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A Potentiometric Study on Complex Formation of Silver(I) Ion with Glycine and β-Alanine in Aqueous Solution

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The complex formation of silver(I) ion with glycine and β-alanine was studied at 25 °C in an aqueous solution containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium by means of potentiometric titrations. At a relatively low pH region, the $AgHL^+$ complex (L^- represents glycinate and β-alaninate ions) was formed, in which the silver ion was coordinated with the carboxyl group of the ligands. At a medium pH range, the AgL and AgL_2^- complexes were formed. From the formation constants of the complexes, it is suggested that the silver ion within the complexes may be coordinated with the amino group of the ligands and the interaction between the metal ion and the carboxyl group within the complexes is so weak that the interaction does not appreciably stabilize the complexes. At the highest pH region, the hydrolyzed species $Ag(OH)L^-$ was formed.

In previous papers,[1,2] we have reported the complex formation reactions of silver(I) ion with some aliphatic diamines. In these cases, not only mononuclear complexes but also polynuclear, protonated, and hydrolyzed complexes were formed, and their formation constants were discussed in connection with the length of the methylene chain within the aliphatic diamines.

Although several investigations of complex formation reactions between silver(I) ion and amino acids have so far been made,[3] the pH ranges covered in most studies were rather limited, so that the formation of only AgL and AgL_2^- complexes have been reported,[4-6] and no further attention has been paid for the formation of protonated and hydrolyzed complexes.

In the present study, we examined the complex formation reactions of silver(I) ion with glycine and β-alanine in aqueous solution where the concentration of hydrogen ions was widely changed ($2 < -\log[H^+] < 11$). The $AgHL^+$ and $Ag(OH)L^-$ complexes were found together with the AgL and AgL_2^- complexes and their formation constants were obtained.

Experimental

Reagents. *Glycine and β-alanine* were recrystallized three times from an ethanol–water mixture and were dried at 80—110 °C in an electric oven. Crystals thus prepared were stored in vacuum.

Other chemicals were the same as those used previously.[1,2]

Measurements. Beckman (Nos. 40495 and 40498) glass electrodes were used in combination with an Orion Digital pH Meter Model 801. The concentration of free silver(I) ion was determined by using an Ag–AgCl electrodes in combination with Takeda Riken Digital Voltmeter (TR-6515). The Kawai-type reference half cell was used,[7] in which an Ag–AgCl electrode was set. The Ag–AgCl electrodes used were prepared according to Brown.[8]

During the potentiometric titrations the total concentration of perchlorate ion was kept constant at 3 mol dm^{-3} by using lithium perchlorate. The concentrations of silver and amino acids were changed over the range of 2.5—10 mmol dm^{-3} and 10—80 mmol dm^{-3}, respectively. The ratio of the total concentration of an amino acid to that of silver ion (C_L/C_{Ag}) ranged from 2 to 32. Measurements were performed at 25.00±0.01 °C in a paraffin oil bath set in a room thermostatted at 25.0±0.5 °C.

Details of the method of measurements were described elsewhere.[1,2]

Results

Titration curves of silver–glycine and silver–β-alanine systems are represented in Figs. 1 and 2, respectively. The value $-\log[H^+]$ was plotted against X ($= -H/C_L$; H stands for the analytical excess concentration of hydrogen ion). Titration data were first analyzed by graphical methods and the composition of the complexes

