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Polarographic Electroreduction of Uranyl Ion in Glycine, DL-Aspartic Acid and Phenylalanine-Aqueous Solutions

E. A. GOMAA*, A. H. EL-ASKALANY** AND M. N. H. MOUSSA

Chemistry Department, Faculty of Science
Mansoura University, Mansoura, Egypt

The electroreduction of uranyl perchlorate in presence of glycine, DL-aspartic acid and phenylalanine were studied by using DC polarography. Glycine and phenylalanine decrease slightly the limiting currents of the two reduction waves with also very small shift in their half wave potentials towards more negative values. DL-aspartic acid shift the half wave potential of the first one electron wave to more complexing direction and changes the second wave from two electron mechanism to one electron processes due to the increase of the pentavalent uranyl ion disproportionation in the presence of the last medium.

INTRODUCTION

The polarogram of uranyl ion in perchlorate medium shows two reduction waves with the least complexing character in comparing with other media[1,2]. The aim of this work is to study the effect of some amino acids on the polarographic behaviour of hexavalent uranyl ion in sodium perchlorate medium.

EXPERIMENTAL

Uranyl perchlorate was prepared by repeating evaporation of uranylnitrate (G. R. Merck) with $HClO_4$, is dissolved in 100 ml water to give 0.01 M uranyl solution. Its exact concentration is determined gravimetrically as U_3O_8. The measurments were done by using a Metrohm E 506 polarograph. The capillary characteristics were $m = 1.47$ mg/sec, $t = 3.6$ s/drop in 0.1 M KCl (open circuit) at a height of 30 cm Hg. Saturated Ag/AgCl electrode is used as a reference electrode.

The amino acids used, glycine, DL-aspartic acid and phenylalanine were of the type Merck, Prolabo and Riedel-De-Haēn AG, respectively. 0.01 M stock solutions of each were prepared.

RESULTS AND DISCUSSION

The polarogram of a 1×10^{-4} M uranyl perchlorate in 0.1 M $NaClO_4$ solution is shown in Fig. 1. The two waves observed are well defined and

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*Present address : Teachers Training College, Salalah, P.O. Boox 19905, Sultanate of Oman.

**Present address : Um-El-Kura University, Faculty of applied science, Mecca, Saudi Arabia.

a study of log $i/i_d - i$ function against potential show that the waves correspond to reversible electrochemical mono and di-electronic exchange

