STUDIES IN THE POLAROGRAPHY OF METAL-AMINO ACID COMPLEXES

Part II. Lead

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INTRODUCTION

MCKENZIE AND MELLOR[1] AND BAPNA AND KARMALKAR[2] have investigated the lead glycinate complex polarographically and reported the formation of 1 : 1 and 1 : 2 and 1 : 1 complexes respectively. Tsai-Teh Lai and Teh-Liang Chang[8] have studied the polarographic behaviour of lead glutamate complexes and reported the formation of several hydroxy complexes. Apart from the above investigations no other polarographic studies have been reported on the lead-amino-acid complexes. In the present paper detailed polarographic investigation of the complexes of lead with glycine, dl-α-alanine, dl-β-alanine, dl-valine, dl-aspartic acid, l-glutamic acid and l-asparagine has been described. A preliminary account[3] of some aspects presented in this paper has already been published. The abbreviations for the amino acids are the same as given in Part I.[4]

EXPERIMENTAL

The details of the experimental procedure have been previously described.[4] The concentration of lead is maintained at 0·5 mM, except for the proportionality experiments. The concentrations of the amino acid anion have been calculated from the pK value of the amino-acids reported in Part I.[4] The polarograms obtained under all conditions were reversible. Hence no polarograms have been given. The measurements have been taken at $30° \pm 0.1°$ C. The value of $m = 1.323$ mg./sec. and 't' is 5 sec. a drop in 1 N KCl.

RESULTS

1. *Effect of pH*

Between pH 11·5 and 12·5 there is precipitation even when the concentration of the amino acid is maintained at 1 M. Above pH 12·5 there is no

precipitation irrespective of the concentration of the amino acid. Below pH 11, there was no precipitation when the concentration of the total amino acid was maintained at 0·2 M with glycine and glutamic acid, 0·3 M with valine and 0·1 M with aspartic acid, asparagine and α-alanine. These concentrations were therefore selected for pH variation studies. In the case of β-alanine, however, there was precipitation even when the concentration of the total amino acid was maintained at 0·5 M. Hence no detailed investigations have been made with this amino acid.

The results of the variation of the half-wave potential with pH for various amino acids are given in Fig. 1. It is found that in all cases a precipitate is formed near about pH 11·5 (marked A in Fig. 1) which redissolves on further increase of pH.

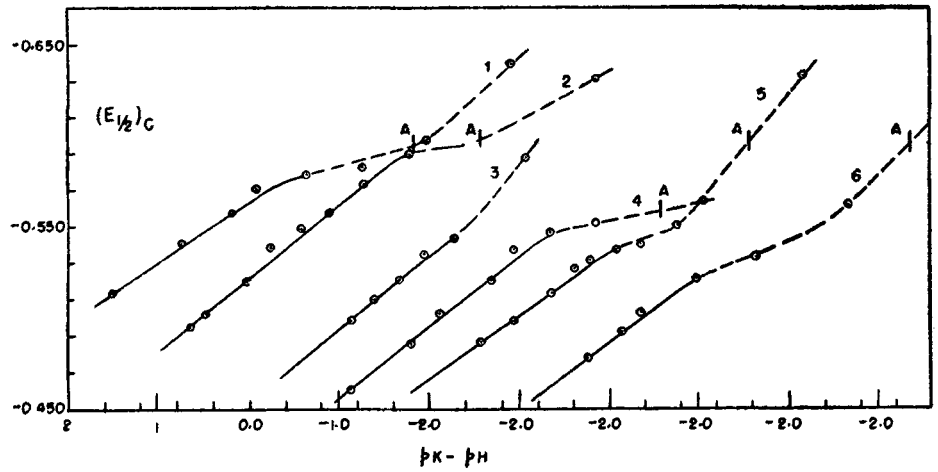

FIG. 1. Variation of half-wave potential with (pK — pH) lead-amino acid anion complexes. Curves 1 to 6 are obtained with aspartate, glycinate, α-alaninate, valinate, glutamate and asparaginate. The *x*-axis is shifted progressively by 1 unit each for curves 2, 3, 4, 5 and 6. The appropriate pH of precipitation is marked A.