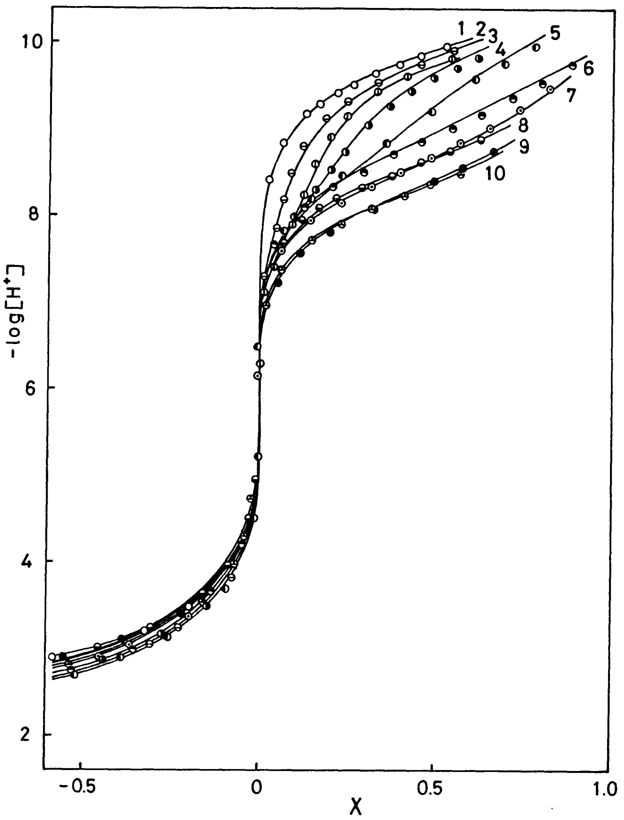

Fig. 1. Titration curves of glycine and silver–glycine solutions.

Curve 1: C_{Ag} (mmol dm^{-3})=0.0, C_L (mmol dm^{-3})=10.13; 2: 2.504, 80.00†; 3: 5.001, 80.00; 4: 2.504, 40.05; 5: 2.504, 20.04; 6: 2.507, 10.08; 7: 5.001, 20.04; 8: 5.001, 10.08; 9: 9.996; 40.05; 10: 9.996, 20.04.

† The concentration of the ligand was changed by dilution during the titration. The solid lines show calculated curves by using the constants in Table 1.

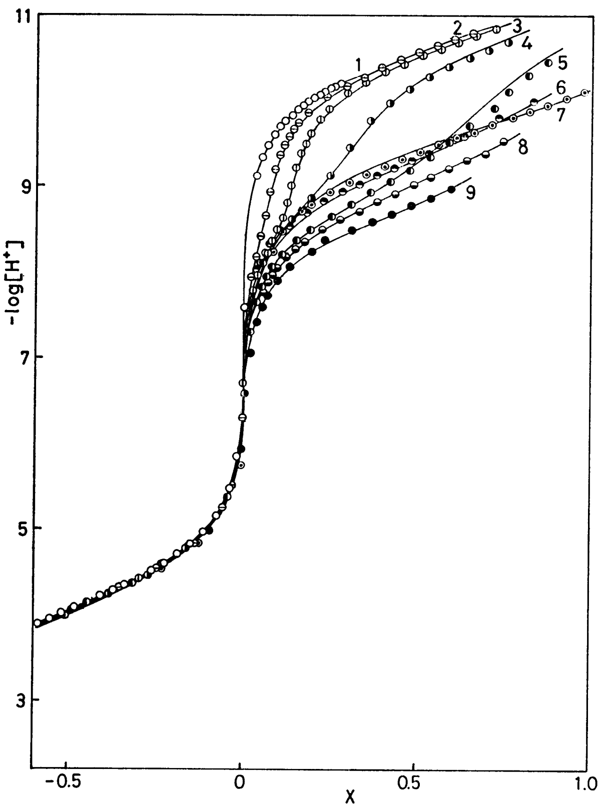

Fig. 2. Titration curves of β-alanine and silver–β-alanine solutions.
Curve 1: C_{Ag} (mmol dm^{-3})=0.0, C_{L} (mmol dm^{-3})= 10.26; 2: 2.546, 80.50†; 3: 5.133, 80.50; 4: 2.546, 40.14; 5: 5.133, 40.14; 6: 5.133, 10.08; 7: 2.546 5.036; 8: 10.05, 20.38; 9: 10.06, 40.14.
† See Fig. 1.

and their approximate formation constants were determined. The formation constants thus obtained were finally optimized by the least-squares method using an electronic computer (FACOM M-160). The least-squares method used was based on a modified MINIQUAD program[9] which minimizes the sum of squared residuals for all mass-balance equations.