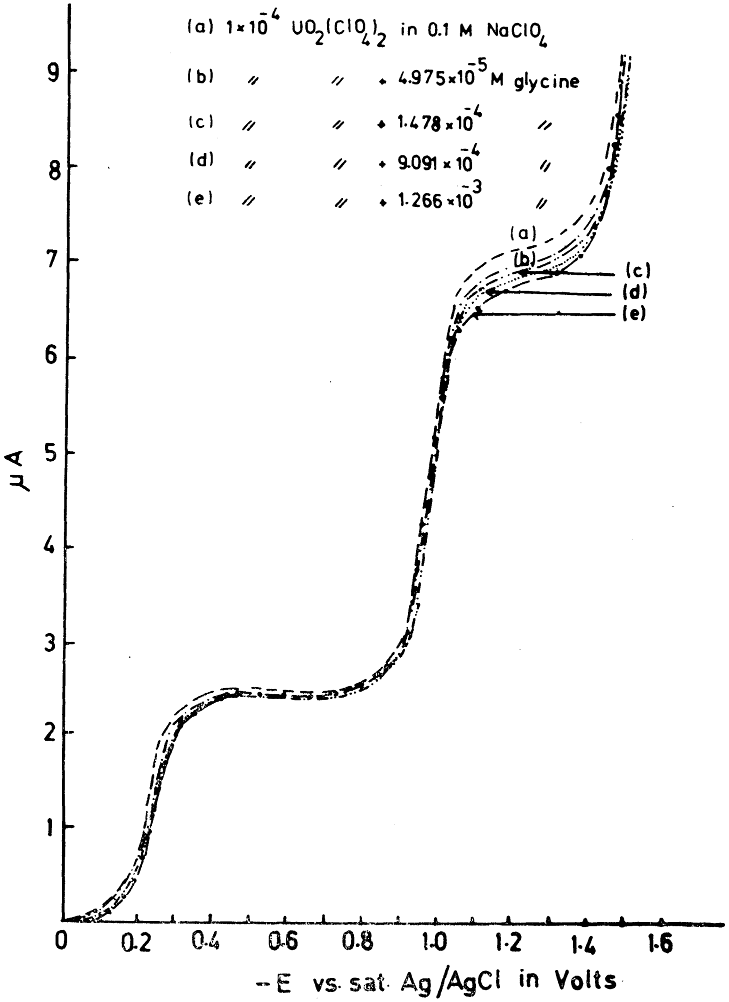


Fig. 1

reactions, respectively. On adding glycine to the above uranyl perchlorate solution in the range of $4.975 \times 10^{-5} - 1.266 \times 10^{-3}$ M, no shift in the half wave potentials of the waves, slight decrease in the limiting current (i_l) of the first wave and detectable decrease in the limiting current of the second wave (Fig. 1 & Table 1).

The polarograms of uranyl perchlorate in presence of different concentration of DL-aspartic acid appear in Fig. 2, show clearly that the limiting current of the second wave decrease gradually till it reach approximately to its half. The process also took place reversibly.

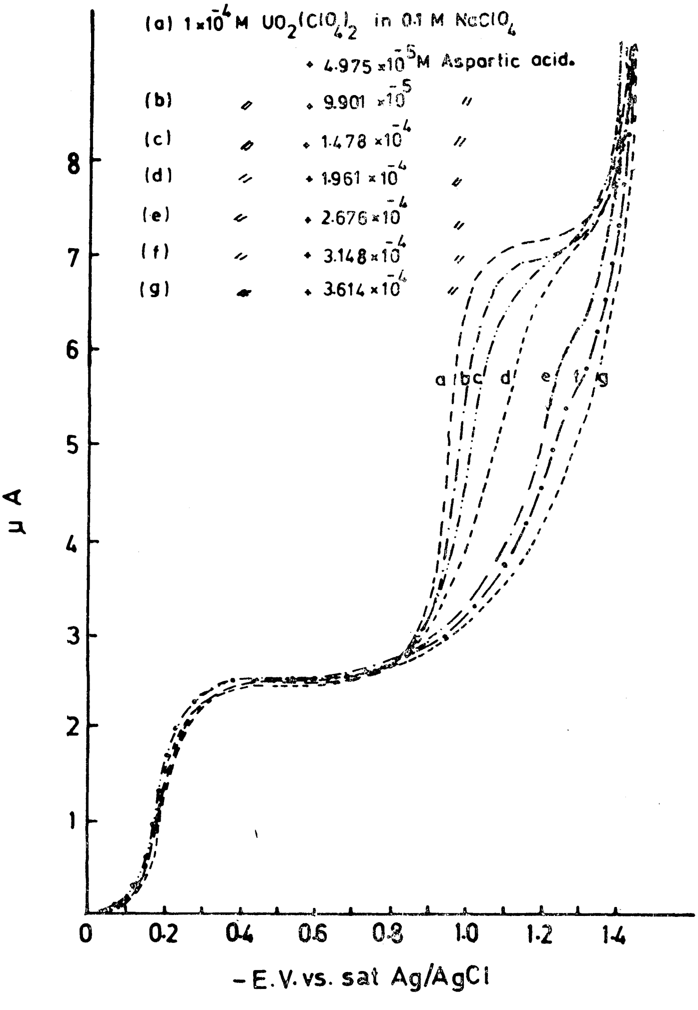


Fig. 2

Fig. 3 shows the effect of phenylalanine on the reduction waves of uranyl perchlorate in 0.1 M-$NaClO_4$ with slight shift in the limiting currents and half wave potentials of both the first and second waves. The interpretation of the results will depend on : (a) inductive effect in the three amino acids used, (b) the pH values of the medium in presence of amino acids, (c) the free energies of reduction for the first and second waves.