2. *Effect of Variation of the Concentration of the Amino Acid Anion at Constant pH (pH Ca* 10 *and* 11)

A pH of 11·3 has been chosen since at this pH all the amino acids are present mostly in the form of anions. Similar experiments have also been conducted at a lower pH value to establish the nature of complexes produced. The lower pH value has been so chosen that at least a maximum of 1·0 M free amino acid anion could be produced in solution. In the case of glycine, α-alanine, β-alanine, aspartic acid and glutamic acid the pH has been maintained at the pK value. In the case of asparagine and valine, since the solu-

bility of the free amino acid is rather low, a pH slightly higher than the pK value is employed (pH 9·8 and 10·2 in asparagine and valine systems). The results are summarized in Table I. The results indicate that in systems containing glycine, aspartic acid and glutamic acid, the half-wave potentials are the same at both pH values for the same concentration of the amino acid anion. However, with α-alanine, asparagine and valine, the half-wave potential is greater at the higher pH value than at the lower pH when the concentration of the amino acid anion is maintained constant. Since the shift corresponds to about 30 millivolts for one pH unit the entry of one hydroxyl group into the complex is indicated. In the case of β-alanine the shift is about 60 millivolts per one pH unit indicating the entry of two hydroxyl groups. It may be pointed out that with β-alanine, there has been a slight

TABLE I

Effect of concentration of amino acid anion on the polarographic behaviour of amino acid complexes of lead

Amino acid	Concentration of amino acid anion M	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4} - E_{1/4}$ volts	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4} - E_{1/4}$ volts
		at pH 9·65		at pH 11·3	
Glycine	0·10	0·564	0·033	0·567	0·028
	0·20	0·581	0·033	0·586	0·028
	0·30	0·591	0·030	0·594	0·028
	0·50	0·607	0·030	0·604	0·032
	1·00	0·622	0·028	0·620	0·032
		at pH 9·70		pH 11·0	
α-Alanine ..	0·10	0·542	0·032	ppt	
	0·20	0·559	0·034	0·590	0·032
	0·30	0·564	0·034	0·599	0·026
	0·50	0·576	0·032	0·609	0·031
	1·00	0·600	0·033	0·630	0·031
		at pH 10·10		at pH 11·6	
β-Alanine ..	0·30	0·512	0·030	0·613	0·030
	0·50	0·534	0·031	0·634	0·026
	1·00	0·555	0·031	0·653	0·034

TABLE I—*Contd.*

Amino acid	Concentration and amino acid anion M	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4}-E_{1/4}$ volts	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4}-E_{1/4}$ volts
		at pH 10·2		at pH 11·0	
Valine	0·20	0·551	0·031	ppt	..
	0·30	0·562	0·028	0·586	0·032
	0·50	0·574	0·032	0·597	0·028
	0·80	0·587	0·032	0·607	0·028
		at pH 9·45		at pH 10·5	
Glutamic acid ..	0·10	0·531	0·033	ppt	..
	0·20	0·551	0·034	0·547	0·032
	0·30	0·563	0·035	0·560	0·030
	0·50	0·576	0·033	0·576	0·032
	0·80	0·594	0·034	0·589	0·034
		at pH 9·60		at pH 11·3	
Aspartic acid ..	0·10	0·577	0·035	0·582	0·033
	0·20	0·592	0·035	0·597	0·035
	0·30	0·603	0·033	0·607	0·033
	0·50	0·613	0.032	0·617	0·033
	0·80	0·625	0·032	0·624	0·032
		at pH 9·80		at pH 11·15	
Asparagine ..	0·10	0·536	0·032	ppt	..
	0·20	0·553	0·031	0·603	0·026
	0·30	0·562	0·032	0·609	0·026
	0·50	0·576	0·034	0·621	0·026
	0·80	0·589	0·031	0·630	0·027

precipitation of lead in all the experiments. However, this does not interfere with the interpretation of the half-wave potential data.

3. *Effect of Sodium Hydroxide on the Polarographic Behaviour of Amino Acid Complexes*

The results obtained with glycine and valine systems are given in Table II. The results obtained with other systems are similar in nature. The half-wave

potentials increase with an increase in the concentration of sodium hydroxide, at all concentrations of amino acids used. However the half-wave potentials are almost independent of the amino acid anion indicating that only pure lead-hydroxy complexes are formed.

TABLE II

Effect of sodium hydroxide on the polarographic behaviour of amino acid complexes of lead

Amino acid	Concentration of amino acid anion M	Concentration of sodium hydroxide M	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4} - E_{1/4}$ volts
Glycine ..	0·10	0·10	0·662	0·031
	0·10	0·90	0·738	0·031
	0·50	0·10	0·658	0·031
	0·50	0·90	0·736	0·031
	0·00	0·10	0·662	0·030
	0·00	0·90	0·736	0·031
Valine ..	0·10	0·10	0·670	0·035
	0·10	1·00	0·761	0·038
	0·50	0·10	0·675	0·038
	0·50	1·00	0·759	0·037

4. *Effect of Sodium Carbonate on the Polarographic Behaviour of the Amino Acid Complexes of Lead*

In presence of sodium carbonate, the solubility of lead is very low. Since lead gets precipitated even in presence of as low as 0·05 M carbonate, no measurements could be made in the case of glutamic acid, valine and β-alanine. The results obtained with other amino acids are given in Table III. The half-wave potentials increase with an increase in the concentration of sodium carbonate. However in contrast to the behaviour in NaOH solutions the half-wave potentials are not independent of the concentration of the amino acid.

