Polarographic Study of Cadmium and Indium Complexes with Alanine

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COMPLEXES of alanine with cadmium and indium have been studied polalographically at 30±0.1°C and ionic strength 0.5M KNO_3. The stability constants of cadmium-alanine complexes were $\beta_1 = 1.3\times10^{14}$, $\beta_1 = 5.0\times10^{7}$ and $\beta_1 = 5.5\times10^{1}$. The data obtained in indium complexes was analysed and the stability constants were evaluted as $\beta_1 = 1.5\times10^{7}$ and $\beta_2 = 3.1\times10^{13}$. The halfwave potential of uncomplexed indium ion which cannot be measured directly owing to the complex nature of the reduction, was calculated as −0.516 V vs. SCE.

AMINO acids have been known to form specific ring compounds with a number of metal ions which fall under the class of inner complex salts. They contain side chain donor atoms that are potentially capable of forming a chelate ring with a metal ion bound at the α-amino nitrogen. A five or six membered ring greatly contributes to the stability of the metal chelate[1] and the presence of nitrogen as the member of the ring adds to the stability of the complexes[2]. Alanine (α-amino propanoic acid) is one of the naturally occuring amino acids which mostly acts as a bidentate ligand with most of the metals and is universally accepted as chelating agent[3,4]. It appears from the literature survey that the study of α-alanine complexes was paid less attention. This paper reports the results of polarographic studies of cadmium and indium complexes with alanine.

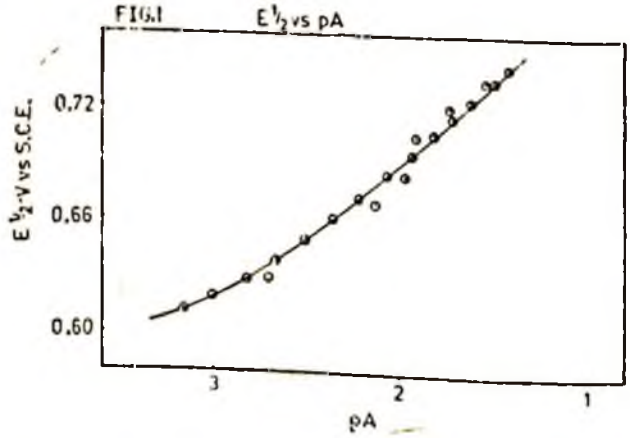
EXPERIMENTAL

Current voltage curves were recorded with a manual polarograph. Potentials were measured against SCE as the reference electrode and dme with capillary constant $m^{\frac{2}{3}}t^{\frac{1}{6}}$ equal to 1.97 $mg^{-\frac{2}{3}}sec^{-\frac{1}{2}}$. Pure nitrogen was passed through the solution before recording the polarograms. The pH of the solutions was measured with a E.C. expandometric pH meter (Model pH 821 B). All measurements were made at 30±0.1°C using Jumo contact thermometer (MS 121) in conjunction with a Jumo relay (EK 15-0). A stock solution of cadmium was prepared by dissolving recrystallised cadmium perchlorate in conductivity water. A stock solution of indium perchlorate was prepared by dissolving indium metal (B.D.H.AnalaR) in nitric acid and fuming it with perchloric acid. These solutions were estimated by standard methods. Alanine (Aldrich) was used without further purification. The reported currents have been corrected for the residual current.

RESULTS AND DISCUSSION

1. *Cadmium System:* Cadmium gave a well defined reversible wave in 0.5 M potassium nitrate with the half-wave potential at −0.579 V vs. SCE. The diffussion controlled nature of the reduction was confirmed as the plots of i vs. $\sqrt{h}$ yielded straight line passing through the origin. In presence of alanine, the reduction was found to be reversible, but the wave shifted to more negative potentials indicating complexation. The concentration of alaninate ion was calculated from the pH of the solution and the pK of alanine, which was determined separately under the experimental conditions as 9.87 by the pH titration technique of Irving and Rossotti[5].

A plot of $E_{\frac{1}{2}}$ (half-wave potential) vs. pA (Fig. 1) resulted in a smooth curve indicating the



presence of more than one complex species of comparable stabilities. Hence, the method of DeFord and Hume[6] was adopted for the evalution of the stability constants.

