A Polarographic Study of the Glycine Complexes of Copper(II), Lead(II), Cadmium(II), and Manganese(II)

Hiroshi Yamashita,* Toru Nozaki, Yoshihito Fukuda, and Toshiyuki Kabata
Department of Resources Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790

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Synopsis. From the polarographic behavior of copper (II), lead(II), cadmium(II), and manganese(II) in aqueous glycine solutions at an ionic strength of 0.4 mol dm^{-3} adjusted with sodium perchlorate, the species of the metal complexes and their stability constants were determined.

Glycine (abbreviated to HL) is included in industrial waste solutions treated by the hydrolysis of protein. Many studies[1,2] on both the compositions and stability constants of the glycine complexes have been carried out by means of a pH titration method, polarography, calorimetry, etc. However, both the species and the stability constants of the mixed-ligand hydroxo-complexes have remained unknown.

In the present work, both the species and stability constants were determined by means of polarography with respect to the copper(II), lead(II), cadmium(II), and manganese(II) complexes. From the experimental results, it is pointed out that those complexes would be formed within high pH ranges.

Experimental

Apparatus. Current-potential curves were obtained using Yanagimoto (Model PA-102) polarographic analyzer. The used dropping mercury-electrodes (DME) had mercury flow rates (m) of 1.273 to 2.758 mg s^{-1}. The drop time (t) was between 2.70 and 5.82 s in distilled water at −1.0 V vs. SCE. The mercury reservoir was 60 cm in height. The DME potential was referred to at the saturated calomel electrode (SCE). The temperatures of the solutions were maintained by the use of a water thermostat at 25±0.1 °C. High-purity nitrogen gas was bubbled through the solutions in order to remove any oxygen gas dissolved in the solutions. The pH values of the solutions were measured after polarographic measurements with a Toa Electronics Ltd. (Model HM-30S) pH meter.

Reagents. Stock solutions of metal ions were prepared by converting metal nitrates into perchlorates with perchloric acid, which had been redistilled under 50—70 mmHg (1 mmHg=133.322 Pa) at 40 °C. The solutions were diluted to a constant volume with redistilled water and were standardized by chelatometric titration with EDTA. A standard solution of glycine was prepared by dissolving a weighed amount of glycine in redistilled water.

Procedures. Acid dissociation-constants of glycine were measured by means of pH titration[3] at an ionic strength of 0.4 mol dm^{-3} and 25 °C. Both the compositions and stability constants of the glycine complexes were determined by a dc polarographic method under the following conditions: an ionic strength of 0.4 mol dm^{-3}; a metal concentration of 8.0×10^{-5} mol dm^{-3}; glycine concentrations from 8.0×10^{-3} to 2.0×10^{-1} mol dm^{-3}, and a temperature of 25 °C. The ionic strengths of the solutions were adjusted with sodium perchlorate.

Results and Discussion

Reversibility of the Electrode Reactions. The reversibility of the electrode reaction was tested under the following conditions: in the cadmium(II) system, pH values from 2.4 to 12.5; in the manganese(II) system, from 6.3 to 9.1; in the copper(II) system, both from 2.1 to 4.0 and from 8.0 to 12.7; and in the lead(II) system, both from 2.1 to 7.0 and from 11.5 to 12.4.

As mentioned in the procedues section, plots of the potential (E) vs. $\log i/(i_l-i)$ exhibited straight lines under the experimental conditions with respect to polarograms of copper, lead, cadmium, and manganese in the aqueous glycine solutions. The slopes of the lines were from 29.0 to 33.2 mV of the potential so that electrode reactions could be regarded as reversible.

Compositions and Stability Constants of the Complexes. At constant metal and glycine concentrations, the dependence of the half-wave potential, $E_{1/2}$, on the pH is shown in Fig. 1. In the ranges of the dashed lines in Fig. 1, polarograms of the complexes could not to be analyzed due to both poor reversibility in the copper system and the formation of a precipite in the lead system. The half-wave potential, $E_{1/2}$, shifted more negatively with increasing pH, and reached a constant value in the high pH ranges. Beyond about 12.0, the potential, moreover, shifted negatively. In Fig. 2 at pH>12.0, the dependence of the half-wave potential on the pH is shown for various glycine concentrations. From their results, it is

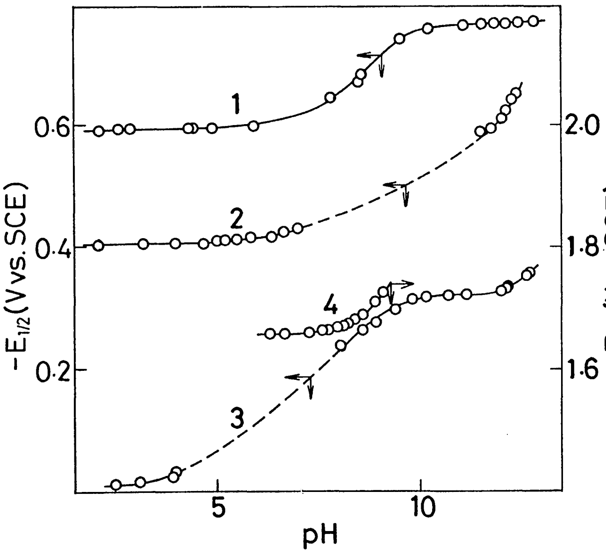

Fig. 1. Effect of pH on the half-wave potential ($-E_{1/2}$).
1: Cd(II), 2: Pb(II), 3: Cu(II), 4: Mn(II), [M(II)]= 8.0×10^{-5} mol dm^{-3}.
[Glycine] (mol dm^{-3}) 1: 4.0×10^{-2}, 2: 8.0×10^{-3}, 3: 4.0×10^{-3}, 4: 2.0×10^{-1}.
I=0.4 mol dm^{-3}, 25 °C.