5. *Effect of Ammonia and Ammonium Nitrate on the Polarographic Behaviour of Amino Acid Complexes of Lead*

The results given in Table IV indicate that the half-wave potentials become more negative with an increase in the concentration of the amino acid anion, when the concentration of ammonia is maintained constant. However the half-wave potentials are independent of the concentration of ammonia at the same concentration of the amino acid anion.

TABLE III

Effect of sodium carbonate on the polarographic behaviour of amino acid complexes of lead

Amino acid	Concentration of amino acid anion M	Concentration of sodium carbonate M	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4} - E_{1/4}$ volts
Glycine ..	0·30	0·10	0·608	0·034
	0·30	0·30	0·624	0·033
	0·30	1·00	0·638	0·034
	0·60	0·10	0·623	0·031
	0·60	0·30	0·636	0·032
	0·60	1·00	0·653	0·031
α-Alanine ..	0·50	0·05	0·627	0·031
	0·50	0·25	0·646	0·034
	0·50	0·50	ppt	..
	1·00	0·05	0·608	0·033
	1·00	0·25	0·626	0·034
	1·00	0·50	ppt	..
Aspartic acid ..	0·10	0·10	0·588	0·033
	0·10	0·30	0·601	0·034
	0·10	1·00	0·619	0·033
	0·30	0·10	0·616	0·033
	0·30	0·30	0·629	0·035
	0·30	1·00	0·643	00·33
Asparagine ..	0·50	0·05	0·620	0·031
	0·50	0·50	0·646	0·034
	1·00	0·05	0·640	0·030
	1·00	0·50	0·668	0·033

6. *Effect of Concentration of Lead on Diffusion Current Constant*

The possibility of employing amino acid complexes of lead for the polarographic estimation of lead has been tested in base solutions where the solubility of lead is sufficiently high. The diffusion current constant of lead has been determined in presence of glycine, aspartic acid, glutamic acid, and asparagine at pH 11 and also in presence of 1 M NH_4OH and 1 M NH_4NO_3. Since the addition of amino acids to alkaline solutions of lead does not offer any additional advantage in the estimation of lead these experiments have not been conducted. Since the solubility of lead is very low in presence of Na_2CO_3 even in solutions containing 1 M amino acid, amino acids are not

suitable for the estimation of lead in presence of Na_2CO_3. However, in presence of amino acids lead becomes sufficiently soluble in ammoniacal solutions for it to be estimated polarographically. The results are presented in Table V. It can easily be observed that the agreement between diffusion

TABLE IV

Effect of ammonium hydroxide and ammonium nitrate on the polarographic behaviour of amino acid complexes of lead

Amino acid	pH	Concentration of amino acid anion M	Concentration of ammonia M	$-E_{1/2}$ *vs.* S.C.E. volts	$E_{3/4} - E_{1/4}$ volts
Glycine	9·50	0·040	1·301	0·533	0·033
	9·60	0·143	1·402	0·568	0·032
	9·70	0·560	1·575	0·596	0·032
	9·22	0·028	0·750	0·523	0·034
	9·32	0·097	0·853	0·555	0·034
	9·72	0·546	1·140	0·597	0·030
α-Alanine ..	9·50	0·039	1·301	0·513	0·032
	9·60	0·130	1·402	0·549	0·032
	9·80	0·557	1·575	0·574	0·032
	9·22	0·025	0·750	0·496	0·034
	9·42	0·070	0·920	0·520	0·035
	9·82	0·569	1·199	0·576	0·033
β-Alanine ..	9·50	0·020	1·301	0·488	0·032
	9·60	0·073	1·402	0·506	0·030
	9·95	0·430	1·680	0·543	0·032
Valine	9·40	0·048	1·193	0·518	0·035
	9·50	0·160	1·301	0·550	0·034
	9·70	0·645	1·494	0·585	0·035
Aspartic acid ..	9·40	0·039	1·193	0·541	0·034
	9·50	0·135	1·301	0·573	0·032
	9·75	0·591	1·544	0·603	0·035
Glutamic acid ..	9·40	0·048	1·193	0·520	0·031
	9·50	0·261	1·301	0·540	0·033
	9·70	0·645	1·502	0·570	0·040
Asparagine ..	9·40	0·077	1·193	0·523	0·035
	9·40	0·230	1·193	0·559	0·033
	9·50	0·806	1·301	0·578	0·033

