Studies on Uranyl Complexes. II. Unidentate Carboxylate Coordination in Uranyl Complexes of α-, β-, and γ-Amino Acids: A Polarographic Study[††]

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Polarographic investigation of uranyl complexes with potentially bidentate α-, β-, and γ-amino acids have been carried out. The polarographic behaviour of these complexes as a function of pH and ligand concentration has revealed the nature of binding to be unidentate carboxylate coordination in the complexes. The amino group is not involved in coordination. The relative stabilities of α-, β-, and γ-amino acid complexes are discussed.

While the chelates formed by amino acids with 3d metal ions have been fairly well characterized, the amino acid complexes of *f* block metal ions have received relatively much less attention. Even among the few investigations carried out on uranyl–amino acid complexes reports are conflicting regarding the chelating ability of the amino acids towards this ion, and the effect of ring size and substituents of the complexes. Cefola *et al.*,[1] Farooq *et al.*,[2] and Tewari *et al.*[3] have postulated chelation involving the carboxyl oxygen and the amino nitrogen in uranyl complexes with glycine, α-alanine, asparagine and glutamine, while Li *et al.*[4] and Feldman *et al.*[5] have suggested that the amino nitrogen is not involved in coordination in uranyl complexes of glycine, serine, aspartic acid and glutamic acid.

The present investigation is oriented primarily towards establishing the nature of binding in uranyl complexes with simple amino acids, *i.e.* to find whether complexation occurs through the amino nitrogen and carboxyl oxygen leading to chelation or whether the ligand is bound only through the carboxyl oxygen. When a complex is reduced under polarographic conditions, the magnitude of the shift in $E_{1/2}$ relative to the simple aqua ion is a measure of the stability of the complex. A chelate complex shows, because of its higher stability, a much larger shift in $E_{1/2}$ than a non-chelate one. Further the amino acid ligand (anion) on liberation from the complex undergoing polarographic reduction gets protonated depending on pH conditions. A study of the polarographic behaviour under varying pH conditions yields useful information on the way in which the ligand is bound as an anion or as a zwitter ion and so on, from which the nature of binding can be inferred.[6,7] Stability constants obtained from polarographic measurements of the complexes are reported.

Experimental

The effect of varying pH on the $E_{1/2}$ of uranyl complexes at constant concentration of ligand and the effect of varying ligand concentration on $E_{1/2}$ at constant pH were investigated by measuring the $E_{1/2}$ values for solutions containing 8×10^{-4} M (M=mol dm^{-3}) $UO_2(ClO_4)_2$ maintained at a constant ionic strength of 0.1 M with respect to $NaClO_4$ and at a temperature of 30.0±0.1 °C. The polarograms were recorded with an automatic Metrimpex type OH 105 Universal Polarograph with a three-electrode set up. Some of the complexes were studied with a manual set up consisting of the polarographic bridge of Physics Instruments Co., in conjunction with a Multiflex galvanometer for measuring diffusion currents and a Leeds Northrup K 3 Universal Potentiometer for measuring the applied potentials. The electrode characteristics were: h=40.0±0.5 cm, t=3.85 s, and $m^{2/3}t^{1/6}=4.25$ mg$^{2/3}$ s$^{-1/2}$. The $E_{1/2}$ values were measured to an accuracy of ±0.5 mV and were reproducible to ±2 mV. The reversibility of each system studied was checked by logarithmic analysis or by measuring the difference in $E_{1/4}-E_{3/4}$ values. The reduction of UO_2^{2+} ion was found to be a reversible one electron process with an $E_{1/2}$ of −0.175 V (*vs.* SCE).

Conductometric titrations of the sodium salts of the ligands against uranyl perchlorate were performed for determining the maximum number of ligand molecules coordinated to the uranyl ion. A direct-reading conductance meter (Toshniwal Conductivity Analyser type L 01.06) provided with a cell of cell constant 0.738 was used. All pH measurements were made with an Elico pH meter (Model L I.10T). The dissociation constants of the amino acids were determined potentiometrically. All the chemicals used were of BDH or Fluka puriss grade.

