalent transition metal ions having an octahedral coordination structure.

In this work, therefore, we investigated the complexation of silver(I) ion with glycinate and β-alaninate ions by potentiometry and calorimetry in water and in 0.2 mole fraction dioxane-water mixture, and solvent effects on the thermodynamic quantities of formation of the metal complexes in these solvents are discussed. Solubilities and enthalpies of solution of the [AgL] (L$^-$=gly$^-$ and β-ala$^-$) complexes and some related compounds were also determined in these solvents. The Gibbs energies of transfer of Ag$^+$ and H$^+$ from water to various dioxane-water mixtures were potentiometrically determined. By combining the thermodynamic quantities thus obtained, thermodynamic quantities of transfer of single species from water to the 0.2 mole fraction dioxane-water mixture were evaluated.

Experimental

Reagents. All chemicals used were of reagent grade. *Lithium glycinate* and *lithium β-alaninate* were prepared by mixing equimolar amounts of glycine or β-alanine and lithium hydroxide in methanol and recrystallized twice from methanol, and then dried at 100 °C in a vacuum oven. *Sodium β-alaninate* was prepared with sodium methoxide by a similar procedure to that used for lithium β-alaninate. *Silver(I) glycinate* and *silver(I) β-alaninate* were prepared by dissolving silver(I) nitrate in aqueous glycine or β-alanine solution, and then by adding sodium hydroxide in the solution. The silver(I) glycinate and silver(I) β-alaninate crystals thus prepared were filtered, washed with methanol and ether, and then dried in vacuum in a dark desiccator at room temperature.

Other chemicals were prepared and purified as described elsewhere.[2,6,7]

Measurements. Potentiometric and calorimetric measurements were carried out in a room thermostated at (25.0±0.2) °C. All test solutions prepared for the measurements contained 3 mol dm^{-3} LiClO$_4$ as a constant ionic medium.

Formation constants were determined by potentiometric measurements which were carried out in a liquid paraffin bath controlled at (25.00±0.02) °C. A test solution containing metal, ligand and hydrogen ions was titrated with a lithium hydroxide solution, and pH of the test solution was determined by using a glass electrode in combination with an Ag-AgCl electrode as a reference. The method of measurements was the same as that described in previous papers.[2–7]

Enthalpies of complexation were calorimetrically determined by measuring in a water bath thermostated at

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†Present address: Department of Chemistry, Texas A & M University, Colledge Station, Texas 77840, U.S.A.

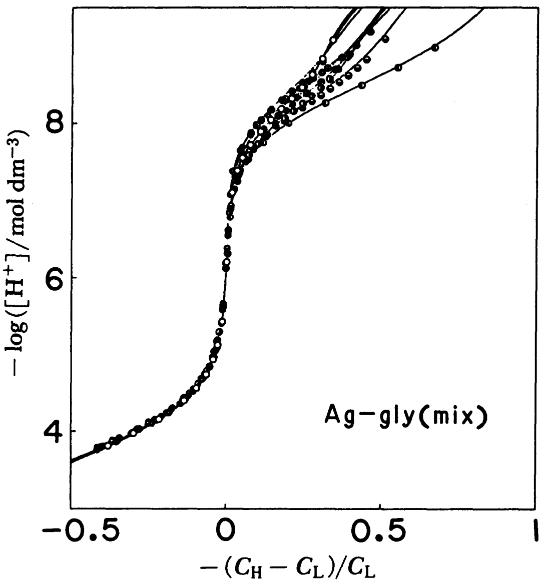

Fig. 1. Potentiometric titration curves for the silver(I)-glycinate system in the 0.2 mole fraction dioxane-water mixture. Initial concentrations of the metal and ligand ions, C_M/mmol dm^{-3} and C_L/mmol dm^{-3}: 2.385, 10.10 (⊙); 2.387, 13.99 (●); 2.926, 13.44 (◉); 3.763, 17.29 (⊕); 3.773, 23.94 (○); 4.741, 18.14 (◒); 5.611, 26.90 (◑); 5.626, 37.25 (◎); 5.801, 11.08 (◐).
The concentrations of the metal and ligand ions were changed by dilution during the titrations. The solid lines show the curves calculated by using the constants in Table 1.

(25.000±0.007) °C. An initial test solution contained silver(I) and ligand ions, and hydrogen ions of relatively low concentration, and was titrated with a perchloric acid solution. Details of measurements were described elsewhere.[3–5,8,9]

The Gibbs energies of transfer of silver(I) ion and proton from water to dioxane-water mixtures were potentiometrically determined by using an Ag-AgCl and a glass electrodes, respectively, in combination with an Ag-AgCl electrode as a reference, and the total concentrations of the relevant ions were kept constant with varying solvent composition in a test solution.

Solubilities of the mono(glycinato)- and mono(β-alaninato)silver(I) complexes were determined in water and in the 0.2 mole fraction dioxane-water mixture, each solution containing 3 mol dm^{-3} $LiClO_4$ and a small amount of glycine or β-alanine in order to prevent hydrolysis of the metal ion, after the solution was equilibrated for more than two weeks in a thermostated room at (25.0±0.2) °C. Concentrations of silver(I) ion in these solution at equilibrium were gravimetrically determined as AgCl. Net concentrations of the [AgL] (L^-=gly$^-$ and β-ala$^-$) complexes in the solutions were calculated by taking into account the distribution of the glycinato and β-alaninato complexes of silver(I) in each solvent.

