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Polarographic and Conductometric Studies of Uranyl Ion in Sulphuric Acid-Ethanol Media

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The polarographic behaviour of uranyl ion in sulphuric acid solutions shows three reduction waves. On adding ethanol the first wave splits into two waves and the second wave disappears, whereas the third wave disappears by increasing the percentage of ethanol in the medium. From the conductivity measurements of uranyl ion in sulphuric acid-ethanol solutions, the dissociation degrees and the association constants were calculated. The results were discussed in view of the solvation volumes and the free energies of solution.

INTRODUCTION

The polarogram of uranyl perchlorate consists of two waves in perchloric acid solutions[1,2], but by the addition of sulphuric acid three waves are obtained. The aim of this work is to study the effect of ethanol on the polarographic behaviour of uranyl ion in sulphuric acid solutions.

EXPERIMENTAL

Uranyl perchlorate was prepared from uranyl nitrate hexahydrate (Merck) as described in a previous paper[3]. The concentration of uranyl ion was determined gravimetrically as U_3O_8. Sulphuric acid (AnalaR) and ethanol (BDH) were used. The polarograms were recorded by using a Radiometer Metrohm Polarecord E 506 polarograph and polarography stand of the type Metrohm E 505. The capillary characteristics were $m = 1.771$ mg-sec and $t = 3.5$ sec in 0.1N KCl at a height of 35 cm Hg. A saturated calomel electrode (SCE) was used as a reference electrode. Conductivity measuring bridge of Electronic Instruments Limited (Kent) was used. The densities of the solutions under consideration were measured by using an electric balance PM 460 and 1 ml measuring bottle.

RESULTS AND DISCUSSION

Polarographic Behaviour of Uranyl Ion

The electroreduction of 1 mM uranyl perchlorate in presence of 0.1N H_2SO_4 and different percentages of ethanol is represented by the polarograms shown on Fig. 1. Three reduction waves are obtained in the absence

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of ethanol which correspond to the reduction of U(VI) → U(V) → U(IV) → U(III)[2], with $E_{1/2}$'s −0.22, −0.95 and −1.10 volts vs. SCE. On adding

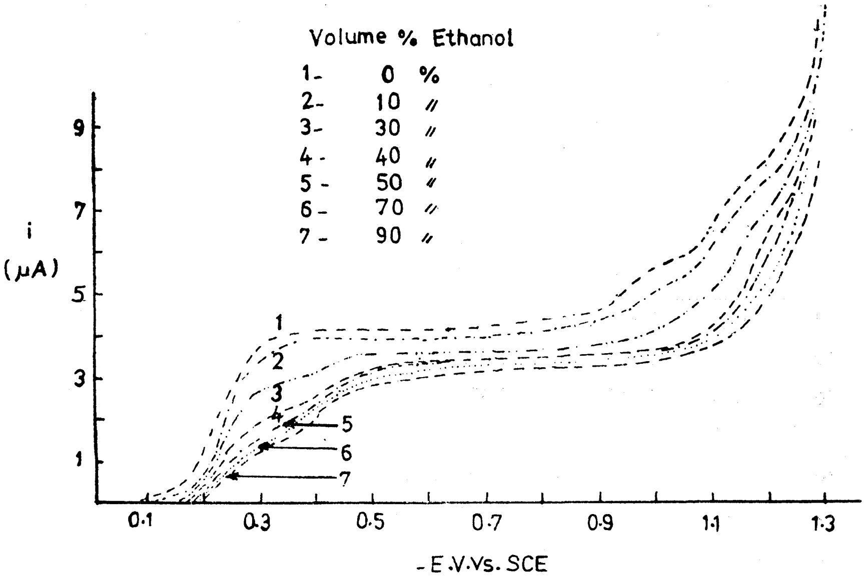

Fig. 1. Polarograms of 1 mM uranyl perchlorate in 0.1N H_2SO_4 plus different percentages of ethanol at 25°C.

ethanol the first wave splits into two waves and the second wave then followed by the third wave disappears gradually. It was found experimentally that by increasing the sulphuric arcid concentration above 0.1N H_2SO_4 two polarographic waves are seen; therefore our experimental part here will be limited to the effect of ethanol on the three reduction waves of uranyl ion.

