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Some Reversible and Irreversible Electrode Processes at DME. A Study on Uranyl and Zinc Complexes of L-Hydroxyproline in Aqueous and Aqueous-Methanolic Solutions

P. C. Rawat and C. M. Gupta*
Department of Chemistry, M.R. Engineering College, Jaipur, India
**Chemical Laboratories, University of Rajasthan, Jaipur, India*

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Complexes of zinc and uranyl ions with L-hydroxyproline (LHP) have been investigated by polarographic method of analysis at 25±1 and 35±1 °C. At pH 4.5, formation of uranyl-LHP complex was observed with metal to ligand ratio of 1: 1 in aqueous and aqueous-methanolic solutions. The stability constant for the complex species is $\log K_c = 1.50$, 1.30, 1.61, 1.87 in aqueous (25 °C), aqueous (35 °C), aqueous-methanolic (10% v/v) and aqueous-methanolic (50% v/v) media respectively. Between pH 3.0—12.0, zinc-LHP complex has been observed to be reduced irreversibly at DME. Detailed investigations have been reported on the system at 25±1 °C and 35±1 °C at pH 10.0 in varying concentrations of the ligand. Kinetic parameters—the formal rate constant $K^\circ_{f,h}$ and transfer coefficient α have been calculated.

Owing to their numerous advantages and interesting properties, amino-acids are finding an increasingly wider applications in chemical technology, biochemistry and various fields of analytical chemistry. Moreover, this class of compounds is characterstically provided with two or more functional groups, the donor atoms from which are capable of combining with a metal atom and, so situated in the molecule, that they permit the formation of a chelate ring with the metal atom as the closing member. L-hydroxyproline (LHP) is one such compound and there are scanty references[1–4] as to the chelate forming capabilities of this acid. The paper is a continuation of our earlier insestigations on the complex forming abilities of L-hydroxyproline with different metal ions. The properties of Cd(II) and Pb(II) complexes have been previously investigated in aqueous and aquo-nonaqueous media.[5] There is however, no reference in literature to the study of uranyl–LHP and zinc–LHP system, and hence the present work has been initiated. The present communication describes the nature of the complexes formed between uranyl ion or zinc ion with LHP by polarographic technique of analysis.

Experimental

L-Hydroxyproline (W. Germany) and AnalaR(BDH) potassium nitrate, potassium chloride, zinc sulphate and uranyl nitrate were used. All solutions were prepared in air free conductivity water. Gelatin at a concentration of 0.004% in final solutions was found satisfactory as maxima suppresor in uranyl–LHP system. No maxima supressor was used in zinc–LHP Studies.

Polarographic waves were recorded with a manual polarograph using a H-cell in conjunction with saturated calomel electrode as reference electrode. The DME had the characterstics: −2.768 mg/s and $t=2.8$ s (in $\mu=0.5$ M KNO_3 or KCl at −1.15 V *vs.* SCE).

The experiments were performed with 0.5 mM uranyl or zinc in varying concentrations of LHP (0.0 to 0.035 M). Ionic strength was kept constant at $\mu=0.5$ M by adding requisite amounts of KNO_3 (Zinc–LHP system) and KCl (Uranyl–LHP system). Dilute solutions of HCl or NaOH (0.01 M) were used for adjusting pH of the solutions on a Cambridge bench pattern (null-deflection type) pH meter.

Studies on the systems were performed at two temperatures 25±1 °C and 35±1 °C in order to calculate thermodynamic parameters.

Our earlier investigations[5–9] on the behaviours of complexation processes in aqueous-aquo-nonaqueous mixtures furnished significant polarographic data pertaining to stability and composition of the complex species. In sequence to these studies, uranyl–LHP system was further investigated under identical conditions in aqueous-methanolic solutions (10—50% v/v).

Uranyl–LHP system has been throughout studied in weakly acid media (pH=4.5) at $\mu=0.5$ M KCl, in order to obtain diffusion controlled, reversible and one electron reduction of U(VI) to U(V) at DME.[10]

Results and Discussion

Uranyl–LHP System. *Reduction*: Uranyl ion in LHP gives a one electron reduction at DME which is diffusion controlled and reversible, as revealed by constant values of $i_d/h^{1/2}_{eff}$, the temperature coefficient (1.1—1.5%) and slope of the conventional log i/i_d-i plots (60±3) mV. The wave nature remained the same in all the experimental conditions studied.