Enthalpies of solution of the mono(glycinato)- and mono(β-alaninato)silver(I) complexes and related species were measured by dissolving a given amount of crystals of the relevant species in water and in the mixture, each containing 3 mol dm^{-3} $LiClO_4$. Procedures of the measurements and analysis of data were described in a previous paper.[9]

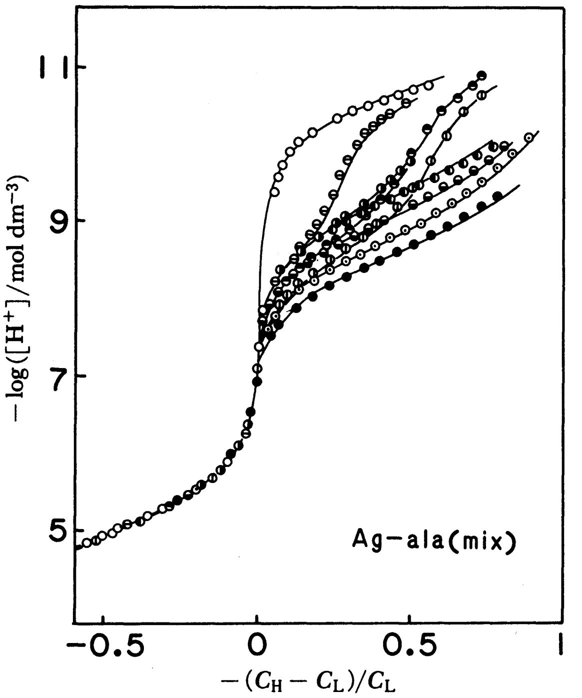

Fig. 2. Potentiometric titration curves for the silver(I)-β-alaninate system in the 0.2 mole fraction dioxane-water mixture. Initial concentrations of the metal and ligand ions, C_M/mmol dm^{-3} and C_L/mmol dm^{-3}: 0.0, 10.03 (○); 2.559, 5.246 (◐); 2.559, 10.12 (◑); 2.559, 20.15 (⊖); 4.997, 10.12 (◓); 4.997, 20.15 (◒); 4.997, 40.90 (⦶); 10.07, 20.15 (⊙); 10.07, 40.90 (●).
The concentrations of the metal and ligand ions were changed by dilution during the titrations. The solid lines show the curves calculated by using the constants in Table 1.

Determination of Formation Constants and Enthalpies. In advance of determining formation constants and enthalpies of complexation of metal ion with ligands, protonation constants and enthalpies of protonation of each ligand had been determined by potentiometry and calorimetry, respectively. The thermodynamic quantities thus obtained were kept constant in the course of the analysis of the formation constants and enthalpies of formation of the glycinato and β-alaninato complexes of Ag(I). Details of the analysis of potentiometric and calorimetric data were described previously.[3–5]

Results and Discussion

Potentiometric titration curves obtained for silver(I) glycinate and β-alaninate systems in the 0.2 mole fraction dioxane-water mixture are depicted in Figs. 1 and 2, respectively. The potentiometric data were first analyzed by the same graphical procedure as that used in a previous work.[2] For both systems, the graphical analysis indicated the formation of [AgL], $[AgL_2]^-$, and $[AgHL]^+$ over the pH range 3—10. In the silver(I)-β-alaninate system, the formation of $[Ag(OH)L]^-$ was also indicated at pH>8. Formation constants of these complexes were refined by the least-squares method, the

Table 1. The Least-Squares Refinements of Overall Formation Constants, $\log\beta_{pqr}$, of the $[Ag_pH_qL_r]^{(p+q-r)+}$ (L^-=gly$^-$ or β-ala$^-$) Complexes in the 0.2 Mole Fraction Dioxane–Water Mixture Containing 3 mol dm^{-3} $LiClO_4$ as a Constant Ionic Medium at 25 °C

$\beta_{pqr}=[Ag_pH_qL_r^{(p+q-r)+}]/[Ag^+]^p[H^+]^q[L^-]^r$

	Species	Glycinate	β-Alaninate
$\log\beta_{011}$	[HL]$^{a)}$	10.22$^{b)}$	10.86(0.03)
$\log\beta_{021}$	$[H_2L]^+$	13.81$^{b)}$	15.84(0.03)
$\log\beta_{111}$	$[AgHL]^+$	10.93(0.04)	11.63(0.03)
$\log\beta_{101}$	[AgL]	3.77(0.01)	4.02(0.22)
$\log\beta_{102}$	$[AgL_2]^-$	7.76(0.01)	8.31(0.03)
$\log\beta_{1-11}$	$[Ag(OH)L]^-$	—	−6.97(0.3)

Values in parentheses refer to 3σ where σ denotes a standard deviation. a) Zwitterion: $^+H_3NCH_2COO^-$ or $^+H_3NCH_2CH_2COO^-$. b) Ref. 4.