TABLE 1

Cadmium-alanine system; Values of F_j functions. Cd = 0.4 mM ; KNO_3 = 0.5M ; $m^{\frac{2}{3}} t_0^{\frac{1}{6}} = 1.97\ mg^{\frac{2}{3}} sec^{-\frac{1}{2}}$; $E_{\frac{1}{2}(s)} = -0.579$ V vs. SCE ; $i_{d(s)} = 3.14\ \mu A$

pA	(A) $\times 10^4$ M	F_0 (A) Exptl.	F_1 (A) $\times 10^{-1}$	F_2 (A) $\times 10^{-6}$	F_3 (A) $\times 10^{-1}$	F_0 (A) Calc.
3.2	6.31	12.73	1.859	8.859	6.12	12.57
3.0	10.00	25.58	2.458	11.580	5.58	24.50
2.8	15.85	55.58	3.443	13.520	5.38	56.06
2.6	25.12	152.40	6.027	18.810	5.50	152.38
2.4	39.81	484.60	12.14	27.23	5.59	479.00
2.2	63.10	1669.00	26.43	39.83	5.52	1663.12
2.0	100.00	6194.00	61.93	60.63	5.56	6131.0
1.8	158.50	23080.00	145.60	91 05	5.43	23363.0
1.6	251.20	93010.00	370.2	146'90	5.65	90662.5
1.5	316.20	188600.00	596.4	188.20	5.78	179787.1
1.4	398.10	380200.00	995.0	239.50	5.89	355778.6

$\beta_1 = 1.3 \times 10^4$; $\beta_2 = 5.0 \times 10^6$; $\beta_3 = 5.5 \times 10^9$.

TABLE 2

Indium-alanine systems values of F_j functions. In = 0.20mM, KNO_3 = 0.5m, $M^2\ t^{\frac{1}{6}} = 1.97\ mg^{\frac{2}{3}}_{\pi}\ sec^{-\frac{1}{2}}$; $E_{\frac{1}{2}(m)} = 0.536$ V vs S C E ; $i_{d(m)} = 1.20\mu A$.

pA	(A) $\times 10^{-4}$ M	F_1''(A)	F_1''(A) $\times 10^{-7}$	F'_2(A) $\times 10^{-13}$	F_0''(A) (calc)
8.4	0.3981	—	—	—	—
8.2	0.6310	1.804	1.269	—	2.070
8.0	1.000	2.900	1.900	4.000	2.810
7.8	1.5850	4.197	2.018	3.27	4.157
7.6	2.5120	6.814	2.315	3.25	6.724
7.4	3.9810	12.30	2.839	3.36	11.885
7.2	6.3100	22.24	3.366	2.96	22.80
7.0	10.00	45.08	4.409	2.91	47.00
6.8	15.850	102.70	6.401	3.09	102.62
6.6	25.120	233.60	9.260	5.09	234.28
6.4	39.810	543.00	13.610	3.04	552.11
6.2	63.100	1361.00	21.550	3.18	1329.64
6.0	100.00	3212.00	32.100	3.06	3251.00
5.8	158.50	7310.00	46.120	2.82	8025.8

$\frac{\beta'_0}{F'_0(m)} = 0.10$ $\frac{\beta'_1}{F'_0(m)} = 1.5 \times 10^8$; $\frac{\beta'_2}{F'_0(m)} = 3.1 \times 10^{15}$

$\beta_1 = 1.5 \times 10^9$, $\beta_2 = 3.1 \times 10^{16}$

Three complexes were indentified with the stability constants $\beta_1 = 1.3 \times 10^4$, $\beta_2 = 5.0 \times 10^6$ and $\beta_3 = 5.5 \times 10^9$. The values obtained in the present work were compared with those of the other workers (Nageswara Rao and Subramanya[7] and Smith et al[8]). The present work was carried out at lower ionic strength (0.5 M potassium nitrate) and the values of stability constants obtained were much higher. Thus it was observed that a decrease in ionic strength of the medium increases the formation and the stability of the complexes which is in agreement with the findings of Debye[9]. It was also seen that the initial value(log β_1) was not obtained by Nageswara Rao et al as the experimental conditions were different. The results are depicated in Table 3.

TABLE 3

Cadmium-alanine system : Stability constants

Supporting electrolyte KNO_3 M	Temp. °C	Log β_1	Log β_2	Log β_3	Ref.
1.0	30	—	7.36	9.15	7
2.0	25	5.13	7.82	9.16	8
0.5	30	4.11	6.70	9.74	present work

