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A Polarographic Study of the Complex Formation Equilibria of Lead(II) Ions with Glutamate and Ethylenediamine-*N*,*N'*-diacetate Anions

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Synopsis. In this experiment, the complex formation equilibria of the lead(II) ions with glutamic and ethylenediamine-*N*,*N'*-diacetic acids were studied by using the polarographic method. The lead(II) ion forms 1 : 1- and 1 : 2-ratio complexes with glutamic acid, while, with ethylenediamine-*N*,*N'*-diacetic acid, it forms only a 1 : 1-ratio complex, PbX^0.

Previously,[1] the present author reported in his polarographic study of the lead(II) ions in aspartate and iminodiacetate solutions that the lead(II) ion forms 1 : 1- and 1 : 2-ratio complexes with aspartate and iminodiacetate anions. The lead(II) ion also can form stable complexes with Glut* and EDDA* anions. However, no systematic equilibrium study of the complex formation reactions of the lead(II) ion with Glut and EDDA anions had been reported. In this connection, it seemed to be worthwhile to determine the equilibria of the lead(II) ion with Glut and EDDA anions. In this paper, the present author will determine the solution equilibria of the lead(II) ion with Glut and EDDA anions by using a polarographic technique.

Experimental

Reagents. The preparation of a lead(II) nitrate solution has been described previously.[1] The Gult and EDDA were recrystallized from their aqueous solutions. The ionic strength of the sample solution was adjusted to 0.30 by adding an appropriate amount of $NaClO_4$. The other chemicals used were of an analytical reagent-grade and were used without further purification.

Apparatus and Experimental Procedures. All the apparatus and the experimental procedures employed in this study were the same as those described previously.[1] The characteristic feature of the DME used was also described previously.[2] For the EDDA system, an acetate buffer solution was used. In the Glut system, no buffer reagent was used, because all the sample solutions contained an appropriate amount of uncomplexed Glut and had enough buffer capacity.

Results and Discussion

Lead(II) ions in Glut (8.50<pH<9.40) and EDDA (3.00<pH<4.00) solutions exhibited single reversible waves, which are diffusion-controlled in nature. In Glut solutions of pH's higher than 9.50, the 1.0 mM lead(II) ion yielded a white precipitate. Therefore, the equilibrium study of the Glut system was conducted in sample solutions containing the 0.30 mM lead(II) ion at pH's lower than 9.50. Since the Glut anion can act as a bidentate or tridentate ligand in the complexation reaction, the lead(II) ion will form 1 : 1- and 1 : 2-ratio complexes with the Glut anion. Therefore, the following relation can be derived for the lead(II)-Glut system:[1]

$$\text{Antilog}\left(\frac{\Delta E_{1/2}}{0.0296}+\log\frac{k_{Pb}}{k_{PbG}}\right) = K'_{PbG}\cdot[\text{Glut}]_f + K'_{PbG}\cdot K^{G'}_{PbG_2}\cdot[\text{Glut}]_f^2 \qquad (1)$$

where $\Delta E_{1/2}$ indicates the shift of the half-wave potential by the complex formation and where K'_{PbG} and $K^{G'}_{PbG}$ are, respectively, the conditional first and second successive formation constants of the lead(II)-Glut complex. By using the above relation, the solution equilibrium between the lead(II) ion and the Glut anion was studied. A typical result obtained is reproduced in Fig. 1. From the intercept and slope of the straight line in Fig. 1, K_{PbG} and $K^{G}_{PbG_2}$ were estimated to be 5.0×10^4 and $7.0_0\times 10^2$ respectively.

The limiting current of the lead(II) ion in the EDDA solution decreased with an increase in the concentration of the uncomplexed EDDA, $[X]_f$. This decrease can be ascribed to the formation of a lead(II)–EDDA complex. If the aquo lead(II) ion coexists with the 1 : 1-ratio EDDA complex, one can derive the following equation for the conditional formation constant of a 1 : 1-ratio lead(II)-EDDA complex, K'_{PbX}, by combining the relation given by Kacena and Matousek[3] and the Ilkovic equation:

$$K'_{PbX}[X]_f = \frac{(i_d)^2_{Pb}-(i_d)_0^2}{(i_d)_0^2-(i_d)^2_{PbX}} \qquad (2)$$

where $(i_d)_{PbX}$ and $(i_d)_{Pb}$ are the diffusion currents of complexed and uncomplexed lead(II) ions respectively,