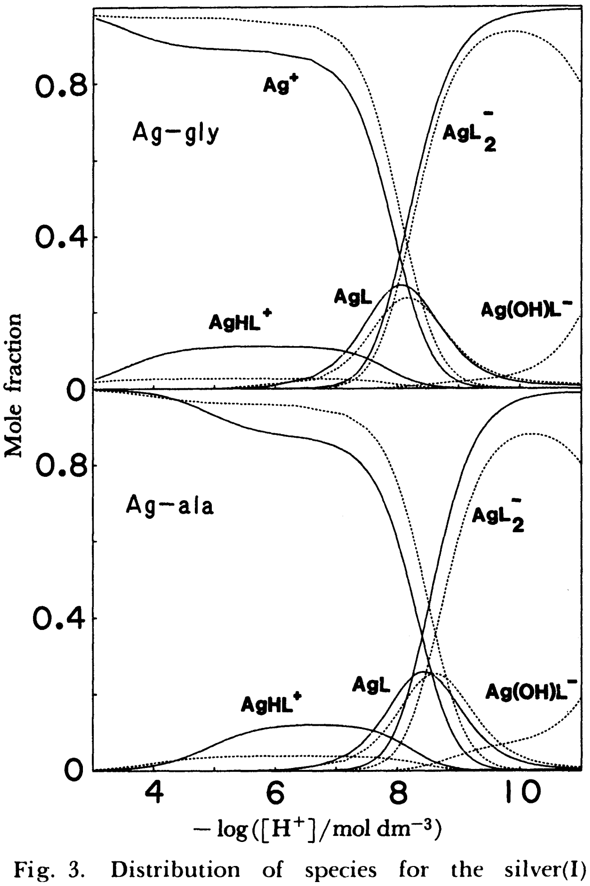

Fig. 3. Distribution of species for the silver(I) glycinate and β-alaninate systems in the 0.2 mole fraction dioxane–water mixture (the solid lines) and in water (the broken lines), both solutions containing 5 and 25 mmol dm^{-3} of silver and ligand ions, respectively, in each system.

results being summarized in Table 1, together with the protonation constants of the ligands. As seen in Figs. 1 and 2 by the solid lines, the theoretical titration curves calculated by using the formation constants in Table 1 well fitted the experimental points over the whole pH range examined in each metal-ligand system. The distribution of species of the silver(I) glycinate and β-alaninate systems in the mixture is shown in Fig. 3.

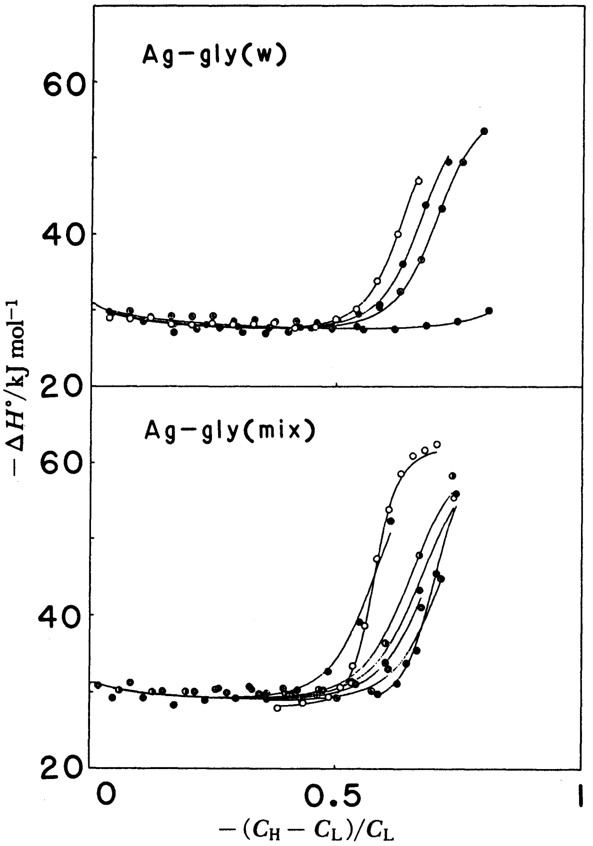

Fig. 4. Calorimetric titration curves of the silver(I)-glycinate system in water and in the 0.2 mole fraction dioxane–water mixture. Initial concentrations of the metal and ligand ions, C_M/mmol dm^{-3} and C_L/mmol dm^{-3}: 15.57, 31.81 (◎); 15.28, 43.09 (⊙); 14.77, 43.46 (●) and 15.21, 47.44 (○) in water and 5.098, 14.64 (⊕); 5.019, 14.91 (◑); 5.476, 15.40 (◉); 4.779, 15.98 (◎); 6.355, 17.18 (⊙); 12.56, 35.21 (●) and 16.41, 56.09 (○) in the mixture.
The solid lines show the calculated curves obtained by using the constants in Tables 1 and 2.