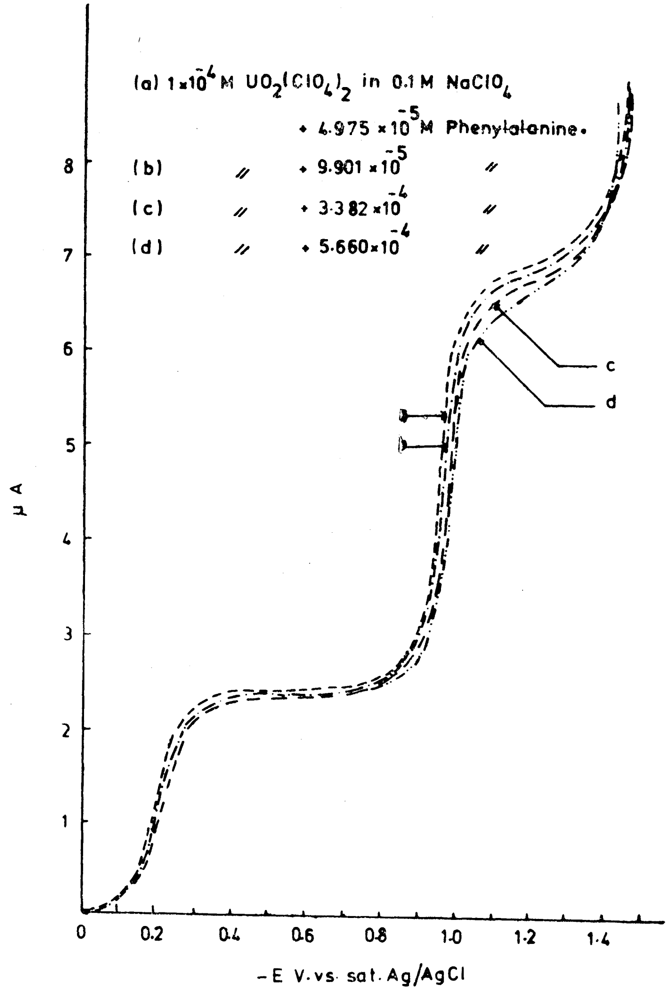
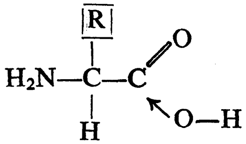
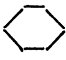


Fig. 3



R = H (Glycine)

= —COOH, (DL-aspartic acid)

= —CH_2, (phenylalanine)

As mentioned in Ref. 3, the carboxylic group in DL-aspartic acid has more inductive effect than the phenyl group in phenylalanine. The measured pH values of the saturated solutions of glycine, DL-aspartic acid and phenylalanine in water are 5.54, 2.34 and 6.76, respectively. Also the free energies of reduction of the hexavalent uranyl ion in presence of the amino acids under consideration were calculated by the use of the following equation:

$$\Delta G^0 = -nFE^0_{1/2} \text{ (vs. H.E.)} \tag{1}$$

as explained in literature[4,5], where n the number of electrons, F faraday constant and $E^0_{1/2}$ (vs. H.E.) is the half wave potential transferred from reference saturated Ag/AgCl electrode to hydrogen electrode[4]. The transfer free energies ΔG^0_t were calculated by subtracting their values from the reference value (in absence of any amino acids) and the resulted data are tabulated in Table 1.

TABLE 1

HALF WAVE POTENTIALS ($E_{1/2}$), LIMITING CURRENTS (i_l), FREE ENERGIES OF TRANSFER (ΔG_t^0) OF URANYL ION (1×10^{-4} mole) IN PRESENCE AND ABSENCE OF SOME AMINO ACIDS

Amino acid concentration in mole/l	$E_{1/2}$ in volts		i_l in μA	
	1st wave	2nd wave	1st wave	2nd wave
Without amino acids	−0.22	−0.955	2.50	7.20
(1) *Glycine*				
(a) 4.975×10^{-5}	−0.22	−0.955	2.45	7.00
(b) 1.478×10^{-4}	−0.22	−0.965	2.40	6.90
(c) 9.091×10^{-4}	−0.22	−0.965	2.40	6.80
(d) 1.266×10^{-3}	−0.22	−0.965	2.35	6.70
(2) *DL-aspartic acid*				
(a) 4.975×10^{-5}	−0.20	−0.970	2.50	7.10
(b) 9.901×10^{-5}	−0.205	−0.990	2.55	6.90
(c) 1.478×10^{-4}	−0.210	−1.020	2.55	6.90
(d) 1.961×10^{-4}	−0.210	−1.060	2.55	6.90
(e) 2.676×10^{-4}	−0.215	−1.115	2.60	6.00
(f) 3.148×10^{-4}	−0.215	−1.160	2.65	5.80
(3) *Phenylalanine*				
(a) 4.975×10^{-5}	−0.210	−0.970	2.40	6.85
(b) 9.901×10^{-5}	−0.210	−0.980	2.40	6.75
(c) 3.382×10^{-4}	−0.215	−0.990	2.35	6.65
(d) 5.660×10^{-4}	−0.220	−1.000	2.30	6.50

TABLE 1 (contd.)