In a lower pH range where most acids are present as HL the following equilibrium between silver ion and an amino acid may be assumed:

$$p\mathrm{Ag}^+ + r\mathrm{HL} = \mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q-r)+} + (r-q)\mathrm{H}^+. \tag{1}$$

The equilibrium constant of Eq. 1 is defined as follows:

$$\kappa_{pqr} = \frac{[\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q-r)+}][\mathrm{H}^+]^{r-q}}{[\mathrm{Ag}^+]^p[\mathrm{HL}]^r} = \beta_{pqr}/\beta_{011}^r, \tag{2}$$

where β_{pqr} denotes the overall formation constant of the $\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q-r)+}$ complex:

$$\beta_{pqr} = [\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q-r)+}]/[\mathrm{Ag}^+]^p[\mathrm{H}^+]^q[\mathrm{L}^-]^r. \tag{3}$$

The material balance of the metal ion gives the following equation:

$$\frac{C_{\mathrm{Ag}} - [\mathrm{Ag}^+]}{[\mathrm{Ag}^+]} = \phi - 1$$
$$= \sum_p\sum_q\sum_r p\kappa_{pqr}[\mathrm{Ag}^+]^{p-1}[\mathrm{H}^+]^{-(r-q)}[\mathrm{HL}]^r. \tag{4}$$

If we assume as a first approximation that only one complex is formed in the pH range, the following equation can be readily derived:

$$\log(\phi-1) - \log[\mathrm{HL}] = \log p\kappa_{pqr} + (p-1)\log[\mathrm{Ag}^+]$$
$$-(r-q)\log[\mathrm{H}^+] + (r-1)\log[\mathrm{HL}]. \tag{5}$$

Since the amount of the $\mathrm{Ag}_p\mathrm{H}_q\mathrm{L}_r{}^{(p+q-r)+}$ complex formed was small, the concentration of the free ligand, HL, was approximated to the total concentration of the ligand, *i.e.*, $[\mathrm{HL}] \approx C_{\mathrm{L}}$. The plots of $\log(\phi-1) - \log C_{\mathrm{L}}$ against $-\log[\mathrm{H}^+]$ for the silver(I)-β-alanine system are shown in Fig. 3 as an example. The plots were practically independent of the total concentrations of both silver ion and the ligand and fell on an almost single straight line with the slope zero. Therefore, $p-1=0$, $r-1=0$ and $r-q=0$ were obtained, and thus, the complex formed was identified to be the AgHL^+ complex.

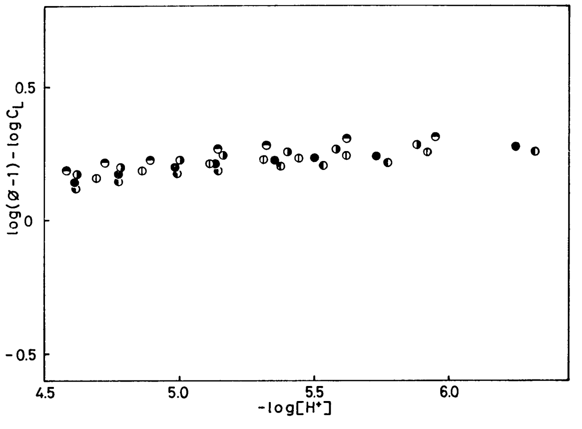

Fig. 3. Plots of $\log(\phi-1) - \log C_{\mathrm{L}}$ *vs.* $-\log[\mathrm{H}^+]$ in the silver–β-alanine system. Symbols are the same as those used in Fig. 2.

Graphical procedures were applied to the estimation of the composition and approximate formation constants of other complexes over the whole pH region. Formation of the complexes, AgL, AgL_2^- and $\mathrm{Ag(OH)L}^-$ were estimated. The formation constants of the complexes thus evaluated by the graphical procedures were further refined by the least-squares method. The assumptions

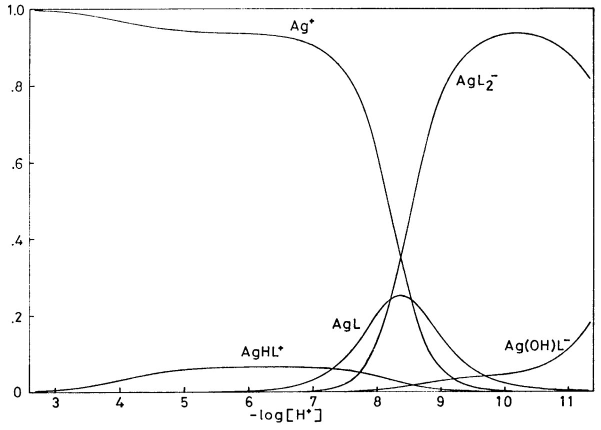

Fig. 4. Distribution of silver–β-alanine complexes. C_{Ag}=5 mmol dm^{-3}, C_{L}=40 mmol dm^{-3}.