Calorimetric titration curves obtained for the silver(I) glycinate and β-alaninate systems are depicted in Figs. 4 and 5, respectively. Enthalpies $-\Delta H°/\mathrm{kJ\,mol^{-1}}$ $(=q/(\delta v C_{H,tit})$, where q and δv denote the heat evolved and the volume of an aliquot of the titrant added, respectively, at each titration point and $C_{H,tit}$ stands for the concentration of $HClO_4$ in the titrant solution) were plotted against the degree of neutralization X $(=-(C_H-C_L)/C_L$, where C_L and C_H denote the total concentration of glycine or β-alanine and hydrogen ion, respectively) of ligand in a solution. The calorimetric data in water were analyzed by using the formation constants of the complexes determined in a previous work.[2)]

As seen in Fig. 3, the formation of $[AgHL]^+$ is weak, so that the enthalpy of formation of the complex was not determined with a sufficient accuracy in each system. The enthalpy of formation of $[Ag(OH)L]^-$ was not also obtained with a reasonable reliability under the present experimental conditions.

The enthalpies of protonation of glycinate and β-alaninate ions and of complex formation of Ag(I) with glycinate and β-alaninate ions in water (w) and in the 0.2 mole fraction dioxane-water mixture (mix) obtained by the least-squares method are summarized in Table 2. The theoretical titration curves calculated by using the formation constants and enthalpies of complexes in Tables 1 and 2 are drawn by the solid lines in Figs. 4 and 5, respectively, which well reproduced the experimental points in each system.

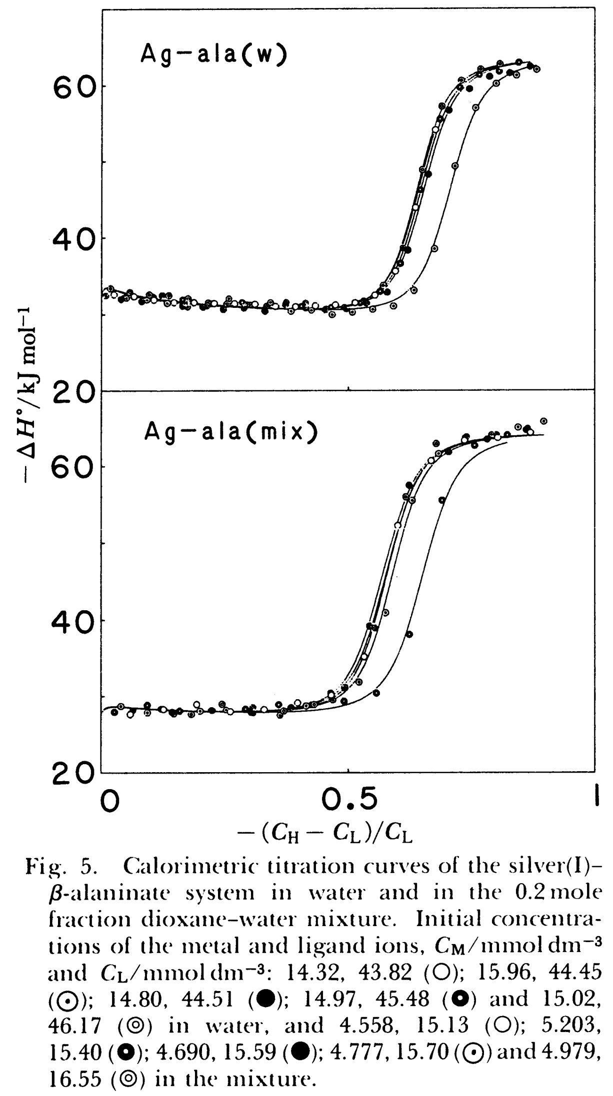

Fig. 5. Calorimetric titration curves of the silver(I)–β-alaninate system in water and in the 0.2 mole fraction dioxane–water mixture. Initial concentrations of the metal and ligand ions, C_M/mmol dm^{-3} and C_L/mmol dm^{-3}: 14.32, 43.82 (○); 15.96, 44.45 (⊙); 14.80, 44.51 (●); 14.97, 45.48 (◉) and 15.02, 46.17 (◎) in water, and 4.558, 15.13 (○); 5.203, 15.40 (◉); 4.690, 15.59 (●); 4.777, 15.70 (⊙) and 4.979, 16.55 (◎) in the mixture.
The solid lines show the calculated curves obtained by using the constants in Tables 1 and 2.

Thermodynamic quantities, $\log(K_n/\mathrm{mol^{-1}\,dm^3})$, $\Delta G_n^\circ/\mathrm{kJ\,mol^{-1}}$, $\Delta H_n^\circ/\mathrm{kJ\,mol^{-1}}$ and $\Delta S_n^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the stepwise formation of $[\mathrm{H}_n\mathrm{L}]^{(n-1)+}$ (L$^-$=β-ala$^-$) and $[\mathrm{AgL}_n]^{(1-n)+}$ (L$^-$=gly$^-$ and β-ala$^-$) are listed in Table 3, together with the difference, $P_n(\mathrm{mix})-P_n(\mathrm{w})$ (P=log K, ΔG°, ΔH°, and ΔS°), between the relevant quantities in water and in the mixture.