Effect of Ligand Concentration: A cathodic shift in $E_{1/2}$, coupled with decrease in diffusion current with increasing concentration of the ligand (0.0—0.035 M) indicates complexation. The plot of $E_{1/2}$ *vs.* $-\log C_X$ results in a straight line (Fig. 1). It is therefore reasonable to conclude the complex being reduced is composed of only one species. The number of ligand/uranyl ion as estimated by expression[11]

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Table 1. Polarographic data for UO_2^{2+}-LHP system in aqueous 25±1 °C(a), 35±1°C(b), 10% methanolic(c), and 50% methanolic (d) media (UO_2^{2+}=0.5 mM, KCl=0.5 M, pH=4.5)

Concn of Ligand M	(a) $-E_{1/2}$ (*vs.* SCE) V	(a) i_d μA	(b) $-E_{1/2}$ (*vs.* SCE) V	(b) i_d μA	(c) $-E_{1/2}$ (*vs.* SCE) V	(c) i_d μA	(d) $-E_{1/2}$ (*vs.* SCE) V	(d) i_d μA
0.0	0.204	1.976	0.195	2.280	0.205	1.596	0.260	1.406
0.02	0.205	1.862	0.196	2.204	0.211	1.406	0.272	1.216
0.03	0.215	1.900	0.202	2.223	0.216	1.406	0.283	1.102
0.04	0.220	1.824	0.209	2.166	0.223	1.368	0.289	1.102
0.05	0.225	1.710	0.212	2.143	0.228	1.482	0.293	1.121
0.06	0.230	1.634	0.215	2.014	0.233	1.464	0.300	1.102
0.07	0.234	1.634	0.219	2.014	0.237	1.482	0.306	1.102
0.08	0.240	1.596	0.225	1.976	0.243	1.464	0.311	1.120

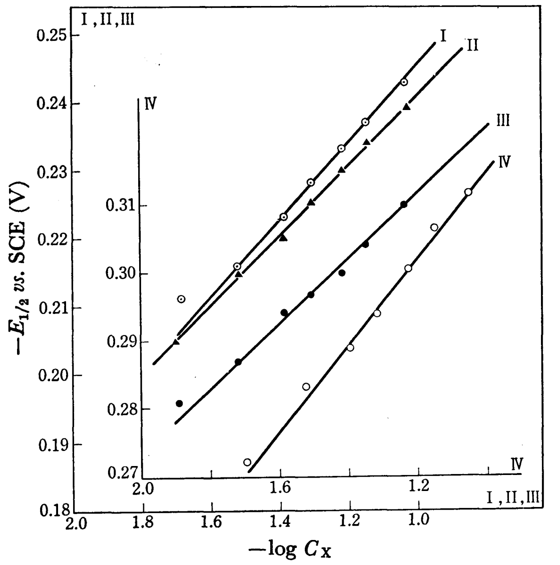

Fig. 1. Plots of $E_{1/2}$ *vs.* $-\log C_x$ for UO_2^{2+}-LHP system at 25 °C (▲), 35 °C (●), 10% methanolic (⊙), and 50% methanolic (○) media.

$$p = -\frac{d(E_{1/2})_c}{d\log C_x} \Big/ \frac{RT}{0.4343nF}$$

is found to be unity. The overall formation constant $\log K_C$ as derived from expression.[11]

$$\Delta E_{1/2} = (E_{1/2})_c - (E_{1/2})_s = \frac{RT}{0.4343nF}\log\beta_p + P\cdot\frac{RT}{0.4343nF}\log C_x$$

and other polarographic data for different temperature and media are summarised in Table 1.

Effect of Non-aqueous Media: The stability constant $\log K_C$ is found to increase with increasing non-aqueous concentration (methanol) in the media. This suggests stronger metal to ligand binding in the media. This is quite significant and in conformity with our earlier studies on different systems[5-9] and also with similar studies by other workers.[12-14]

Effect of Temperature: Stability constants $\log K_C$ value shows a decrease at increased temperature. This establishes exothermic nature of the interaction between U(VI) and LHP. The thermodynamic constants ΔG, ΔH, and ΔS as calculated from standard equations[15] are summarized in Table 2.