Table 1. Stability Constants of Complexes (I=0.4 mol dm^{-3}, 25 °C)

$\log \beta_{ij}$	Cu(II)	Pb(II)	Cd(II)	Mn(II)
ML	8.26±0.1 8.46(I=0.2)$^{a)}$ 8.14±0.02(I=0.5)$^{b)}$	5.3±0.1 5.11(I=1.0)$^{a)}$ 5.47(I=0)$^{b)}$	4.94±0.1 6.0(I=0.1)$^{a)}$ 4.14(I=1.0)$^{b)}$	0.94±0.2 2.65(I=0.5)$^{a)}$
ML_2	15.42±0.1 15.29(I=0.2)$^{a)}$ 14.97±0.1(I=0.5)$^{b)}$	7.8±0.1 7.08(I=1.0)$^{a)}$ 8.86(I=0)$^{b)}$	8.30±0.1 8.08(I=1.0)$^{a)}$ 7.60(I=1.0)$^{b)}$	4.7(I=0.5)$^{a)}$
ML_3	17.34±0.1 16.25(I=0.1)$^{a)}$	10.0±0.1	9.73±0.1 9.78(I=1.0)$^{a)}$ 9.74(I=1.0)$^{b)}$	
M(OH)L	14.59±0.1	9.9±0.1	6.57±0.1	6.65±0.2
$M(OH)L_2$	17.31±0.1	11.1±0.1	9.59±0.1 9.27(I=1.0)$^{a)}$	
$M(OH)_2L$	15.86±0.1	12.7±0.1	9.31±0.1	
$M(OH)_2L_2$	18.85±0.1	13.6±0.1	11.81±0.1	
$M(OH)_3L$	17.85±0.1	14.7±0.1		
$M(OH)_4L$		17.3±0.1		

a) Ref. 1. b) Ref. 2.

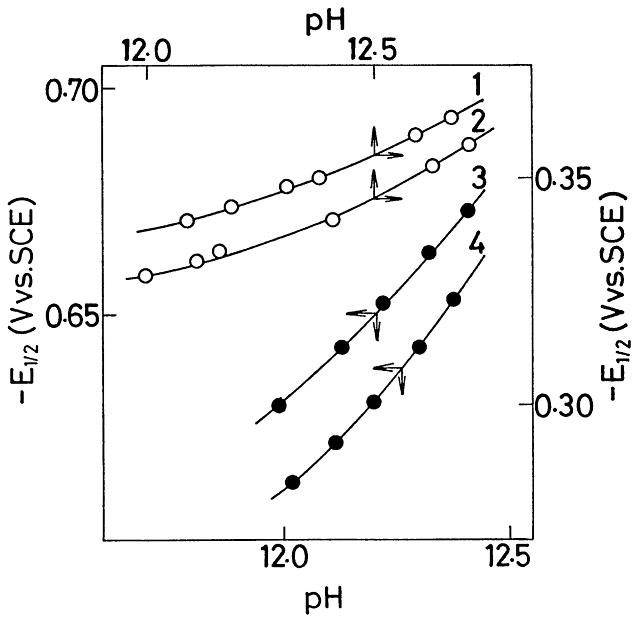

Fig. 2. Effect of pH on the half-wave potential ($-E_{1/2}$).
O: Cu(II), ●: Pb(II), [M(II)]=8.0×10^{-5} mol dm^{-3}.
[Glycine] (mol dm^{-3}) 1: 6.0×10^{-3}, 2: 4.0×10^{-3}, 3: 3.0×10^{-2}, 4: 8.0×10^{-3}.
I=0.4 mol dm^{-3}, 25 °C.

considered that mixed-ligand hydroxo-complexes coordinated both L^- and OH^- to their metals, according to Eq. 1. Therefore, both the compositions and over-all stability constants, β_{ij}, of mixed complexes were determined as described previously.[4] In this method, Eq. 2 was used while also applying the Schaap's equation:[5]

$$M^{2+} + iOH^- + jL^- \rightleftarrows M(OH)_iL_j^{2-(i+j)} \quad (1)$$

$$\begin{aligned} F_{00}(OH, L) &\equiv \sum \beta_{ij}[OH]^i[L]^j \\ &= \text{antilog}\,[0.435(nF/RT)\{(E_{1/2})_s - (E_{1/2})_c\} \\ &\quad + \log I_s/I_c], \end{aligned} \quad (2)$$

where $(E_{1/2})_s$ is the half-wave potential of simple metal ions, $(E_{1/2})_c$ is the potential of the metal complexes, I_s is the diffusion current-constants of the metal ions, and I_c is a constant of the metal complexes. By considering the coordination number of metal ions, OH^- and L^-, the values of β_{ij} were determined by a previously described method.[4] Both the compositions and stability constants of the complexes, thus obtained in this work, are shown in Table 1 together with the values obtained in the literature. The β_{ij} values of copper(II), lead(II), and cadmium(II) were in fair agreement with the values found in the literature. The complexing ability of glycine with their metals increased in the following order: manganese(II)< cadmium(II)<lead(II)<copper(II). From the results, it is considered that the reactivity of glycine with its metals contributed to the electrostatic effect.

References

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