Polarography of Uranyl-Mandelate Complexes

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(Received November 2, 1972)

Abstract

The uranyl ion in mandelic acid solution has been investigated by polarography. The chelate species formed was found to be UO_2A^+ at $\text{pH} < 3.8$. The diffusion coefficient of chelate decreases with increasing pH value and the square root of the ionic strength. When $\text{pH} > 5.8$, an irreversible and diffusion-controlled wave was obtained due to the hydroxylation of the chelate species. The kinetic parameters of the electrode reduction were found to be that K_s is in the order of 10^{-4} cm/sec and α is 0.32 ± 0.01 .

Introduction

The complex formation of mandelic acid with europium¹⁾, gallium²⁾ and lanthanum³⁾ has been investigated. Varma and Agarmal⁴⁾ have studied the uranyl-mandelate complexes by potentiometric and spectrophotometric methods and have shown that the metal-ligand ratio of the complex is 1:1 and that the complex hydrolyzed above pH 3.1.

In this work, the polarographic characteristics, the diffusion coefficient and the kinetic parameters of the electrode reaction for the uranyl-mandelate system are reported.

Experimental

Apparatus—All polarograms were recorded with a Yanagimoto Pen-Recording Polarograph Model p8 at $25 \pm 0.1^\circ\text{C}$. The characteristics of the DME were: $m = 1.397$ mg/sec and $t = 4.96$ sec at 73.6 cm mercury height in a 0.15 M NaClO_4 solution at an applied potential of -0.36 V *vs.* SCE. Oxygen was eliminated by passing a purified hydrogen through the solution.

The pH values of the solutions were adjusted with perchloric acid or sodium hydroxide and determined by a Toa Denpa HM-5A glass electrode pH meter.

Chemicals—The stock solution of 0.1 M uranyl perchlorate was prepared and analyzed as described in the earlier paper⁵⁾.

A 0.2 M stock solution of Dl-mandelic acid (HA) was prepared by dissolving 7.607 g of the acid (chemically pure grade, Kanto Chemical Co.) in distilled water and diluting to 250 ml.

A 0.15 M sodium perchlorate was used as a supporting electrolyte and no maximum suppressor was needed through this work.

Results and Discussion

The polarographic characteristics of the uranyl-mandelate complexes were studied systematically over the pH range 1.20 to 9.10 with the ligand concentrations varying from 0.004 *M* to 0.40 *M*. It is obvious from Table 1 that one-electron reversible reduction waves were obtained at lower pH values (e.g., at pH > 5.20 for [HA] = 0.40 *M* and at pH < 3.85 for [HA] = 0.004 *M*). The limitation of pH values with respect to various ligand concentrations for reversible waves can be observed from the dashed line in Fig. 1.

The temperature coefficient of the half-wave potential was obtained to be -0.34 mV per degree for a solution containing 1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.1 *M* mandelic acid and 0.15 *M* NaClO_4 at pH 3.21. The mean value of $i_d/h^{1/2}$ is 0.370 ± 0.003 (Table 2). These data demonstrate that the electrode reactions are reversible and diffusion-controlled processes.

Table 1. Polarographic characteristics and reversibility of uranyl-mandelate complex.
(1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.15 *M* NaClO_4)

C_{HA}, M	pH	$-E_{1/2}, V$ vs. SCE	$\frac{-\Delta E_{d.e.}}{\Delta \log \frac{i}{i_d - i}}$	$i_d, \mu A$
0.40	1.60	0.178	0.058	4.36
	2.50	0.220	0.056	4.90
	3.72	0.285	0.055	3.15
	4.45	0.310	0.056	2.49
	5.20	0.315	0.056	2.01
0.10	1.20	0.178	0.060	3.45
	2.50	0.195	0.056	3.36
	3.21	0.231	0.056	3.18
	4.40	0.284	0.058	2.25
	5.00	0.290	0.056	1.83
0.05	2.32	0.178	0.053	2.52
	3.60	0.225	0.059	2.50
	4.20	0.258	0.057	1.74
	4.47	0.203	0.058	1.80
0.02	1.40	0.178	0.056	3.45
	2.30	0.178	0.058	2.70
	3.50	0.208	0.056	2.67
	4.05	0.230	0.056	2.16
	4.30	0.240	0.057	2.10
0.01	2.00	0.178	0.056	2.67
	3.42	0.190	0.057	2.40
	3.90	0.210	0.057	2.42
	4.20	0.215	0.058	2.43
0.004	1.80	0.178	0.056	3.21
	2.50	0.178	0.057	2.13
	3.50	0.185	0.056	2.64
	3.85	0.195	0.056	2.70

Fig. 1. The limitation of pH values with respect to various ligand concentrations for reversible waves.