Gibbs Energies and Enthalpies of Transfer of Proton, and Silver(I), Glycinate and β-Alaninate Ions from Water to the 0.2 Mole Fraction Dioxane-Water Mixture. Changes in activities of proton and silver(I) ion in dioxane-water mixtures relative to those in water were determined by measuring emfs of a cell constructed with a glass and an Ag–AgCl electrodes in combination with an Ag–AgCl electrode as a reference, in which the total concentrations of relevant ions were kept constant with varying solvent composition. In each case of proton and silver(I) ion, the difference in emfs, $\Delta E=E(\mathrm{mix})-E(\mathrm{w})$, was obtained as a function of the concentration of dioxane in the mixtures, the result being shown in Fig. 6. As seen in Fig. 6, the ΔE values were independent of the concentrations of relevant ions, but depended on the solvent composition. Thus, ΔE is represented by Eq. 1:

$$\Delta E = (RT/F)\ln\{y(\mathrm{mix})/y(\mathrm{w})\} + \{E_\mathrm{j}(\mathrm{mix}) - E_\mathrm{j}(\mathrm{w})\}, \quad (1)$$

where y and E_j stand for the activity coefficient and the liquid junction potential of a species at the interface between a test solution and a salt bridge (an aqueous solution or 0.2 mole fraction dioxane-water mixture containing 3 mol dm^{-3} LiClO$_4$ as an ionic medium) and F denotes the Faraday constant. Since the difference in emfs was not influenced by the change of the composition of the salt bridge, the term $\{E_j(\mathrm{mix})-E_j(\mathrm{w})\}$ should be negligibly small. In these measurements, therefore, the ΔE values observed for proton and silver(I) ion could be attributed to the Gibbs energy of transfer of a relevant ion from water to the mixture:

$$\Delta G_\mathrm{t}^\circ = RT\ln\{y(\mathrm{mix})/y(\mathrm{w})\} = F\Delta E. \quad (2)$$

The $\Delta G_\mathrm{t}^\circ$ values of proton and silver(I) ion from water to the 0.2 mole fraction dioxane-water mixture were thus obtained to be 1.9 and 3.1 kJ mol^{-1}, respectively.

Solubilities of the mono(glycinato)- and mono(β-

Table 2. The Least-Squares Refinements of Overall Enthalpies, $\Delta H_{\beta pqr}^\circ$/kJ mol^{-1}, of Formation of $[\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r]^{(p+q-r)+}$ (L$^-$=gly$^-$ or β-ala$^-$) in Water(w) and in the 0.2 Mole Fraction Dioxane-Water Mixture (mix), Each Solution Containing 3 mol dm^{-3} LiClO$_4$ as a Constant Ionic Medium at 25 °C

	Species	Gly$^-$(w)	Gly$^-$(mix)	β-Ala$^-$(w)	β-Ala$^-$(mix)
$\Delta H_{\beta 011}^\circ$	[HL]$^{a)}$	−57.9$^{b)}$	−62.7$^{b)}$	−63.8(0.5)	−64.5(0.3)
$\Delta H_{\beta 021}^\circ$	$[\mathrm{H_2L}]^+$	−63.4$^{b)}$	−73.0$^{b)}$	−73.0(0.5)	−78.8(0.4)
$\Delta H_{\beta 101}^\circ$	[AgL]	−25.7(1.1)	−30.3(1.6)	−28.2(0.8)	−34.5(1.4)
$\Delta H_{\beta 102}^\circ$	$[\mathrm{AgL_2}]^-$	−62.2(0.5)	−69.4(0.8)	−67.1(0.4)	−74.6(0.7)

Values in parentheses refer to 3σ where σ denotes a standard deviation. a) Zwitterion: $^+\mathrm{H_3NCH_2COO^-}$ or $^+\mathrm{H_3NCH_2CH_2COO^-}$. b) Ref. 4.

Table 3. Thermodynamic Quantities, $\log(K_n/\mathrm{mol^{-1}\,dm^3})$, $\Delta G_n^\circ/\mathrm{kJ\,mol^{-1}}$, $\Delta H_n^\circ/\mathrm{kJ\,mol^{-1}}$, and $\Delta S_n^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the Stepwise Formation of $[H_nL]^{(n-1)+}$ (L^-=β-ala$^-$) and $[AgL_n]^{(1-n)+}$ (L^-=gly$^-$ or β-ala$^-$) in Water and in the 0.2 Mole Fraction Dioxane-Water Mixture, and Their Differences in the Solvents

	Water	0.2 Mole Fraction Dioxane-Water Mixture	Difference
H^+-β-ala$^-$ system			
$\log K_1$	10.65	10.86	0.21
$\log K_2$	4.03	4.98	0.96
ΔG_1°	−60.9	−62.1	−1.2
ΔG_2°	−23.0	−28.5	−5.5
ΔH_1°	−63.8	−64.5	−0.7
ΔH_2°	−9.2	−14.3	−5.1
ΔS_1°	−10	−8	2
ΔS_2°	46	48	2
Ag^+-gly$^-$ system			
$\log K_1$	3.28	3.77	0.51
$\log K_2$	3.68	3.99	0.36
ΔG_1°	−18.7	−21.6	−2.9
ΔG_2°	−21.0	−22.8	−1.8
ΔH_1°	−25.7	−30.3	−4.6
ΔH_2°	−36.5	−39.1	−2.6
ΔS_1°	−23	−29	−6
ΔS_2°	−52	−55	−3
Ag^+-β-ala$^-$ system			
$\log K_1$	3.58	4.02	0.44
$\log K_2$	3.88	4.29	0.41
ΔG_1°	−20.4	−23.0	−2.6
ΔG_2°	−22.2	−24.5	−2.3
ΔH_1°	−28.2	−34.5	−6.3
ΔH_2°	−38.9	−40.1	−1.2
ΔS_1°	−26	−39	−13
ΔS_2°	−56	−52	4