Results and Discussion

The ligands chosen were glycine, DL-α-alanine, DL-2-aminobutyric acid, β-alanine, 4-aminobutyric acid and isobutyric acid, all except the last one potentially bidentate ligands capable of forming five-, six-, or seven- membered rings. Isobutyric acid was chosen as a reference ligand having only unidentate function through its carboxyl group. A comparison of the shift in $E_{1/2}$ for polarographic reduction of the amino acid complexes with that for the isobutyrate complex would show whether chelation occurs or not, and if it occured, yield information correlating ring size and stability of the complex.

Effect of pH *on the* $E_{1/2}$ *of the Complexes.* The manner in which $E_{1/2}$ depends on pH often provides useful information regarding the electrode reactions and the different species existing under different pH conditions and thus the mode of binding in the complex.

The coordinating(donor) atom exists in the protonat-

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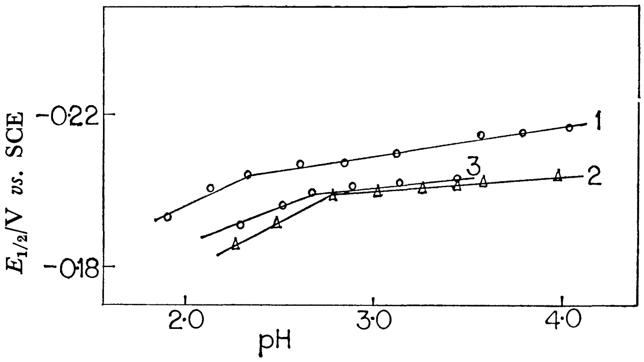

Fig. 1. Uranyl-α-amino acid complexes: plot of pH *vs.* $E_{1/2}$. 1: Glycinate, 2: α-alaninate and 3: DL-2-aminobutyrate. Concentrations: $[UO_2^{2+}]=0.0008$ M, [glycine]=0.1067 M, [α-Alanine]=0.09114 M, [2-aminobutyric acid]=0.1063 M.

TABLE 1. STABILITY CONSTANTS OF URANYL COMPLEXES OF α-, β- AND γ-AMINO ACIDS

Complex	Dissociation constants of ligands		pH range	$\log \beta UO_2(HL)_2^{2+}$
	pK_{COOH}	$pK_{NH_3^+}$		
Glycinate	2.45	9.69	2.5—4.0	2.14
α-Alaninate	2.48	9.67	2.7—4.0	2.15
2-Aminobutyrate	2.36	9.60	2.7—4.0	2.12
β-Alaninate	3.60	10.07	3.5—4.3	3.49
4-Aminobutyrate	4.04	10.26	3.00—4.10 and 4.1—5.4	4.44
Isobutyrate	4.76	—	3.00—4.8	5.66[a)]

a) $\log \beta_{ML_2}$

ed form over a range of pH, and complexation takes place with deprotonation. On polarographic reduction of the complex, the liberated ligand will recombine with protons if pH conditions suit such protonation. In solutions of pH greater than the p*K* of the coordinating group, protonation would not occur. If, however, the solution pH is below the p*K* of the coordinating group, the released ligand will get protonated. A plot of the variation of the measured $E_{1/2}$ with pH would show breaks corresponding to the p*K* values of the coordinating groups present in the ligand.

For the potentially bidentate amino acid with amino and carboxyl groups as possible coordinating groups the following relationships between $E_{1/2}$ and pH are valid.

1. At $pH<pK_{COOH}<pK_{NH_3^+}$:

$$E_{1/2} = E_s^\circ - \frac{0.0591}{n}\log \beta_{ML_p} - p\frac{0.0591}{n}\log K_1K_2[L^-] - 2Z\frac{0.0591}{n}pH.$$

2. At $pH=pK_{COOH}<pH<pK_{NH_3^+}$:

$$E_{1/2} = E_s^\circ - \frac{0.0591}{n}\log \beta_{ML_p} - p\frac{0.0591}{n}\log K_2[L^-] - Z\frac{0.0591}{n}pH.$$

3. At $pH>pK_{NH_3^+}>pK_{COOH}$:

$$E_{1/2} = E_s^\circ - \frac{0.0591}{n}\log \beta_{ML_p} - p\frac{0.0591}{n}\log [L^-].$$

Here K_1 and K_2 correspond to pK_{COOH} and $pK_{NH_3^+}$ respectively. $E_{1/2}$ is the half-wave potential of the complex and E_s° is the standard reduction potential of the cation $\simeq E_{1/2}$ of the uncomplexed aqua ion; β_{ML_p} is the overal stability constant of the complex ML_p, and *Z* is the number of protons involved in the electrode reaction.