TABLE V

Effect of concentration of lead on the diffusion current constant

Concentration of lead mM	Diffusion current constant $i_d/c.m.^{2/3} t^{1/6}$	Concentration of lead mM	Diffusion current constant $i_d/c.m.^{2/3} t^{1/6}$
B.S. = 1·0 M, glycinate; x=1·686		B.S. = 1·0 M asparaginate; x= 1·682	
0·50	3·01	0·50	2·65
1·00	2·98	1·00	2·63
3·00	2·97	3·00	2·62
B.S. = 1·0 M glutamate; x=1·680		B.S. = 0·5 M aspartate; x=1·670	
0·50	2·51	0·50	2·76
1·00	2·48	1·00	2·75
2·00	2·48	3·00	2·78
B.S. = 1·0 M glycinate + 1·0 M Na_2CO_3; x=1·672		B.S. = 0·5 M aspartate + 1·0 M Na_2CO_3; x= 1·676	
0·50	2·30	0·50	2·35
1·00	2·28	1·00	2·34
2·00	2·16	2·00	1·92
B.S. = 1·0 M glutamate + 0·1 M Na_2CO_3; x=1·681		B.S. = 1·0 M glycinate + 1·0 M NH_4OH + 1·0 M NH_4NO_3; x=1·655	
0·50	1·76	0·50	3·16
1·00	1·74	1·50	3·19
2·00	1·76	4·00	3·22
B.S. = 1·0 M asparaginate + 1·0 M NH_4OH + 1 M NH_4NO_3; x=1·673		B.S. = 1·0 M glutamate + 1 M NH_4OH + 1 M NH_4NO_3; x=1·684	
1·00	2·57	1·00	2·63
4·00	2·64	4·00	2·60
B.S. = 0·5 M aspartate + 1·0 M NH_4OH + 1·0 M NH_4NO_3; x= 1·707			
1·00	2·63		
4·00	2·65		

B.S. = Base solution; $x = m^{2/3} t^{1/6}$ in $mg.^{2/3} sec.^{-1/2}$

D.C.C. measured at − 1·00 volts *vs.* S.C.E.

current constant values obtained at different concentrations of the metal is quite satisfactory.

Discussion

1. *Effect of pH*

Laitinen and others[5] obtained the following equation relating to the half-wave potential of the metal-amino acid complexes.

$$(E_{1/2})_c = (E_{1/2})_s + 0{\cdot}0296 \log K_d + 0{\cdot}0296\, p.\,(pK - pH) - 0{\cdot}0296\, p.\, \log [HA] \text{ at } 25^\circ \text{ C.}$$

where

$(E_{1/2})_c$ = half-wave potential of the complex metal ion,

$(E_{1/2})_s$ = half-wave potential of the simple metal ion,

K_d = dissociation constant of the complex,

[HA] = total concentration of the amino acid.

The plot of $(E_{1/2})_c$ *Vs.* (pK—pH) at low concentrations of the ligand (amino acid anion) should give a straight line whose slope gives the number of ligands attached.

The plots given in Fig. 1 indicate that the plots are all straight lines till the pH value goes above the pK by 0·1 to 0·7 units for the amino acids. If only one complex is produced one can expect a straight line up to a pH value of (pK—1) since the concentration of the free amino acid can be considered to be a constant within 5% till that pH. When the pH is greater than (pK—1) the value of log [HA] can no longer be regarded as constant. Hence $E_{1/2}$ *Vs.* (pK—pH) plot must fall off with an increase in the pH value. Since the plots of $E_{1/2}$ *vs* (pK—pH) are straight lines in the lead-amino acid systems, it can be concluded that more than one complex is present.