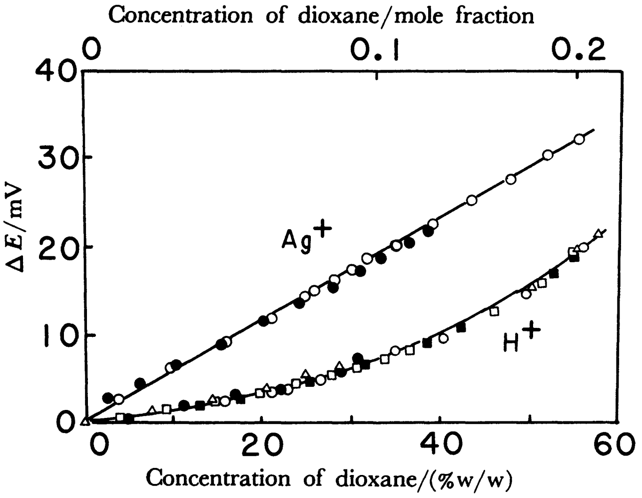

Fig. 6. Emfs obtained as a function of the dioxane concentration in dioxane-water mixtures. An aqueous solution (w) and the 0.2 mole fraction dioxane-water mixture (mix), each containing 3 mol dm^{-3} $LiClO_4$, were used as the salt-bridge solutions. Emfs measured in solutions of the same concentration of Ag^+ or H^+ ion (5—20 mmol dm^{-3}) are plotted with the same symbol.

alaninato)silver(I) complexes were determined in water and in the 0.2 mole fraction dioxane-water mixture. The net solubilities (Γ/mol dm^{-3}) of the complexes were evaluated by taking into account the distribution of species in each solution, the result being given in Table 4. The Gibbs energy of transfer of [AgL], ΔG_t°([AgL]), from water to the mixture was calculated:

$$\Delta G_t^\circ([\mathrm{AgL}]) = -RT\ln\{\Gamma_{\mathrm{mix}}([\mathrm{AgL}])/\Gamma_{\mathrm{w}}([\mathrm{AgL}])\}, \quad (3)$$

which is related to the Gibbs energies of transfer of relevant ions, $\Delta G_t^\circ(Ag^+)$ and $\Delta G_t^\circ(L^-)$, and the Gibbs energies of formation of [AgL], ΔG_1°, in water and in the mixture given in Table 3:

$$\Delta G_1^\circ(\mathrm{mix}) - \Delta G_1^\circ(\mathrm{w}) = \Delta G_t^\circ([\mathrm{AgL}]) - \Delta G_t^\circ(\mathrm{Ag^+}) - \Delta G_t^\circ(\mathrm{L^-}). \quad (4)$$

Since all the values except for $\Delta G_t^\circ(L^-)$ have been determined, the $\Delta G_t^\circ(L^-)$ values for glycinate and β-alaninate ions were determined.

Crystals of silver(I) glycinate and β-alaninate which were in equilibrium with the solution may involve some water molecules such as Aggly·(1/2)H_2O.[10] In this case, the ΔG_t°([AgL]) value involves the contribution of the Gibbs energy of transfer of a half mole of water from water to the mixture. However, the $\Delta G_t^\circ(H_2O)$ value is about −0.4 kJ mol^{-1},[11] and thus, the contribution of water was neglected.

The enthalpies of solution of $AgClO_4$, β-alanine, sodium β-alaninate, and silver(I) glycinate and β-alaninate in water and in the 0.2 mole fraction

Table 4. Solubilities, Γ/mol dm^{-3}, and Enthalpies of Solution, ΔH°_s/kJ mol^{-1}, of the Mono(glycinato)- and Mono(β-alaninato)silver(I) Complexes and Some Related Species in Water and in the 0.2 Mole Fraction Dioxane–Water Mixture at 25 °C, and the Enthalpies of Transfer, ΔH°_t/kJ mol^{-1}, of the Species from Water to the Mixure

	Water	0.2 Mole Fraction Dioxane–Water Mixture	ΔH°_t
Γ([Aggly])$^{a)}$	7.37×10^{-3}	6.10×10^{-4}	
Γ([Agala])$^{a)}$	9.24×10^{-3}	6.55×10^{-4}	
ΔH°_s([Aggly])$^{b)}$	33.2	36.3	3.1
ΔH°_s([Agala])$^{b)}$	25.6	24.8	−0.8
ΔH°_s($AgClO_4$)	8.6	−17.9	−26.6
ΔH°_s([Hala])	9.5	16.3	6.8
ΔH°_s(Naala)$^{c)}$	−19.4	−9.2	10.2

a) Concentration of [AgL] corrected by taking into account the distribution of species in each solution. b) Dissolved in solutions containing excess ligand ions to yield $[AgL_2]^-$, and the measured enthalpy of solution was corrected for the enthalpy for the reaction, $[AgL]+L^-=[AgL_2]^-$. c) Dissolved in solutions containing 0.01 mol dm^{-3} NaOH.

dioxane–water mixture are summarized in Table 4.