The slope $d(E_{1/2})/d(pH)$ of each region of the $E_{1/2}$ *vs.* pH diagram is equal to $0.0591/n\ Z$, where *Z* is the number of protons involved in the electrode reactions which will be 2, 1, and 0 at $pH<pK_{COOH}$, $pK_{COOH}<pH<pK_{NH_3^+}$, and $pH>pK_{NH_3^+}>pK_{COOH}$, respectively.

Uranyl-α-Amino Acid Complexes. The variation of $E_{1/2}$ as a function of pH was investigated between pH 1.80 and 4.0 with all the three α-amino acid complexes. The $E_{1/2}$ *vs.* pH diagrams (Fig. 1) show breaks at pH values 2.35 for glycinate, 2.70 for α-alaninate, and 2-aminobutyrate complexes. The pK_{COOH} values of these acids are presented in Table 1. Below pH 1.80 the $E_{1/2}$ values were found to be independent of pH with a constant value of −0.175 V (*vs.* SCE). Since this is the $E_{1/2}$ of the uncomplexed aqua uranyl cation, the inference is that no complexation occurs. Beyond pH 4.0 the polarograms were distorted possibly due to hydrolysis. In the region of $pH>pK_{COOH}$, the $E_{1/2}$ values were very nearly independent of pH upto about pH 4 in all the cases. With the experimental pH below the $pK_{NH_3^+}$ of the acids concerned, the amino group, if involved in coordination, would get protonated at the electrode surface on liberation when the complex undergoes polarographic reduction. No such protonation was indicated from the experimental studies. The inference is that the amino group is not involved in coordination. In other words, no chelate ring is formed.

The effect of the ligand concentration was investigated at pH 3.15±0.1 for glycinate, 3.25±0.1 for α-alaninate, and at pH 3.5±0.1 for 2-aminobutyrate complex. The plots of $E_{1/2}$ *vs.* log HL[10)] for all the three complexes gave a (*p*-*q*) (where *p* and *q* are the number of ligands attached to the metal in the oxidised and reduced forms respectively) value of two in the ligand concentration range of 0.17—0.6 M. Since polarographic reduction of the complexed $(UO)_2^{2+}$ ion occurs only to the lower oxidation state (UO_2^+) and not to the metallic state, the variation of $E_{1/2}$ with ligand concentration will indicate only the difference in the number of ligands coordinated to the higher and lower oxidation states and thus only the ratio of stability constants of the complex between the oxidized and reduced forms can be determined.[8)] However, if the absolute value of '*p*' or '*q*' is known, it is possible to calculate the individual stability constants.[9)] The value of '*p*' was found to be two from conductometric titrations. Figure 3 gives the conductemetric titration of the sodium salt of α-alaninate against uranyl perchlorate. The break at 5 ml of uranyl perchlorate corresponds to the formation of the complex species with the metal: ligand ratio of

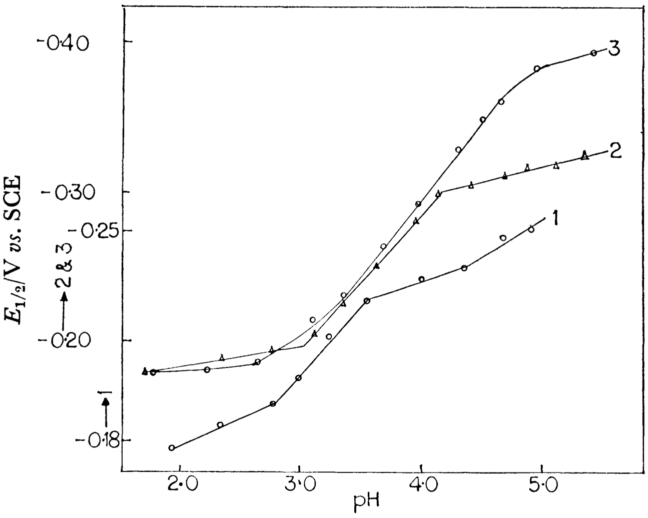

Fig. 2. Variation of $E_{1/2}$ with pH for uranyl complexes. 1: β-Alaninate, 2: 4-aminobutyrate and 3: isobutyrate. Concentrations: $[UO_2^{2+}]=0.0008$ M, [β-alanine]$=0.1007$ M, [4-aminobutyric acid]$=0.1008$ M, [isobutyric acid]$=0.100$ M.