The results obtained have been analyzed assuming the existence of Pb A and Pb A_2 employing the equation developed by McKenzie and Mellor.[1] In this equation the term log I_m/I_c has been omitted since the error introduced is quite small. The plots of

$$\frac{\text{antilog}\left[\frac{1}{0{\cdot}03007}\{(E_{\frac{1}{2}})_s - (E_{\frac{1}{2}})_c\}\right] - 1}{C_A} \textit{ Vs. } C_A \text{ at } 30^\circ \text{ C.}$$

(where C_A = concentration of the amino acid anion) are given in Figs. 2 and 3. The plots are straight lines. The intercept gives the value of β_{PbA} and the slope

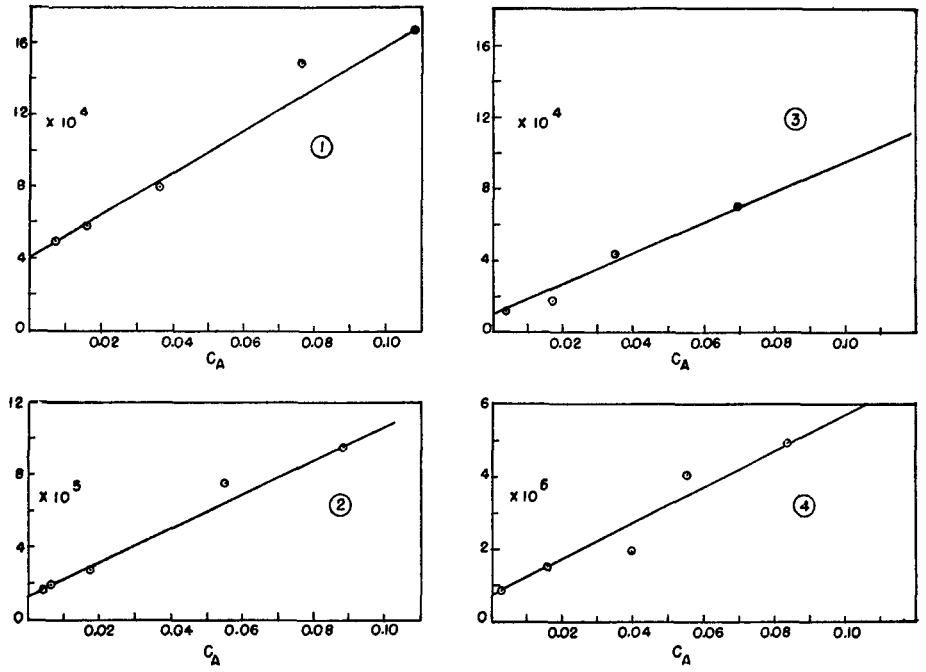

FIG. 2. Plots of antilog $1/0{\cdot}03007\ \{(E_{1/2})_s - (E_{1/2})_c\}$ *Vs.* concentration of (1) glutamate, (2) glycinate, (3) valinate and (4) aspartate in lead-amino acid anion systems.

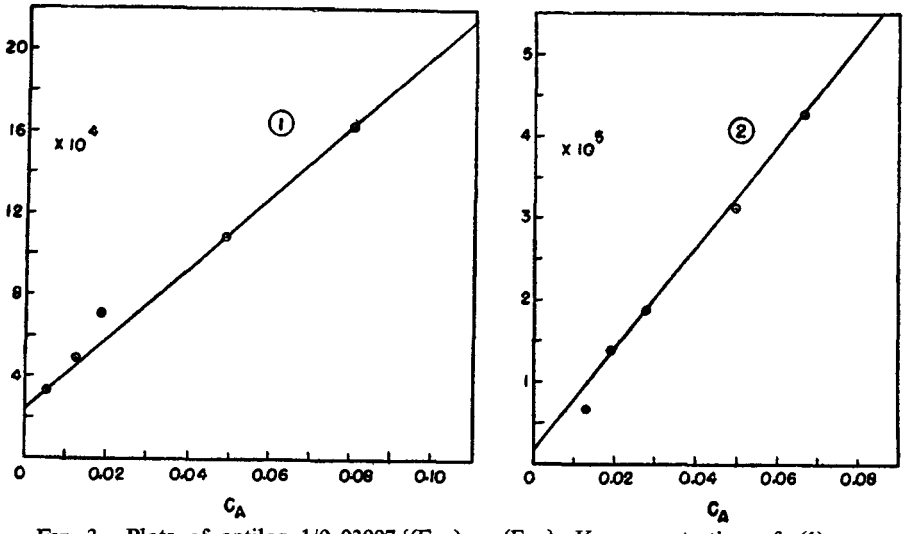

FIG. 3. Plots of antilog $1/0{\cdot}03007\ \{(E_{1/2})_s - (E_{1/2}\}_c$ *Vs.* concentration of (1) asparaginate and (2) α-alaninate in lead-amino acid anion systems.

the value of β_{PbA_2}. The logarithm of stability constants of Pb $(gl)_2$, Pb $(aspt)_2^{2-}$ and Pb $(glut)_2^{2-}$ obtained in the above analysis, *viz.*, 6·97, 7·69

and 6·07 compare favourably with the values 7·08, 7·38 and 6·22 obtained at higher concentrations of the amino acid anion, justifying the assumptions made in the above analysis. The stability constants of all the complexes are given in Table VI.