Table 2. Thermodynamic constants for UO_2^{2+}-LHP system

Temp. (°C)	$\log K_c$	ΔG kcal	ΔH (kcal)	ΔS (cal/deg/mol)
25±1	1.50	−2.04	—	—
35±1	1.30	−1.83	−8.4	−21.3

L-Hydroxyproline is an amino-acid with pK_1=9.58 and pK_{12}=1.93.[16] Therefore at pH (4.5) on which the system has been investigated, the predominant ligand species must be a dipole molecule rather than the L-hydroxyprolinate ion. In the light of this discussion the complex species and electrode reaction can be possibly formul ated as under.

$$UO_2^{2+} + HL\ (\text{dipole molecule}) \rightleftharpoons [UO_2(HL)]^{2+}$$

UO_2^{2+} and $[UO_2(HL)]^{2+}$ co-exist and undergo electrode reaction

$$UO_2^{2+} + [UO_2(HL)]^{2+} + H^+ + 2e \rightleftharpoons 2UO_2^+ + (HL\text{-}H)^+$$

Zinc-LHP System. *Reduction*: Zinc in LHP (Zn=0.5 mM, μ=0.5 M KNO_3, LHP=0.125 M) was initially investigated in a wide range of pH of the solutions (3.0 to 12.0) at 25±1 °C. The metal ion was observed to give a well defined, diffusion controlled wave in all the solutions. The conventional log plots were linear, but the resulting slopes were not found to be in agreement with the theoretical values, thus indicating the irreversible nature of the electrode reaction. However, the H.W.E.T. shifted towards more negative values with increase in pH suggesting formation of a stable, soluble Zn–LHP complex. Further, studies on the system were preferred at pH=10.0.

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TABLE 3. POLAROGRAPHIC DATA FOR Zn–LHP SYSTEM AT 25±1 °C (a) AND 35±1 °C (b) (Zn=0.5 mM, KNO_3 μ=0.5 M, pH=10.0)

Concn of ligand M		$-E_{1/2}^{0}$ (*vs.* SCE) V	Slope of log plots. mV	i_d μA	αn	$D_0^{1/2}$ 10^{-3}	$K^{0}_{f,n}$
0.005	(a)	1.238	43	3.002	1.26	2.11	9.22×10^{-25}
	(b)	—	—	—	—	—	—
0.015	(a)	1.288	45	2.850	1.20	2.00	9.59×10^{-25}
	(b)	1.266	41	3.306	1.32	2.32	9.70×10^{-26}
0.020	(a)	1.295	46	2.964	1.18	2.08	1.77×10^{-24}
	(b)	1.273	42	3.306	1.29	2.32	2.93×10^{-25}
0.025	(a)	1.303	47	2.85	1.15	2.00	3.32×10^{-24}
	(b)	1.280	43	3.306	1.26	2.32	7.03×10^{-25}
0.030	(a)	1.309	50	2.774	1.08	1.95	4.47×10^{-23}
	(b)	1.285	45	3.154	1.20	2.22	4.23×10^{-24}
0.035	(a)	1.315	52	2.736	1.04	1.92	1.92×10^{-22}
	(b)	1.290	49	3.040	1.11	2.14	1.55×10^{-22}

Effect of Concentration of the Ligand: The zinc–LHP reduction wave, however remained irreversible and diffusion controlled in all the concentrations of the ligand (0.0 to 0.035 M) corresponding to 0.5 mM zinc at μ=0.5 M (KNO_3) and pH=10.0. The wave nature did not change at higher temperature 35±1 °C as well.

Kinetic Parameters: From Koutecky's[17] treatment of irreversible waves as modified by Meites and Israel[18] it follows that for a cathodic wave (at 25 °C) with $E_{1/2}$ more then -1.0 V *vs.* SCE

$$E_{\mathrm{DME}} + 0.2412 = \frac{0.05915}{\alpha n}\log\frac{1.349K^{\circ}_{\mathrm{f.h}}}{D_0^{1/2}} - \frac{0.0542}{\alpha n}(\log i/(i_d - i) - 0.546\log t) \quad (1)$$

and

$$E^{\circ}_{1/2} = -0.2412 + \frac{0.05915}{\alpha n}\log\frac{1.349K^{\circ}_{\mathrm{f.h}}}{D_0^{1/2}} \quad (2)$$

The kinetic parameters have thus been calculated by employing Eqs. (1) and (2). The αn was obtained by equating the slope of the straight line plot E_{DME} *vs.* ($\log i/(i_d-i)$ -0.546 $\log t$) with $0.0542/\alpha n$. The same plot gives the intercept where the quantity being plotted along the abscissa is zero, which is equal to the parameter $E_{1/2}$ defined by the Eq. (2), which was then used to calculate $K^{\circ}_{\mathrm{f.h}}$. The values of $K^{\circ}_{\mathrm{f.h}}$ and αn at 25±1 °C and 35±1 °C (using analogous equations valid at this temperature) in various concentrations of the ligand are summarized in Table 3. From the perusal of the results, it is obvious that the electrode reaction is highly irreversible and increased concentration of the ligand further adds to the irreversibility of the reaction. There is no significant change in this character even at higher temperature.

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