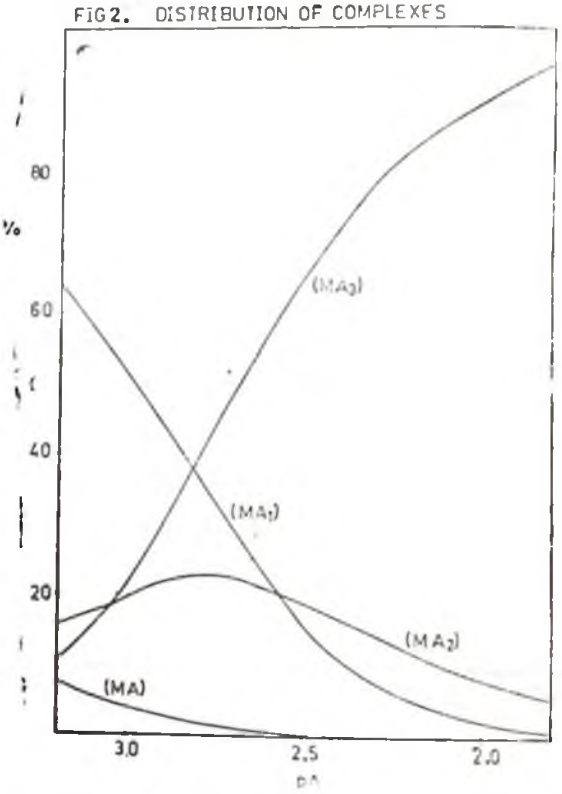
The distribution of cadmium as various complex species at different ligand concentrations was also calculated from

$$\beta_1 (A)^1/F_o (A) = (MA_i)/C_u \qquad (1)$$

where the right hand side gives the ratio of the concentration of the species MA_i to that of the total metal. The results are depicted in Fig. 2.

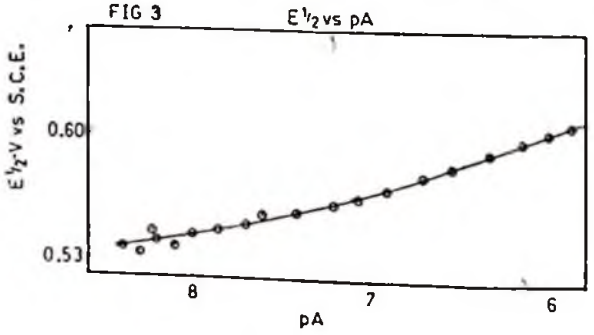
2. *Indium System* : Indium gives poorly defined waves in absence of complexing media. Hence the polarogram of 'simple' indium ion was not obtained in the presence of supporting electrolyte 0.5 potassium nitrate (ill-defined and extended[10]). However it was found that in presence of alanine, the reduction was found to be reversible and the wave was well defined. Polagrams of indium were obtained in presence of various concentrations of alanine at different pH (3 to 5). The plot of $E^1/_2$ vs. pA was a smooth curve (Fig. 3) indicating the presence of different species whose stabilities differ greatly.

FIG 2. DISTRIBUTION OF COMPLEXES



The data, however, could not be analysed by DeFord and Hume's method because of lack of simple ion value. Hence the method suggested by

FIG 3 $E^1/_2$ vs pA



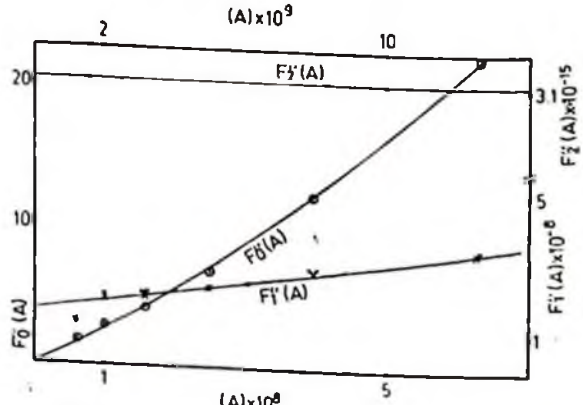


FIG 4 F' FUNCTIONS

(A)x10⁸FOR Fδ(A) AND Fi'(A)
(A)x10⁹FOR Fi'(A)

Momcki and Ogawa[11] was applied for tee evaluation of stability constants.

The half wave potential and the diffusion current corresponding to pA 8.4 were taken as $E^{1}/_{2}(m)$ and $id_{(m)}$ respectively. The function E_{o}'' (A) was calculated from the values obtained from the plot of $E_{\frac{1}{2}}$ vs. pA and was solved by the graphical method (Fig.4). The results are presented in Table 2. Two complexes were identified as $\beta_1 = 1.5 \times 10^{9}$, $\beta_2 = 3.1 \times 10^{16}$.

The half wave potential of the uncomplexed ('simple') ion was also calculated by this method and found to be −0.516 V vs. SCE which compares well with the value obtained by other workers [12 13].

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