TABLE VI

*Formulae and thermodynamic constants for lead amino acid complexes**

Formula	$-\log K_d$	ΔF° K. cals.	E. *vs.* N.H.E. (volts)	Formula	$-\log K_d$	ΔF° K. cals.	E. *vs.* N.H.E. (volts)
$Pb(gl)_1^+$	5·11	7·08	0·283	$Pb(aspt)_2^{2-}$ ..	7·38	10·24	0·352
$Pb(gl)_2$	7·08	9·83	0·343	$Pb(aspt)_1$	5·88	8·16	0·307
$Pb(\alpha\text{-al})_2(OH)_1^-$ ..	9·85	13·66	0·426	$Pb(glut)_2^{2-}$ ..	6·22	8·63	0·317
$Pb(\alpha\text{-al})_2$	6·83	9·47	0·334	$Pb(glut)_1$	4·60	6·38	0·268
$Pb(\alpha\text{-al})_1^+$ ..	4·18	5·80	0·255	$Pb(aspg)_2(OH)_1^-$ ..	10·02	13·91	0·431
$Pb(\beta\text{-al})_2(OH)_2^{2-}$ ..	12·11	16·79	0·494	$Pb(aspg)_2$	6·23	8·64	0·317
$Pb(val)_2(OH)_1^-$ ..	9·41	13·06	0·413	$Pb(aspg)_1^+$ ..	4·36	6·05	0·261
$Pb(val)_2$	5·89	8·17	0·307	$Pb(gl)_2(CO_3)_1^{2-}$ ..	8·61	11·95	0·389
$Pb(val)_1^+$	4·02	5·58	0·250	$Pb(aspt)_2(CO_3)_1^{4-}$ ..	8·88	12·31	0·397

* ΔF° = Free energy for deissocialcon of the complex.
E = Standard potencial for the formation of the complex.

2. *Effect of Concentration of Amino Acid Anion at Constant pH*

Since the half-wave potentials are practically the same at pH 9·65 and 11·30 (Table I) at constant concentration of glycinate, aspartate and glutamate ions, it may be concluded that hydroxy group does not enter the complex under these conditions. Application of Lingane's equation to the shift in the half-wave potential at various concentrations of glycinate, aspartate and glutamate ions indicate the entry of two groups.

In lead-asparagine, lead-valine and lead-α alanine systems, the half-wave potentials have shifted by about 30 millivolts per pH unit, at constant amino acid anion concentration indicating the formation of a monohydroxy complex.

The half-wave potential shifts, at different amino acid anion concentrations, indicate the entry of two amino acid anion groups. In lead-β alanine system similar argument leads to the following formula:

$$Pb\ (\beta\text{-al})_2\ (OH)_2^{2-}.$$

The plots of $E_{1/2}$ *Vs.* log C_A given in Figs. 4 and 5 are straight lines. These plots are used to obtain the value of $E_{1/2}$ at log $C_A = 0$ for calculating the stability constants.

3. *Complex Formation in Sodium Hydroxide Solutions*

It has already been pointed out that mixed hydroxy complexes are not formed. Application of Lingane's equation indicates that a complex with three hydroxyl groups is formed. The dissociation constant of the hydroxy complex ($10^{-11.7}$) compares favourably with that calculated from the results obtained by Lingane ($10^{-11.8}$ in 1 M solutions of sodium hydroxide).

4. *Complex Formation in Sodium Carbonate Solutions*

Subrahmanya[6] has reported the formation of mixed complexes of lead with ethanolamine and carbonate. In the present work evidence is obtained for the formation of Pb $(gl)_2\ CO_3^{2-}$ and Pb $(aspt)_2\ CO_3^{4-}$. In the case of α-alanine and asparagine conclusions regarding the composition of the complexes formed are more involved since at pH 9 to 10 lead forms mixed hydroxy complexes in presence of both these amino acids. The shift obtained by varying the concentration of sodium carbonate at constant concentration of amino acid anion (0·5 and 1·0 M) corresponds to the entry of one carbonate group. Since the potentials with 0·50 and 1·0 M amino acid anion + 0·05 M sodium carbonate are very close to those in 0·50 and 1·00 M amino acid anion, it is not possible to get at the composition of the complex.