The relation between log $i/i_d - i$ against E in volts (analysis of the waves) are straight lines; from their slopes the values of αn_a are obtained for all the waves represented in Fig. 1. By plotting log i against log h (mercury height relations) straight lines were obtained. The slopes of the different waves are approximately 0.5, indicating that the electrode processes are mainly diffusion controlled. The free energies of reduction and their transfer values from 0% ethanol as the reference solvent to the mixed solvents under consideration for uranyl ion are calculated by applying eq. 1[4,5].

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

where $E^0_{1/2}V$ (vs. HE) = $E_{1/2}V$ (vs. SCE) + 0.247. The calculated ΔG values and their transfer values ΔG_t from 0% ethanol to mixed solvents are given in Table I.

TABLE 1

FREE ENERGIES AND FREE ENERGIES OF TRANSFER FROM WATER TO MIXED ETHANOL MEDIA FOR 1 mM URANYL ION IN MIXED 0.1N H_2SO_4 AND ETHANOL SOLVENTS AT 25°C IN kJ/mol

Vol. % of EtOH	Ethanol mole fraction (X_s)	1st wave ΔG		1st wave ΔG_t		X_s EtOH	2nd wave ΔG	2nd wave ΔG_t	3rd wave ΔG	3rd wave ΔG_t
		1st or 1st splitted wave	2nd splitted wave	1st or 1st splitted wave	2nd splitted wave					
0	0	−2.123		0		0	134.135	0	252.734	0
10	0.080	−0.483		1.640		0.080	137.609	3.474	253.313	0.579
20	0.164	1.255		3.378		0.164			258.523	5.789
30	0.252	2.702	1.496	4.825	3.619	0.252			267.498	14.764
40	0.344	4.439	1.583	6.562	3.706					
50	0.441	6.079	1.621	8.202	3.744					
70	0.648	7.817	1.641	9.930	3.764					
90	0.876	9.457	1.669	11.580	3.792					

Reduction Mechanism

The reduction mechanism was suggested by considering two facts: (1) the αn_a values indicate that the reduction takes place by two electrons for the first wave in absence and presence of 10% ethanol and one electron for all the other waves; (2) the mecury height relations indicate the reversibility and diffusibility of the waves.

It is seen that the reduction process of the first wave corresponds to the reduction of hexavalent uranyl ion to pentavalent one as:

$$\underset{\text{U(VI)}}{2UO_2^{++} + SO_4^{--}} + 2e^- \rightleftharpoons \underset{\text{U(V)}}{(UO_2)_2SO_4} \qquad (2)$$

On adding ethanol this first wave splitted into two waves at and above 20% ethanol. The sum of the heights of the two splitted waves is approximately equal to the height of the first unsplitted wave. The reduction mechanism of the splitted first wave may take place as explained in eq. 3 with the reduction of U(VI) to U(V)[6].

$$\underset{\text{U(VI)}}{UO_2^{++} + HSO_4^-} + e^- \rightleftharpoons \underset{\text{U(V)}}{UO_2HSO_4} \qquad (3)$$

The reduction of the first splitted wave may be followed by the reduction of the second splitted wave as:

$$2UO_2HSO_4 + e^- \rightleftharpoons (UO_2)_2SO_4 + H_2 \tag{4}$$

This mechanism was done as above because of the behaviour of ethanol in shifting the dissociation of sulphuric acid to HSO_4^- rich position[7]. The other two waves are corresponding to the reduction of pentavalent uranyl ion to the tetravalent and trivalent uranyl ions, respectively as shown in eq. 5[8].

$$\underset{U(V)}{UO_2^+} \rightarrow \underset{U(IV)}{UO_2} \rightarrow \underset{U(III)}{UO^+} \tag{5}$$

Increasing the percentage of ethanol resulted in the disappearance of the pentavalent wave due to the increase of the disproportionation of U(V) to U(IV) and U(IV) on adding more alcohol[9,10], whereas the disappearance of U(IV) wave was due to the increase in the hydrogen evolution process[10,11].

Conductometric Behaviour of Uranyl Ion

The conductance of 0.5–3 mM uranyl perchlorate in 0.1N sulphuric acid plus different percentage of ethanol was measured at 25°C and from these, the equivalent conductance was calculated. The limiting conductances were also calculated. The limiting conductances (Λ_0) were obtained from Λ vs. $\sqrt{C}$ plots and tabulated in Table 2. Applying eq. (6), the partial molar volume is obtained.