1:2. The value of '*p*', the maximum number of ligands coordinated to the metal is thus 2. Since (*p*-*q*) values determined polarographically are also found to be equal to two, it is evident that '*q*' is zero and that UO_2^+ ion does not form a complex. The stability constants of the complexes calculated using Lingane equation[10] give the $\log \beta_{M(HL)_2^{2+}}$ values presented in Table 1.

The similarity in the nature of binding in these complexes is evident from (a) the identical nature of the $E_{1/2}$ *vs.* pH curves, (b) the similar $\Delta E_{1/2}$ values for similar concentrations of the ligands under similar conditions of pH and (c) the close similarity in the $\log \beta_{M(HL)_2^{2+}}$ values. The low $\log \beta_{M(HL)_2^{2+}}$ values are indicative of the absence of chelation. The electrode reaction for all the three complexes may be expressed in the general form (at $pH > pK_{COOH}$)

$$UO_2(HL)_2^{2+} + e^- \rightleftharpoons UO_2^+ + 2HL,$$

HL being the zwitter ion of the type of $H_3N^+-CH_2-COO^-$.

Uranyl-β-Alaninate Complex. The variation of $E_{1/2}$ with pH investigated in the pH region of 1.90—4.90 indicated that below pH 1.90 complexation did not occur and beyond pH 4.90 the polarograms were distorted. The $E_{1/2}$ *vs.* pH diagram (Fig. 2) showed a break at pH 3.5 corresponding to pK_{COOH} of β-alanine (*cf.* Table 1). In the pH region between 2.75 and 3.5 the $d(E_{1/2})/d(pH)$ slope has a value of 0.055 corresponding to the involvement one proton per metal atom in the reduction process. The variation of $E_{1/2}$ with ligand concentration indicated the (*p*-*q*) value to be one. However, conductometric titrations of the sodium salt of β-alanine with uranyl perchlorate indicated the value of '*p*' to be two. It is evident that one ligand molecule is coordinated to the UO_2^+ ion. The electrode process may be formulated as (at $pH < pK_{COOH}$)

$$UO_2(HL)_2^{2+} + H^+ + e^- \rightleftharpoons UO_2(HL)^+ + H_2L^+$$

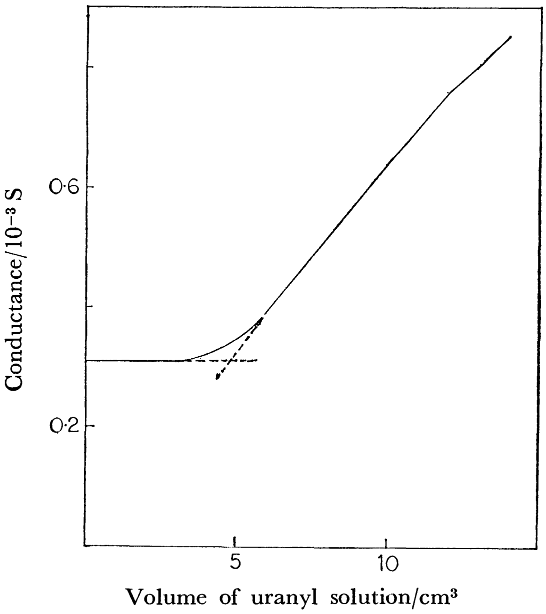

Fig. 3. Concudctometric Titration of sodium salt of α-alanine *vs.* uranyl perchlorate. 10 ml of ligand (0.08072 M)+100 ml water titrated against uranyl perchlorate (0.0801 M).

H_2L^+ being the species $H_3N^+-(CH_2)-COOH$.