5. *Complex Formation in Presence of Ammonia and Ammonium Nitrate*

As in the cadmium system,[4] the pH changes accompanying the mixing of the reagents have to be taken into account in interpreting the half-wave potential data. The results obtained (Table IV) indicate that at the concentration of the amino acid anion the half-wave potentials of solutions containing

(*a*) amino acid anion only;

(*b*) amino acid anion + different concentrations of ammonia are practically the same indicating that the nature of the complexes in all

the solutions is the same. It can therefore be concluded that ammonia does not enter the complex under these conditions. The composition of the various complexes present in ammoniacal solutions is the same as in pure amino acid anion solutions, under the same pH conditions.

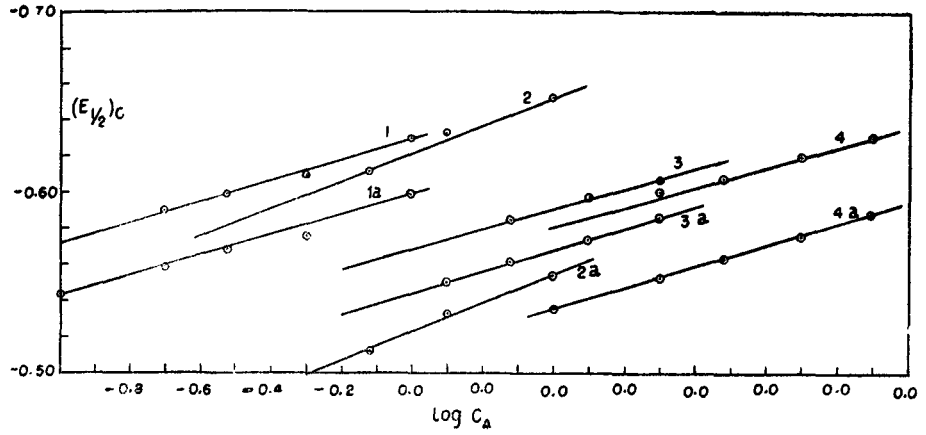

FIG. 4. Variation of half-wave potential with log concentration of amino acid anion in lead-amino acid systems. Curves 1 to 4 are obtained with α-alaninate (pH 11·0), β-alaninate (pH 41·6), valinate (pH 11·0), and asparaginate (pH 11·15) while curves 1 *a* to 4 *a* are obtained with α-alannate (pH 9·7), β-alaninate (pH 10·1), valinate (pH 10·2) and asparaginate (pH 9·8). The *x*-axis is shifted by 0·4 units for β-alaninate and valinate and by 0·6 units for asparaginate.

6. *Thermodynamic Data from Polarographic Measurements*[6]

In the present work the stability constants of pure complexes have been determined mostly by Lingane's method, employing the plot of $E_{1/2}$ *Vs.* log concentration of the amino acid anion. For mixed complexes where the half-wave potentials in 1 M solution of the ligands are not available, the following extension of Lingane's formula for pure complexes is used:

$$(E_{\frac{1}{2}})_{\text{complex ion}} - (E_{\frac{1}{2}})_{\text{simple ion}}$$

$$= \frac{0\cdot06014}{n} \log K_d - p_1 \frac{0\cdot06014}{n} \log C_{x_1} - p_2 \frac{0\cdot06014}{n} \log C_{x_2}.$$

The modified Hume and Deford's equation (employed by McKenzie and Mellor[1]) has been used to obtain the formation constants of 1 : 1 and 1 : 2 complexes of lead in glycine, α-alanine, valine, aspartic acid, glutamic acid, and asparagine systems. The half-wave potential of lead ion at 30° C. in 1 normal KNO_3 is taken to be −0·409 V *Vs.* S.C.E.[7] The standard potential

for the reduction reaction $Pb^{2+} + 2e = Pb$ at 30° C. is taken to be equal to −0·130 V *Vs.* N.H.E.[7] The thermodynamic data on different complexes noticed in the present work are given in Table VI.