TABLE 2

EQUIVALENT CONDUCTANCE AND LIMITING CONDUCTANCE VALUE FOR DIFFERENT URANYL ION CONCENTRATION IN MIXED 0.1N H_2SO_4-ETHANOL SOLUTIONS

Vol. % EtOH	Λ (cm² ohm⁻¹ mole⁻¹) 0.5 mM UO_2^{2+}	1 mM UO_2^{2+}	2 mM UO_2^{2+}	3 mM UO_2^{2+}	Λ_0 (cm² ohm⁻¹ mole⁻¹)
0	42.5	35	25	17	61
20	29	23	14.5	8	44
40	14.2	11	7	4	21.5
60	5.7	4.5	2.9	1.8	8.3
80	1.52	1.2	0.78	0.44	2.26

$$V^0 = \frac{M}{d_0} - \frac{1000}{C}\left(\frac{d - d_0}{d_0}\right) \tag{6}$$

where M is the molecular mass of the solute, C its concentration, d_0 and

d are the densities of solvent and solution, respectively. From the constant value of packing density (the relation between van der Waals and partial molar volume) for high molecular weights[12], the van der Waals radii (r_w) were estimated by applying eq. (7) after King[12].

$$P = \frac{V_w}{V^0} = 0.661 \pm 0.017 \qquad (7)$$

where P is the packing density. The calculated V^0 values from densities and V_w's from eq. (7) for 1 mM uranyl ion solutions are given in Table 3.

TABLE 3

DENSITIES, PARTIAL MOLAR VOLUMES AND VAN DER WAALS VOLUMES OF 1 mM UO_2^{2+} IN MIXED 0.1N H_2SO_4 + ETHANOL SOLVENTS AT 25°C

Vol. % of EtOH	d_0 g./cm³	d g./cm³	V° cm³/mole	V_W cm³/mole
0	1.0112	1.0123	462.64	305.81
20	0.9848	0.9850	475.97	314.62
40	0.9524	0.9572	487.33	322.13
60	0.9207	0.9195	506.75	334.96
80	0.8679	0.8824	523.59	346.09

The association constants for the self-association of uranyl ions in mixed sulphuric acid-ethanol solutions can be evaluated by using the Fuoss-Shedlovsky equation[13,14].

$$\frac{1}{\Lambda} = \frac{K_A C \Lambda \gamma_{\pm} S(Z)}{\Lambda_0^2} + \frac{1}{\Lambda} \qquad (8)$$

where $\gamma_{\pm}$ is the mean activity coefficient, estimated from the extended Debye-Hückel equation[15] as

$$\log \gamma_{\pm} = -\frac{1.824 \times 10^6 \sqrt{C}/(T \cdot \epsilon)^{3/2}}{1 + 50.29 \times 10^8/(T \cdot \epsilon)^{1/2} \cdot (r_w)\sqrt{C}} \qquad (9)$$

C is the concentration, ϵ is the medium dielectric constant and r_w is the solvated radius (van der Waals radius) evaluated as explained before. The Fuoss-Shedlovsky function was calculated as explained in ref. 16. From the known parameter in Eq. (9), the unknown association constants (K_A) for 1 mM UO_2^{2+} ions in mixed solvents under consideration are calculated and in Table 4 tabulated. The degree of dissociation (α) was

TABLE 4

SOLVATED RADII (r_w),FUOSS-SHEDLOVSKY FUNCTIONS $S(Z)$, ACTIVITY COEFFICIENTS ($\gamma\pm$), ASSOCIATION CONSTANTS (K_A) AND DISSOCIATION DEGREES (α) FOR 1 mM UO_2^{++} IN MIXED 0.1N H_2SO_4-ETHANOL SOLVENTS AT 25°C

Vol. % EtOH	r_w (Å)	$S(Z)$	$\log\gamma\pm$	K_A	α
0	4.798	1.0126	−0.015	2.024×10^5	0.581
20	4.844	1.0274	−0.018	2.030×10^5	0.537
40	4.882	1.0320	−0.024	1.570×10^5	0.528
60	4.946	1.0310	−0.034	9.928×10^4	0.559
80	5.000	1.0340	−0.051	6.214×10^4	0.549

calculated from eq. (10) for 1 mM UO_2^{2+} and given also in Table 4.

$$\alpha = \frac{\Lambda S(Z)}{\Lambda_0} \tag{10}$$

It was thus concluded from the results in Tables 1–4 that an increase in ethanol percentages was followed by an increase in free energies of reduction (ΔG and ΔG_t) shifted to less negative and more positive values, increase in the partial molar volumes (V^0), increase in the van der Waals volumes (V_w), increase of the association constants (K_A) and decrease in the dissociation degrees (α), due to more solvation.

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