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POLAROGRAPHIC STUDY OF URANYL-AMINO ACIDS COMPLEXES—I: U(VI) IN GLYCINE, DL-α AND β-ALANINES AND HISTIDINE

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ABSTRACT

Complexation of glycine (gl), dl-α alanine (α-al), β-alanine (β-al) and histidine (hist.) with uranium(VI) has been followed polarographically in aqueous medium. Stability constants (at 26 ± 0·5° C) at 0·5 M ($NaClO_4$) ionic strength have been determined by graphical and numerical methods. Glycine formed two complexes with their respective stability constants: log $\beta_1 = 1{\cdot}34 \pm 0{\cdot}04$, log $\beta_2 = 2{\cdot}72 \pm 0{\cdot}02$; α-alanine formed three complexes with their stability constants: log $\beta_1 = 2{\cdot}04 \pm 0{\cdot}02$, log $\beta_2 = 2{\cdot}08 \pm 0{\cdot}04$, β_3 is negative indicating the absence of 1 : 3 complex species, and log $\beta_4 = 3{\cdot}85 \pm 0{\cdot}04$; β-alanine gave one complex species with: log $\beta_1 = 3{\cdot}41 \pm 0{\cdot}01$ and histidine also formed one complex species with log $\beta_1 = 1{\cdot}45 \pm 0{\cdot}05$.

INTRODUCTION

THE uranyl ion UO_2^{++} is the most commonly occurring entity in uranium(VI) chemistry. A large number of complexes of amino acids have been studied by potentiometry and spectrophotometry with metals[1]. In contrast, only a small number of uranyl complexes have been described polarographically with amino acids. The present paper deals with the polarographic investigations of U(VI)-gl, U(VI)-α-al, U(VI)-β-al and U(VI)-hist. systems at 26° ± 0·5° C in the pH range of 4·8 to 5·0.

EXPERIMENTAL

Materials and Methods

Uranyl nitrate and the complexing agents used were of BDH AnalaR grade, except histidine which was obtained from V.P. Chest Institute, New Delhi. Sodium perchlorate (E. Merck) was used to maintain the ionic strength constant at 0·5 M. All solutions were prepared in glass distilled water.

Half-wave potentials and diffusion currents were measured on Cambridge Recording Polarograph. De-oxygenation of the solutions was achieved by purified nitrogen gas. The saturated calomel electrode (SCE) was used as a reference electrode. The half-wave potentials were obtained from the log-plots. The dropping mercury electrode (DME) had the following characteristics:

$t = 3{\cdot}1$ sec. in 0·5 M $NaClO_4$ (open circuit) and $m = 1{\cdot}96$ mg sec^{-1}.

The cell resistance was found to be low in all cases.

RESULTS AND DISCUSSION

(i) *Uranyl-glycine system*

In each solution the concentration of uranyl nitrate was maintained constant at 1 mM while glycine concentrations varied from 0·02 M to 0·35 M. The half-wave potential of the one electron reduction of U(VI) was 0·180 V, which increased in the presence of glycine to a more negative value indicating complex formation (Table I).

The relationship between $-(E_{1/2})_c$ and log C_L where C_L is the ligand concentration, was not linear but gave a smooth curve formed by the super-position of two segments, showing the existence of 1 : 1 and 1 : 2 complex species. The method of DeFord Hume[2] gave the following values for the stabilities:

log $\beta_1 = 1{\cdot}34 \pm 0{\cdot}040$ and log $\beta_2 = 2{\cdot}72 \pm 0{\cdot}02$.

These values do not quite agree with those obtained potentiometrically by M. Cefola *et al.*[3] owing to the differences in ionic strength, electrolyte used and temperature.

(ii) *Uranyl-dl-α-alanine and uranyl-β-alanine systems*

The concentrations of dl-α-alanine and β-alanine varied from 0·01 M to 0·27 M and from 0·01 M to 0·26 M respectively (Table I). dl-α-alanine formed 1 : 1, 1 : 2 and 1 : 4 complexes. A negative value of β_3 indicated the absence of 1 : 3 complex species in the solution. DeFord–Hume method yields the following values for the stabilities:

log $\beta_1 = 2{\cdot}04 \pm 0{\cdot}02$, log $\beta_2 = 2{\cdot}08 \pm 0{\cdot}04$ and log $\beta_4 = 3{\cdot}85 \pm 0{\cdot}02$.

Only one complex (1 : 1) was detected with β-alanine (Table I). Stability constant, calculated by Lingane method[4], was log $\beta_1 = 3{\cdot}41 \pm 0{\cdot}01$.