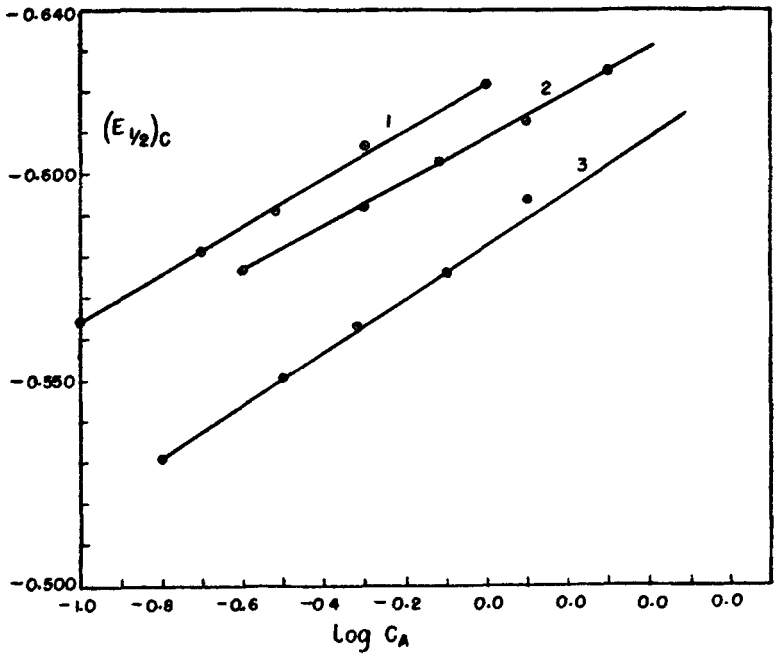

FIG. 5. Variation of half-wave potential of lead with log concentration of amino acid anion, n lead-amino acid systems. Curves 1 to 3 are obtained with glycinate, aspartate and glutamate. The *x*-axis is shifted by 0·2 unit each for aspartate and glutamate.

7. *Comparison with the Previous Work*

The value 7·08 obtained in the present work for $-\log K_d$ of Pb $(gl)_2$ compares well with the value of 7·4 reported by McKenzie and Mellor[1] by the polarographic method, considering the variation in experimental conditions. Bapna and Karmalkar[2] reported a value of 5·27 for $-\log K_d$ of Pb $(gl)^+$ and Keefer[9] obtained a value of 5·17 for the same complex by the solubility method. The value obtained in the present study 5·11 agrees well with these values. Tsai-Teh and Teh Liang Chang[8] reported the formation of mixed hydroxy glutamate complexes such as Pb $(glut)_1$ $(OH)^-$, Pb $(glut)_2$ $(OH)^{3-}$ and Pb $(glut)_3$ $(OH)^{5-}$ at pH 8·3. The results reported in the present work do not support the formation of such complexes. It is evident from the data presented in Table I that hydroxy group does not enter the complex and that only Pb $(glut)_2^{2-}$ is formed below pH 10·5 when the concentration of glutamate is between 0·10 and 0·80 M.

Summary

1. The polarographic behaviour of glycine, α-alanine, β-alanine, valine, aspartic acid, glutamic acid and asparagine complexes of lead has been studied at various pH values and in presence of (1) NaOH, (2) Na_2CO_3 and (3) $NH_4NO_3 + NH_4OH$. All the polarographic waves have been found to be reversible.

2. Experiments conducted on the effect of variation of pH, *i.e.*, $7 < pH < 9$ (varying slightly in different cases), on half-wave potential keeping the total concentration of amino-acid have indicated the formation of Pb A and Pb A_2. The data have been analysed employing the equations developed by DeFord and Hume as modified by McKenzie and Mellor.

3. Only pure complexes are produced below pH 11·2 in the case of aspartic acid, glutamic acid and glycine, while mono hydroxy complexes are produced in α-alanine, valine and asparagine systems.

4. It has been found that no mixed hydroxy and mixed ammonia complexes are produced in presence of sodium hydroxide and ammonia-ammonium nitrate, respectively. However evidence is obtained for the formation of mixed carbonate complexes in glycine and aspartic acid systems in presence of sodium carbonate.

5. Thermodynamic data have been calculated from polarographic measurements for 18 complexes.

6. The suitability of incorporating amino acids in base solutions for the polarographic estimation of lead has been tested.

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References

1. McKenzie, H. A. and Mellor, D. P. — *Aust. J. Chem.*, 1961, **14**, 562.
2. Bapna, T. and Karmalkar, H. — *J. Vikram Univ.*, 1957, **3**, 101.
3. Nageswara Rao, G. and Subrahmanya, R. S. — *J. sci. industr. res.*, 1962, **21 B**, 193.
4. ———— .. *Proc. Ind. Acad. Sci.*, 1964, **60 A**, 165.

5. Laitinen, H. A., Onstott, E., Bailar, J. C. (Jr.) and Swann, S. — *J. Amer. Chem. Soc.*, 1950, **72**, 2484.

6. Subrahmanya, R. S. .. *Proc. Ind. Acad. Sci.*, 1956, **43 A**, 383.

7. ———— .. *Ibid.*, 1957, **46 A**, 433.

8. Tsai-Teh and Teh Liang Chang — *Anal. Chem.*, 1961, **33**, 1953.

9. Keefer, R. M. and Reiber, H. G. — *J. Amer. Chem. Soc.*, 1941, **63**, 689.