Amino acid concen.	ΔG^0 (kJ/mole)		ΔG_t^0 (kJ/mole)	
	1st wave	2nd wave	1st wave	2nd wave
Without amino acids	2.606	−136.144	0	0
(1) *Glycine*				
(a) 4.975×10^{-5}	2.606	−138.574	0	−1.93
(b) 1.478×10^{-4}	2.606	−138.574	0	−1.93
(c) 9.091×10^{-4}	2.606	−138.574	0	−1.93
(d) 1.266×10^{-3}	2.606	−138.574	0	−1.93
(2) *DL-aspartic acid*				
(a) 4.975×10^{-5}	4.536	−139.539	1.93	−2.895
(b) 9.901×10^{-5}	4.053	−143.399	1.447	−6.755
(c) 1.478×10^{-4}	3.571	−149.189	0.965	−12.545
(d) 1.961×10^{-4}	3.571	−156.909	0.965	−20.265
(e) 2.676×10^{-4}	3.088	−167.524	0.482	−30.880
(f) 3.148×10^{-4}	3.088	−176.209	0.482	−39.563
(3) *Phenylalanine*				
(a) 4.975×10^{-5}	3.571	−139.539	0.965	−2.895
(b) 9.901×10^{-5}	3.571	−141.469	0.965	−4.825
(c) 3.382×10^{-4}	3.088	−143.399	0.482	−6.755
(d) 5.660×10^{-4}	2.606	−145.329	0	−8.685

These free energy values indicate that DL-aspartic acid has more values in comparing with the other acids used, mainly to the bigger inductive effect of its carboxylic acid group.

Reduction Mechanism

The first reduction wave was found to be one electron process due to the reduction of hexavalent uranyl ion to the pentavalent ones as explained before[6].

$$U(VI) + e^- \rightleftharpoons U(V)$$

or

$$UO_2^{++} + e^- \rightleftharpoons UO_2^+ \qquad (2)$$

The first reduction process was followed by two reduction process reversible) of the second wave in presence and absence of the amino acids used as in equation (3)[6].

$$U(V) + 2e^- \rightleftharpoons U(III)$$

or

$$UO_2^+ + 2e^- + 2H^+ \rightleftharpoons UO^+ + H_2O \tag{3}$$

The abnormal decrease in the limiting current of the second wave and its half wave potential shift on more adding DL-aspartic acid was due to the disproportionation of U(V) in this medium. Since the UO_2^+ species is comparatively stable in only narrow pH range (2.0–4.0)[7], where the disproportionation into U^{4+} and UO_2^{2+} is quite slow as:

$$2UO_2^+ + 4H_3O^+ \rightleftharpoons UO_2^{2+} + U^{4+} + 6H_2O \tag{4}$$

with equilibrium constant[8] of $(1.7 \pm 0.3) \times 10^6$.

In acid solution the dismutation of pentavalent uranyl ion takes place more readily as[9]:

$$2H^+ + 2UO_2(OH)_3 \rightleftharpoons UO_2^{2+} + U(OH)_4 + 2H_2O$$

or

$$2H^+ + U_2O_5 + H_2O \rightleftharpoons UO_2^{2+} + U(OH)_4 \tag{5}$$

Further studies[10–12] found that the rate of disproportionation to be (a) increased with increasing hydrogen ion concentration, (b) increased with increasing pH of the organic acids, (c) increased with decreasing pK of the organic acid. For all these factors, DL-aspartic acid show the effective medium on the dismutation of U(V) in comparing with other amino acids. Therefore, the reduction mechanism of the second wave in presence of DL-aspartic acid was changed from two electrons mechanism $U(V) + 2e^- \rightleftharpoons U(III)$ to one electron mechanism as $U(V) + e^- \rightleftharpoons U(IV)$, whereas further reaction as $U(V) \rightleftharpoons U(VI) + e^-$ took place, which increase the limiting current of the first wave as the result of petavalent ion disproportionation.

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