In the pH region beyond pK_{COOH}, the $E_{1/2}$ values were very nearly independent of pH upto about pH 4.30, beyond which once again the $E_{1/2}$ values became pH dependent possibly due to hydrolytic reactions and formation of hydroxo species. The fact that protons are not involved in the reduction process in the pH region between 3.5 and 4.3 leads to the inference that the amino nitrogen is not coordinated to the metal atom. The plot of $E_{1/2}$ *vs.* log HL indicated the value of (*p*-*q*) to be two in the ligand concentration range of 0.1 to 0.7 M. Since the value of '*p*' determined conductometrically was also equal to two, '*q*' was taken to be zero meaning that UO_2^+ ion was not complexed. The electrode reaction in this region is expressed by the following equation at $pK_{COOH} < pH < pK_{NH_3^+}$,

$$UO_2(HL)_2^{2+} + e^- \rightleftharpoons UO_2^+ + 2HL.$$

The stability constant was calculated using Lingane equation, and the $\log \beta_{M(HL)_2^{2+}}$ value was found to be 3.49 ± 0.05.

Uranyl-4-Aminobutyrate Complex. The variation of $E_{1/2}$ with pH (Fig. 2) indicated that below pH 1.70, UO_2^{2+} ion was not complexed and beyond pH 5.4, precipitation occurred for a metal concentration of 8×10^{-4} M and ligand concentration of 0.1 M. The break corresponding to pK_{COOH} (4.04) was observed at pH 4.10. In the pH region 3—4.1 the number of protons involved in the reduction was found to be two. The $E_{1/2}$ values were independent of pH at $pH > pK_{COOH}$, clearly indicating the absence of coordination by the amino nitrogen. The variation of $E_{1/2}$ with ligand concentration investigated at pH 4.9 indicated the value of (*p*-*q*) to be two, and the value of '*p*' was found to be two from conductometric titrations. The electrode processes between pH 3.00 and

4.10 ($pH<pK_{COOH}$)

$$UO_2(HL)_2^{2+} + 2H^+ + e^- \rightleftharpoons UO_2^+ + 2H_2L^+,$$

and at pH 4.9 ($pH>pK_{COOH}$)

$$UO_2(HL)_2^{2+} + e^- \rightleftharpoons UO_2^+ + 2HL.$$

The $\log \beta_{M(HL)_2^{2+}}$ calculated using the Lingane equation was found to be 4.44±0.05.

Uranyl–Isobutyrate Complex. Below pH 2.0 complexation of uranyl was not observed and above pH 5.7 the metal precipitated. The break in the $E_{1/2}$ *vs.* pH relationship (Fig. 2), was observed at 4.8, the pK_{COOH} of the ligand being 4.76. In the pH region below pK_{COOH} the $d(E_{1/2})/d(pH)$ has a value of 0.11 corresponding to the involvement of two protons in the reduction process. The effect of ligand concentration on $E_{1/2}$ was investigated at pH 3.05. The plot of $E_{1/2}$ *vs.* log L^- gave a value of two for (p-q) and the value of 'p' was found to be two from conductometric titrations. The stability constant ($\log \beta_{ML_2}$) was found to be 5.66±0.10. The electrode process may be formulated as ($pH<pK_{COOH}$)

$$UO_2L_2 + 2H^+ + e^- \rightleftharpoons UO_2^+ + 2HL.$$

Conclusions. The $\Delta E_{1/2}$ values for the typical amino acid complexes of uranyl reported here are lower than that for the unidentate complex formed by isobutyric acid. So are the $\log \beta_{M(HL)_2^{2+}}$ values. The results clearly indicate that the amino acids do not form chelate complexes with uranyl ion. Furthermore, the carboxyl group itself is rendered a poorer complexing site because its basicity is lowered by the proximity of the more basic amino group in the same molecule. It may be seen from the figures that $\Delta E_1/_2$ for uranyl ion in the presence of α-, β-, and γ-amino acids are all lower than the value in the presence of isobutyric acid for similar conditions of pH and ligand concentration. If chelate rings had been formed, the $\Delta E_{1/2}$ values would have been larger.

The range of pH in which the complexes undergo reduction reversibly before hydrolysis sets in is also indicative of the relative stabilities of the complexes. For α-amino acid systems the maximum pH upto which hydrolysis can be neglected is 4.0, 4.9 for β-alaninate, 5.4 for 4-aminobutyrate, and 5.7 for isobutyrate complexes.

The order of stability of uranyl complexes in the present investigation turns out to be isobutyrate>4-aminobutyrate>β-alaninate>glycinate=α-alaninate=2-aminobutyrate. This order clearly points to the absence of chelation in uranyl amino acid complexes.

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