○ 0.4M; ● 0.1M; □ 0.05M; △ 0.02M; × 0.01M;
▽ 0.004M

The general formula of the uranyl-mandate complex may be expressed either by $\text{UO}_2(\text{HA})_p^{2+}$ or $\text{UO}_2(\text{A})_p^{2-p}$ and the electrode reactions can be expressed, respectively, as

or

The $(p - q)$ value in Equations (1) and (2) was determined from the plots of $(E_{1/2})_e$ vs. $\log C_{\text{HA}}$, in which $C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$. The slope of $\Delta(E_{1/2})_e / \Delta \log C_{\text{HA}}$ was found to be -0.059 , indicating that $p - q = 1$. Since $p = 1^{4)}$ then the complex species and the electrode reactions (1) and (2) become:

Then, the half-wave potentials for electrode reactions (3) and (4) can be expressed as

Table 2. Variation of limiting current with height of mercury column.
(1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.1 M mandelic acid, 0.15 M NaClO_4)

pH	Height, h_{corr} (cm)	i_d , μA	$i_d/h^{1/2}$
3.21	83.6	3.36	0.367
	73.6	3.18	0.370
	63.6	2.97	0.372
Ave. 0.370 ± 0.003			

$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log \frac{\beta_{RC}}{\beta_{OC}} - 0.059 \log C_{HA} + 0.059 \text{ pH} \\ + 0.059 \log \{[H^+] + K_{HA}\} \quad (5)$$

and

$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log \frac{\beta_{RC}}{\beta_{OC}} - 0.059 \log C_{HA} - 0.059 \log K_{HA} \\ + 0.059 \log \{[H^+] + K_{HA}\} \quad (6)$$

Taking the partial derivative of $-(E_{1/2})_c$ with respect to pH value for Equations (5) and (6), we get

$$-\frac{\partial (E_{1/2})_c}{\partial \text{pH}} = 0.059 \left[1 + \frac{[H^+]}{[H^+] + K_{HA}} \right] \quad (7)$$

and

$$-\frac{\partial (E_{1/2})_c}{\partial \text{pH}} = 0.059 \left[\frac{[H^+]}{[H^+] + K_{HA}} \right] \quad (8)$$

respectively, where $K_{HA} = 3.88 \times 10^{-4}$ for mandelic acid⁶⁾.

The characteristic curves of $-\partial(E_{1/2})_c/\partial \text{pH}$ vs. pH for $\text{UO}_2(\text{HA})^{2+}$ and UO_2A^+ species are shown respectively in curves I and II of Fig. 2, in which the data were calculated from Equation (7) and (8). Curves A, B, C and D in Fig. 2 illustrate the experimental curves which were obtained with a solution containing 1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.10 M mandelic acid, and at ionic strength, respectively, 0.45, 0.16, 0.08 and 0.03 adjusted with enough NaClO_4 . In referring the experimental curves A, B, C and D with the characteristic curves I and II, it was proved that the complex species formed

Fig. 2. Characteristic curves of $-\partial(E_{1/2})_c/\partial \text{pH}$ vs. pH for complex species of $\text{UO}_2(\text{HA})^{2+}$ (curve I) and UO_2A^+ (curve II). (Curves A, B, C and D are experimental at μ 0.45, 0.16, 0.08 and 0.03).

is $\text{UO}_2(\text{A})^+$ rather than $\text{UO}_2(\text{HA})^{2+}$. The deviation of those experimental curves A, B, C and D from the characteristic curve II decreases with decreasing ionic strength of the solution.

Effects of Ionic Strength and pH on the Diffusion Coefficient—In the modified Ilkovic equation⁷⁾

$$i_d = 607 n D^{1/2} m^{2/3} t^{1/6} \left(1 + \frac{AD^{1/2} t^{1/6}}{m^{1/3}} \right) C \quad (9)$$

The concentration C of the reducible substance can be expressed as the complex species concentration of

$$[\text{UO}_2\text{A}^+] = \frac{C_{\text{UO}_2} + \left\{ \frac{C_{\text{HA}} K_{\text{HA}}}{K_{\text{HA}} + [\text{H}^+]} \right\}}{\frac{1}{\beta} + \left\{ \frac{C_{\text{HA}} K_{\text{HA}}}{K_{\text{HA}} + [\text{H}^+]} \right\}} \quad (10)$$

where A is a constant 39 and β_{oc} is 2.93×10^3 ⁴⁾. Substituting the corresponding experimental data for a given pH value into Equations (9) and (10), the diffusion coefficients of the complex UO_2A^+ can be calculated (Tables 3 and 4). The diffusion coefficient decreases with increasing pH value (Table 3) and the square root of the ionic strength (Table 4).