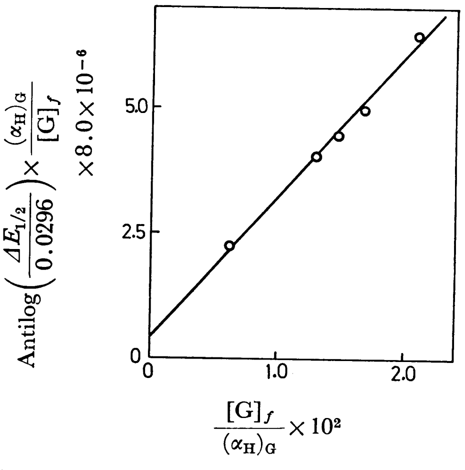

Fig. 1. Determination of formation constants of lead-(II)-Glut complex.
$\mu=0.30$, 25 °C
$[Pb(II)]=0.30$ mM
$[\text{Glut}]_f$ ranged from 50 to 250 mM

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* Glut, glutamate; EDDA, ethylenediamine-*N*,*N'*-di acetate.

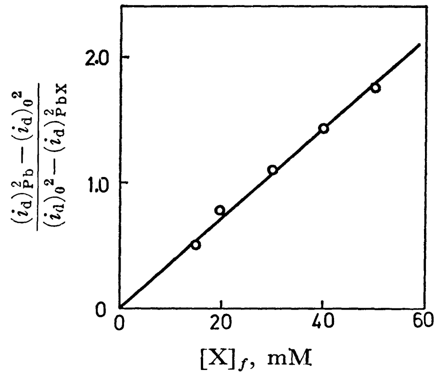

Fig. 2. Determination of formation constant of lead-(II)-EDDA complex.
$\mu=0.30$, 25 °C, pH=3.50
$[Pb(II)]=1.0$ mM, $[Ac]_f=0.06$ M
$[EDDA]_f$ ranged from 15 to 50 mM

and $(i_d)_0$, the apparent diffusion current. As is shown by the straight line in Fig. 2, the plot of the right-hand side of Eq. (2) against $[X]_f$ gave a straight line passing through the point of origin. From the slope of the above linear relation, K_{PbX} was determined to be $10^{10.43}$ ($\mu=0.30$, 25 °C). With the aid of the $\Delta E_{1/2}=0.0296[\log(1+K'_{PbX}\cdot[X]_f)+\log(k_{PbX}/k_{Pb})]$ equation, the effects of the concentrations of hydrogen and EDDA ions were examined by using the K_{PbX} value thus determined. Some typical results thus obtained are shown in Table 1. The agreement between the observed and calculated values can be regarded as satisfactory. Under the present experimental conditions, an acetate anion had practically no effect on the polarographic behavior of the lead(II) ion in the EDDA solution.

The successive formation constants of the lead(II)-Glut complex are nearly identical with those of the corresponding alaninate complex.[4)] This fact may mean that the glutamate anion functions as a bidentate ligand in the complex-formation reaction with the lead(II) ion. The prevalence of bidentate coordination in the complexation reaction of the Glut anion with the metal(II) ion has already been mentioned by Ho *et al.*[5)]

Table 1. The effects of solution pH and concentration of uncomplexed EDDA on the half-wave potential
$\mu=0.30$, 25 °C
$[Ac]_f=0.06$ M

pH	$[X]_f$, mM	$E_{1/2}$ V *vs.* SCE	$\Delta E_{1/2}$[a)], mV Calcd	$\Delta E_{1/2}$[a)], mV Obsd
3.50	20.0	−0.3752	− 7.0	− 6.9
3.50	30.0	−0.3773	− 9.4	− 9.0
3.50	40.0	−0.3801	−11.5	−11.8
3.50	50.0	−0.3823	−13.3	−14.0
3.80	20.0	−0.3843	−17.5	−16.5

a) $(E_{1/2})_{Pb^{2+}}=-0.3683$ V *vs.* SCE was used.

The lead(II)-nitrilotriacetate (NTA) complex has a formation constant larger than that of the lead(II)-triethylenetetraammine (Trien) complex.[4)] This fact may be ascribed to the larger entropy increase in the complexation reaction of the NTA anion due to its highly hydrated carboxylate groups. Therefore, it is not unreasonable to believe that the formation constant of the lead(II)-EDDA complex is larger than that of the Trien complex, but smaller than that of the NTA complex. The K_{PbX} value determined in this study proved the above explanation to be true.

References

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