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TABLE I

U(VI) = 1 mM; $\mu = 0{\cdot}5$ M ($NaClO_4$); $-(E_{1/2})_s = -0{\cdot}180$ V; Temp. = 26 ± 0·5° C

dl-α-al conc. M	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·10	0·12	0·14	0·16	0·18	0·20	0·22	0·24	0·27
$-E_{1/2}$ V	0·188	0·204	0·213	0·220	0·224	0·228	0·232	0·235	0·240	0·245	0·250	0·255	0·260	0·266	0·270	0·275	0·280
i_d μA	3·30	3·22	3·15	3·15	3·08	3·00	3·00	2·92	2·85	2·85	2·85	2·77	2·77	2·70	2·70	2·70	2·70
gl conc. M		0·02	0·04	0·06	0·08	0·10	0·12	0·14	0·16	0·20	0·24	0·28	0·32	0·35			
$-E_{1/2}$ V		0·188	0·204	0·215	0·220	0·228	0·236	0·243	0·248	0·258	0·267	0·275	0·280	0·285			
i_d μA		3·52	3·37	3·22	3·00	2·92	2·92	2·92	2·92	2·85	2·77	2·70	2·70	2·70			
β-al conc. M	0·01	0·02	0·03	0·04	0·05	0·06	0·08	0·10	0·12	0·14	0·16	0·18	0·20	0·23	0·26		
$-E_{1/2}$ V	0·260	0·280	0·290	0·300	0·305	0·310	0·318	0·324	0·329	0·333	0·338	0·340	0·342	0·346	0·350		
i_d μA	3·00	2·85	2·78	2·48	2·25	2·17	1·95	1·87	1·80	1·80	1·73	1·73	1·65	1·65	1·65		
His. conc. M	0·05	0·06	0·07	0·08	0·10	0·12	0·15	0·20	0·24	0·28							
$-E_{1/2}$ V	0·193	0·195	0·197	0·199	0·202	0·205	0·209	0·213	0·216	0·220							
i_d μA	3·08	3·00	2·92	2·85	2·77	2·77	2·77	2·70	2·70	2·70							

(iii) *Uranyl-histidine system*

All the experimental conditions were same as in the previous systems, only the concentrations of histidine varied from 0·02 M to 0·28 M (Table I). Only a single (1 : 1) complex was observed[4] with $\log \beta_1 = 1{\cdot}45 \pm 0{\cdot}05$.

Herasymenko[5] published the first account of the polarographic reduction of uranium. He found that the reduction of the first wave was independent of the acidity of the solution, *i.e.*, the half-wave potential of the reduction is independent of the hydrogen ion concentration and hence the first reduction must be according to the equation

$$UO_2^{++} + e \rightleftharpoons UO_2^{+}$$

The half-wave potential found for this reduction in the present work is $-0{\cdot}180$ V which agrees well with the value obtained by Herasymenko[5].

As reported by Dhaneshwar[6], the hydrolysis and the disproportionation are the two main difficulties in the polarographic study of uranium. Hydrolysis of uranyl ion occurs even at pH 3·0 and at higher pH both the uranyl ion and the complex species are hydrolysed. But Ahrland[7] observed that the complexes could be investigated because of the fact that the complexes are hydrolysed to a small extent as the complexes have low ionic charge and fewer places of coordination. Large excess of the ligand also suppresses the hydrolysis considerably.

Second difficulty is the disproportionation of uranium. But it is negligible[8] above pH 3·0 and hence this effect can also be neglected in the present study as the pH of the solutions is about 5·0. DeFord-Hume method can be applied to the systems only when the reduction at DME takes place to the metallic state. In the present investigation, the uranium(VI) does not get reduced to the zero valence state and hence the method cannot be applied to the present systems. This is tentamount to saying that the stability constants obtained are the ratios of the stability constants of U(VI) to those of U(V). But it is evident from the slopes of the plots of $-(E_{1/2})_c$ *vs.* $\log C_L$ that U(V) does not form complexes with the ligands and therefore DeFord-Hume method can conveniently be applied to the systems.

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WORKSHOP ON *PHYTOPHTHORA* DISEASES OF TROPICAL CULTIVATED PLANTS

The above Workshop will be held at Central Plantation Crops Research Institute, Kasaragod, Kerala 670 124 and also at its Regional Station, Calicut, Kerala 673 011, from 19th to 23rd September 1980. The Workshop will consist of two parts. The first part, to be held at Kasaragod, will comprise presentation of reviews on *Phytophthora* diseases of tropical crops and sessions on various aspects of *Phytophthora* diseases. The Second part, to be held at Calicut will restrict itself to discussions on black pepper *Phytophthora*. The participants may attend either or both the parts. The last date for submission of contributed papers: *Abstracts*—15th May 1980; *Full papers*—30th June 1980. *Contributed papers* : Abstracts should not exceed 200 words in length, and full papers 1500 words. Further details can be had from Dr. N. M. Nayar, Director, Central Plantation Crops Research Institute, Kasaragod, Kerala 670 124.