As to silver(I) glycinate and β-alaninate, the solubilities were too low in both solutions to directly measure the enthalpies of solution of the salts. Therefore, silver(I) glycinate (or silver(I) β-alaninate) was dissolved in a solution containing appropriate concentrations of glycine and lithium glycinate (or β-alanine and lithiun β-alaninate) in order to fully convert the species to $[AgL_2]^-$ in the solution. Thus, the measured enthalpy of solution is represented as the sum of the enthalpy of solution of [AgL], ΔH°_s([AgL]), and the enthalpy of reaction, $[AgL]+L^-=[AgL_2]^-$. Since the latter value is known, the ΔH°_s([AgL]) value was evaluated. Although the reliability of the ΔH°_s([AgL]) is low due to a low solublility of the complex in each solution, the value may account for the corresponding one calculated from the related thermodynamic quantities as will be discussed in a later section.

Since the ΔH°_t($AgClO_4$) and ΔH°_t(Naala) values are represented as the sum of the enthalpies of transfer of relevant ions, the ΔH°_t(Ag^+) and ΔH°_t(β-ala$^-$) values were obtained by subtracting the known ΔH°_t(ClO_4^-) and ΔH°_t(Na^+) values[9] from the ΔH°_t($AgClO_4$) and ΔH°_t(Naala) values, respectively.

β-Alanine exists as the zwitterion in the aqueous solutions, and thus the difference in the ΔH°_s values in these solutions corresponds to the enthalpy of transfer of the zwitterionic β-alanine.

The thermodynamic quantities of transfer of complex species were then evaluated in a following section.

Thermodynamic Quantities of Transfer of Complexes from Water to the 0.2 Mole Fraction Dioxane–Water Mixture. The Gibbs energies of protonation of β-alaninate ion in water, ΔG°_{HL}(w), and in the mixture, ΔG°_{HL}(mix), are related to the Gibbs energies of transfer of β-alanine zwitterion, ΔG°_t([HL]), proton, ΔG°_t(H^+), and β-alaninate ion, ΔG°_t(L^-), from water to the mixture as follows:

$$\Delta G^\circ_{HL}(\mathrm{mix}) - \Delta G^\circ_{HL}(\mathrm{w}) = \Delta G^\circ_t([HL]) - \Delta G^\circ_t(H^+) - \Delta G^\circ_t(L^-). \quad (5)$$

Since all the values except for ΔG°_t([HL]) have been determined, the ΔG°_t([HL]) value was evaluated. Then, the Gibbs energy of transfer of $[H_2L]^+$, ΔG°_t($[H_2L]^+$), was successively obtained by using the corresponding relationship similar to that in Eq. 5.

Similarly, the stepwise Gibbs energies of formation of the bis(glycinato)- and bis(β-alaninato)silver(I) complexes in water, ΔG°_2(w), and in the mixture, ΔG°_2(mix), are related to the Gibbs energies of transfer of the related species in Eq. 6:

$$\Delta G^\circ_2(\mathrm{mix}) - \Delta G^\circ_2(\mathrm{w}) = \Delta G^\circ_t([AgL_2]^-) - \Delta G^\circ_t([AgL]) - \Delta G^\circ_t(L^-). \quad (6)$$

Since the ΔG°_t([AgL]) value has been determined by solubility measurements and the ΔG°_t(L^-), ΔG°_2(w), and ΔG°_2(mix) values were also known as described in a preceding section, the ΔG°_t($[AgL_2]^-$) (L^-=gly$^-$ and β-ala$^-$) values were evaluated.

A similar procedure was applicable for evaluation of the enthalpies of transfer of complex species. In the enthalpy relationship corresponding to Eq. 5, all the values except for ΔH°_t(H^+) in the β-alanine system have been determined, thus, the ΔH°_t(H^+) value was evaluated to be −22.5 kJ mol^{-1}, which is in good agreement with that (−22.7 kJ mol^{-1}) determined in the glycine system. Since the ΔH°_t(H^+), ΔH°_t([HL]), ΔH°_t(Ag^+), and ΔH°_t(L^-) have been determined, the ΔH°_t values of $[H_2L]^+$ and $[AgL_n]^{(1-n)+}$ (n=1 and 2) were calculated. The results are summarized in Table 5, together with the corresponding entropies of transfer of species calculated from the ΔG°_t and ΔH°_t values.

Solvation Structure around Ionic Species in Dioxane–Water Mixtures. Thermodynamic quantities of transfer of ions from water to a dioxane–water mixture reflect the differences in both ion–solvent (solvation of ion) and solvent–solvent interactions in the solvents. In water, water molecules are hydrogen-bonded with each other in the bulk, and ions introduced from the gas phase to water first destroy the hydrogen-bonding water–water bonds and then are coordinated with the water molecules liberated from the structure of water

Table 5. 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–Water Mixture at 25 °C