of the formation of the $AgHL_2$, $AgH_2L_2^+$, and AgOH complexes beside the complexes graphically obtained were all rejected in the course of the least-squares procedures. The final results are summerized in Table 1, together with the formation constants of ethylendiamine and 1,3-propanediamine complexes.[1,2] The solid lines in Figs. 1 and 2 were calculated by Eq. 6:

$$X_{\text{calc}} = \frac{C_L + K_i[H^+]^{-1} - [H^+] - \sum_p\sum_q\sum_r q\beta_{pqr}[Ag^+]^p[H^+]^q[L^-]^r}{C_L}, \tag{6}$$

where K_1 denotes the autoprotolysis constant of water in 3 mol dm^{-3} $LiClO_4$ aqueous solution and is $10^{-13.87\pm0.01}$ mol^{-2} dm^6,[10] and the formation constant β_{pqr} used are those in Table 1. A typical set of distribution curves of the silver–β-alanine complexes is depicted in Fig. 4.

Discussion

The equilibrium constant $K(AgHL/HL)$ for the reaction

$$Ag^+ + HL = AgHL^+ \tag{7}$$

$$K(AgHL/HL) = [AgHL^+]/[Ag^+][HL] \tag{8}$$

can be calculated from the formation constants listed in Table 1. The values $\log K(AgHL/HL)$ for glycine and β-alanine are 0.07 and 0.23, respectively. The values are much smaller than those for diamines (*e.g.*, 2.79 for ethylenediamine), whilst they are very similar to the value for acetic acid (0.36).[11] Thus, the metal ion within the AgHL complex may be coordinated with the carboxyl group of the ligands. The value of $\log K(AgHL/HL)$ for glycine is smaller than that for β-alanine. A stronger electrostatic repulsion between silver ion and the terminal hydrogen ion at the amino group within the silver–glycine complex than that within the silver–β-alanine complex may reduce the stability of the former complex compared with the latter.

TABLE 1. FORMATION CONSTANTS OF THE $Ag_pH_qL_r$ COMPLEXES, $\log \beta_{pqr}$, IN 3 mol dm^{-3} $LiClO_4$ AT 25 °C[a)]

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

Complex	gly^-	β-ala^-	en[2)]	pn[2)]
HL	9.91±0.02	10.65±0.02	10.74	10.96
H_2L	12.60±0.03	14.68±0.03	18.67	20.65
AgHL	9.99±0.20	10.88±0.15	13.53	14.32
AgL	3.28±0.02	3.58±0.03	5.26	6.59
AgL_2	6.96±0.03	7.46±0.03	9.45	9.8
Ag(OH)L	−6.48±0.15	−6.12±0.08	−4.81	−3.57

a) The charge of the complexes is omitted. Uncertainties of the formation constants were estimated as 3σ, where σ denotes the standard deviation.

Stepwise formation constants $\log K(AgL/L)$ and $\log K(AgL_2/L)$ for the reactions, $Ag^+ + L^- = AgL$ and $AgL + L^- = AgL_2^-$, respectively, are readily calculated from the data in Table 1, that is, $\log K(AgL/L) = 3.28$ and $\log K(AgL_2/L) = 3.68$ for the silver–glycine complexes and $\log K(AgL/L) = 3.58$ and $\log K(AgL_2/L) = 3.88$ for the silver–β-alanine complexes. The trend that the $K(AgL_2/L)$ value is larger than the $K(AgL/L)$ value is the same as that found for silver–ammine and silver–monoamine complexes having a linear structure, and is opposite to that observed for silver–diamine complexes in the previous work[2)] in which we reported that they have a distorted tetrahedral structure. These results suggest, therefore, that glycine and β-alanine essentially act as monodentate ligands to the central silver ion and the interaction between the positively charged silver ion and the negatively charged carboxyl group of the ligands may be so weak that it does not appreciably contribute to stabilization of the nitrogen-coordinated complexes.

The equilibrium constants of the hydrolytic reaction of the amino acid silver complexes, $AgL + H_2O = Ag(OH)L^- + H^+$ are given as $\log {}^*K(Ag(OH)L/AgL) = -9.76$ and -9.70 for the glycinato and β-alaninato complexes of silver ion, respectively. These values are slightly larger than those of silver–ethylenediamine (−10.08) and 1,3-propanediamine (−10.16) complexes in the same medium.[2)]

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