The diffusion coefficient is affected by the composition of the solution and can be given by the equation⁸⁾

$$D = D^0 - A\mu^{1/2} \quad (11)$$

where D^0 is the diffusion coefficient in infinitely dilute solution and A is a constant. Combine equation (11) with Ilkovic equation to yield:

$$I^2 = (I^0)^2 - A^2 \mu^{1/2} \quad (12)$$

Table 3. The effect of pH on the diffusion coefficient
(1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.1 M mandelic acid,
0.15 M NaClO_4)

pH	$i_d (\mu\text{A})$	$D \times 10^7 \text{ (cm/sec)}$
2.20	3.63	3.75
2.50	3.36	2.16
3.00	3.26	1.45
3.21	3.18	1.29
3.50	2.89	1.02
4.10	2.43	0.69
4.40	2.25	0.59

Table 4. Effect of ionic strength on the diffusion coefficient
(1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.10 M mandelic acid at
pH 4.2 and enough NaClO_4 to give a certain
ionic strength)

$\mu^{1/2}$	$i_d (\mu\text{A})$	$D \times 10^7 \text{ (cm/sec)}$
1.03	1.83	0.74
0.68	2.07	0.95
0.55	2.24	1.10
0.40	2.40	1.27
0.21	2.43	1.30

or

$$i_d^2 = (i_d^0)^2 - B^2 \mu^{1/2} \quad (13)$$

where (i_d^0) is the diffusion current at infinite dilution.

Equations (11) and (13) infer that the plots of D and i_d^2 versus $\mu^{1/2}$ should give straight lines and the values of D^0 and (i_d^0) can be obtained by extrapolating to infinite dilution. Fig. 3, which shows these plots, were obtained by applying the least-square method for the data in Table 4 and can be expressed in the following two equations.

$$D \times 10^7 = 1.50 - 0.74 \mu^{1/2} \quad (14)$$

and

$$i_d^2 = 6.80 - 3.36 \mu^{1/2} \quad (15)$$

Thus, the diffusion coefficient of UO_2A^+ at infinite dilution was obtained to be 1.50×10^{-7} cm/sec and the corresponding diffusion current constant is equal to 1.60.

Fig. 3. Plot of D and i_d^2 vs. $\mu^{1/2}$
1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.10 M mandelic acid at pH 4.2.

Kinetic parameters of electrode reaction—The curves in Fig. 1 break at the dashed line, beyond the dashed line, when the pH value increasing the wave becomes irreversible due to hydroxylation of the complex⁴⁾. The polarographic characteristics at pH 6.10 are shown in Table 5. The plots of $E_{d.e.}$ vs. $\log i/(i_a - i)$ were found to be good straight lines, but the mean slope for this series is 81.5 ± 2.5 mV. The temperature coefficient of the diffusion current is $0.78\%/^\circ\text{C}$ and the value of $i_d/h^{1/2}$ is 0.125 ± 0.005 . These data show that the electrode reactions are irreversible and diffusion controlled process.

The corrected half-wave potential $E_{1/2}^r$ for a quasi-reversible system can be obtained by plotting $\left[E_{d.e.} + \frac{RT}{nF} \ln \frac{i}{i_a - i} \right]$ against i and by extrapolating it to $i=0$ (Fig. 4)⁹⁾.

The standard rate constant k_s and transfer coefficient α of electrode reaction were determined from the intercept and the slope of the plots of $\log(Z-1)$ vs. $(E_{1/2}^r - E_{d.e.})$ (Fig. 5)⁹⁾. The data obtained for various ligand concentration are listed in Table 5.

Fig. 4. Determination of the corrected half-wave potential.
1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.004 M HA and 0.15 M NaClO_4 at pH 6.10

Fig. 5. Plot of $\log (Z-1)$ vs. $(E_{1/2}^r - E_{d,e.})$

Table 5. Polarographic characteristics and kinetic parameters of uranyl-mandelate chelate.
(1.0 mM $\text{UO}_2(\text{ClO}_4)_2$, 0.15 M NaClO_4 at pH 6.10)

C_{HA} M	$V - E_{1/2}$ vs. SCE	$V - E_{1/2}^r$ vs. SCE	i_d μA	$\frac{-\Delta E_{d,e.}}{\Delta \log \frac{i}{i_d - i}}$	α	$k_s \times 10^4$ cm/sec
0.004	0.550	0.535	1.50	0.080	0.341	5.12
0.010	0.581	0.562	1.32	0.084	0.355	4.63
0.020	0.626	0.589	1.30	0.083	0.324	4.48
0.050	0.647	0.613	1.22	0.079	0.300	4.42
0.100	0.665	0.637	1.05	0.081	0.317	4.33
0.200	0.672	0.653	1.02	0.079	0.337	4.28
0.400	0.680	0.675	0.98	0.083	0.326	4.10

Fig. 6. Plot of $-E_{1/2}^r$ vs. $\log C_{HA}$

The k_s values were found to be of the order of 10^{-4} cm/sec, which indicates that the electrode reduction is quasi-reversible. As the ligand concentration increases, k_s was found to decrease, showing that the irreversibility increases with increasing ligand concentration. The transfer coefficient α was found to be 0.32 ± 0.01 (Table 5).

As shown in Fig. 6, the plot of $-E_{1/2}^r$ vs. $\log C_{HA}$ comes to a straight line, which proves the formation of a single stable complex. Therefore, it was concluded that the irreversible electrode reduction is not caused by the consecutive complex formation; the hydroxylation of the uranyl-mandelate complex slowed down the reduction rate and resulted in the irreversible electrode reduction.

Acknowledgement

The authors thank the National Science Council for financial support of this work.

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