Species	ΔG_t°	ΔH_t°	ΔS_t°
H^+	1.9	−22.7[a)]	−83
gly$^-$	6.0	28.7[a)]	76
β-ala$^-$	6.0	30.0	81
[Hgly][b)]	6.3	1.2[a)]	−17
$[H_2gly]^+$	4.1	−26.3[a)]	−100
[Hala][b)]	7.3	6.8	−2
$[H_2ala]^+$	3.5	−20.8	−82
Ag^+	3.1	−21.9	−84
[Aggly]	6.2	2.4	−13
$[Ag(gly)_2]^-$	10.1	28.6	62
[Agala]	6.6	1.8	−16
$[Ag(ala)_2]^-$	10.3	30.6	68

a) Ref. 9. b) Zwitterion: $^+H_3NCH_2COO^-$ or $^+H_3NCH_2CH_2COO^-$.

in the bulk. Similarly, ions introduced to a dioxane–water mixture may destroy both dioxane–water and water–water bonds. The bonding energies between solvent molecules in a dioxane–water mixture may be different from those in pure water, but the difference is not appreciable in the 0.2 mole fraction dioxane–water mixture because the ΔH_t° value of one mole of water molecules from water to the mixture is not significant (−0.6 kJ mol^{-1}) as compared with the corresponding ΔH_t° values of ions.[9,12] Consequently, it is postulated that thermodynamic quantities of transfer of ions from water to the dioxane–water mixture mainly reflect the change in the ion–solvent interaction in the solvents.

As seen in Table 5, compared to the ΔH_t° and ΔS_t° values of neutral species, the ΔH_t° and ΔS_t° values of cationic species, Ag^+, H^+ and $[H_2L]^+$, are significantly negative, while the ΔH_t° and ΔS_t° values of anionic species, L^- and $[AgL_2]^-$, are remarkably positive.

Negative ΔH_t° values of Ag^+, H^+, and $[H_2L]^+$ from water to the dioxane–water mixture imply that solvation energies of the ions are increased in the mixture compared to those in water. Corresponding negative ΔS_t° values of the cations suggest that solvent molecules solvating the cations are more ordered, i.e., the solvation structure is enhanced, in the dioxane–water mixture than in water. The reverse is the case for anions, L^- and $[AgL_2]^-$, which have positive ΔH_t° and ΔS_t° values. It is expected that solvation energies of the anions are decreased and solvent molecules solvating the anions are less ordered, i.e., the solvation structure is weakened, in the mixture than in water. The enhancement or weakening of solvation structure around ions may occur at the secondary or higher solvation shells because, since both donor and acceptor properties of dioxane are weaker than those of water, metal ions and ligands are expected to be preferentially solvated with water molecules in the primary solvation shell.[9]

The reason why solvation energies of cations are increased and those of anions are decreased by the addition of dioxane to water may be explained by a following consideration:

A water molecule has an oxygen atom as the electron donor (D_w) and two protons as the electron acceptor (A_w). They interact to form hydrogen-bonds in the bulk water and the equilibrium as the following equation may hold:

$$D_w + A_w = D_w\text{–}A_w, \tag{7}$$

where D_w–A_w denotes the formation of a hydrogen-bond between D_w and A_w of water molecules. It should be noted that free D_w or A_w means not only a free water molecule but also a terminal oxygen or hydrogen atom of water within a hydrogen-bonded network chain of water. The equilibrium in Eq. 7 is largely shifted toward the right hand side in pure water at room temperature.

A basic dioxane molecule may act as a donor (D_d) with a comparable donicity with water, because the donor number of dioxane (D_N=14.8) is not largely different from that of water (D_N=18.0).[13] On the other hand, the acceptor ability of dioxane (the acceptor number A_N=10.8) is much smaller than that of water (A_N=54.8).[13] Therefore, when dioxane is introduced in water, a dioxane molecule may interact with water molecules to form hydrogen-bonds through its etherial oxygen atoms as represented by D_d–A_w:

$$D_d + A_w = D_d - A_w \tag{8}$$

Thus, the formation of hydrogen-bonds between dioxane and water molecules will shift the equilibrium in Eq. 7 to result in an increase of the concentration of D_w, while the concentration of A_w decreases with decreasing mole fraction of water in the mixture.

In water-rich dioxane–water mixtures, metal ions and anionic ligands may be preferentially solvated with water molecules. Metal ions thus interact with oxygen donor atoms (D_w) and anionic ligands interact with protons (A_w) of water molecules, and thus, solvated metal ions and anionic ligands are in equilibrium with free D_w and A_w, respectively, of water. In the water-rich 0.2 mole fraction dioxane–water mixture compared to pure water, an increase of the concentration of D_w may therefore lead to an enhanced hydration structure around metal ions, while a decrease of the concentration of A_w may lead to a weakened hydration structure around anions.

In the case of glycine and β-alanine zwitterions in contrast to simple ions, the ΔH_t° value is smaller than the ΔG_t° value, so that the ΔS_t° value is negative. The same trend in the thermodynamic quantities of transfer has been observed for the [AgL] (L^-=gly$^-$ and β-ala$^-$) complexes in Table 5. Therefore, we propose that [AgL] (L^-=gly$^-$ and β-ala$^-$) complexes have similar zwitterionic structures, $^{+}AgNH_2CH_2COO^{-}$ and $^{+}AgNH_2CH_2CH_2COO^{-}$, to those of glycine ($^{+}H_3NCH_2COO^{-}$) and β-alanine ($^{+}H_3NCH_2CH_2COO^{-}$) zwitterions, respectively, both in water and in the dioxane-water mixture examined.

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