Kinetics and Electrochemical Studies of Uranium in Perchlorate and Sulphate Media by Cyclic Voltammetry

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(Received 26th April 2007, revised 18th June 2007)

Summary: The cyclic voltammetric behavior of uranyl ion was investigated at hanging mercury drop electrode in perchlorate supporting electrolyte. The standard heterogeneous electrons transfer rate constant "k_s" for the reduction of uranium from U(VI) to U(V) state was 2.72×10^{-3} cm sec^{-1} in simple perchlorate medium and in the presence of 0.40 mol L^{-1} sulphate ions the value of k_s was 2.56×10^{-3} cm sec^{-1}. The effect of temperature on the values of k_s was investigated and different thermodynamic constants, ΔH^*, ΔS^* and ΔG_{298}^*, were calculated. The values of ΔH^*, ΔS^* and ΔG_{298}^* were 7.97 kJ mol^{-1}, -23.80 J mol^{-1} K^{-1} and 15.06 kJ mol^{-1} in simple perchlorate medium and 3.99 kJ mol^{-1}, -37.70 J mol^{-1} K^{-1}, and 15.22 kJ mol^{-1} in sulphate medium. The stability constants of uranyl sulphate complexes were calculated from the analysis of shift in peak potential of uranyl ions with increasing concentration of sulphate ions. The values of $\log\beta_1$ and $\log\beta_2$ for 1:1 and 1:2 uranyl sulphate complexes were found to be 1.90 ± 0.01 and 2.92 ± 0.02 respectively, which are in close agreement with the literature values.

Introduction

Uranium is an important element because it is used in the production of energy in nuclear reactors. It has numerous other applications particularly in defence. It is a toxic element at low level. It forms complexes with a variety of naturally occurring anions like oxalate, carbonate, sulphate, acetate, etc. and has very long residence time in water [1]. In complexed form, an element becomes more toxic. Study of the complexation behavior of uranyl ion is important for extraction, separation and speciation purposes [2-4]. The complexation of uranyl ion has been studied by different techniques [5-9]. Voltammetry is a reliable method [10] and it can be used for variety of studies [11]. Cyclic voltammetry is a very useful technique but rarely used for complexation study. It is a quick and an accurate method for the determination of stability constants and provides a better understanding of mechanism of an electron transfer process.

The electrochemical reduction of uranyl ion has been studied in both complexing and non-complexing electrolyte media [12-14]. In non-complexing electrolyte media, the uranyl ion is hydrolyzed at pH > 4 [15-18] and in complexing media it is stable up to pH 5 [3]. Due to the hydrolysis of uranyl ion, the diffusion current no longer exists in basic media [16-17]. The redox behavior of uranyl ion needs critical evaluation [19]. Extensive studies have been done on uranium other than the evaluation of heterogeneous electron transfer rate constants.

In electrochemistry the study of rates of electron transfer reaction at an electrode-electrolyte solution interface is a fundamental issue. The electron transfer reaction is one of the basic processes in many chemical fields including organic and inorganic chemistry. Electron transfer is probably the only process for which theoretical models have been proposed [20-22]. Studies on evaluation of heterogeneous electron transfer rate constants for reduction of uranyl ions are scarce and hardly any reliable data is available. The methods described by Nicholson [23] and Klinger and Kochi [24] can be used for the determination of heterogeneous electron transfer rate constants using peak separation method.

In this work, the diffusion coefficient and heterogeneous electron transfer rate constants for uranyl ion have been evaluated. Effect of sulphate ions on rate constant has been studied. Thermo-

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dynamic constants ΔH°, ΔS° and ΔG_{298}° have been determined. Stability constants of uranyl sulphate complexes have also been evaluated by cyclic voltammetry.

Results and Discussion

Cyclic Voltammetric Characteristics of Uranyl Ion

The cyclic voltammogram of uranyl ions at 25 °C in 0.1 mol L^{-1} $NaClO_4$ + 0.1 mol L^{-1} $HClO_4$ solution in the potential range 0.2 to – 0.6 V is shown in Fig. 1. The cathodic peak "C1" appeared at – 0.17 V while the corresponding anodic peak "A1" appeared at – 0.11 V at 50 mV sec^{-1} scan rate. The difference between cathodic peak potential and half-wave potential, which lies at 85.2 % of the way up the peak, was 0.029 V at 50 mV.sec^{-1} scan rate. This value is close to the theoretical value of 0.028 V for reversible one electron transfer process [25].

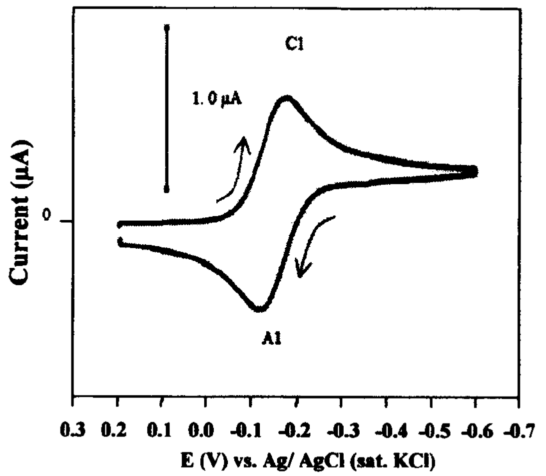

Fig. 1: Cyclic voltammogram of uranyl ion at HMDE in 0.1 mol L^{-1} $NaClO_4$ + 0.1 mol L^{-1} $HClO_4$ solution (scan rate = 50 mV sec^{-1}, E_a=0.2 V, E_c= -0.6 V, $[UO_2^{2+}]$ =5 × 10^{-4} mol L^{-1}).

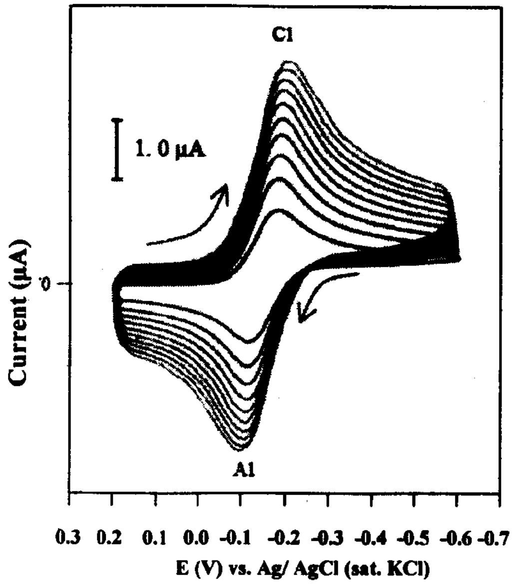

Fig. 2: Effect of scan rate on the cyclic voltammogram of uranyl ion (E_a=0.2 V, E_c= -0.6 V $[UO_2^{2+}]$ = 5 × 10^{-4} mol L^{-1}, $[NaClO_4]$ = 0.1 mol L^{-1}, and $[HClO_4]$ = 0.1 mol L^{-1}, scan rate varied from 100 to 1000 mV sec^{-1} by a step of 100 mV sec^{-1}).

The reversibility of electrode process corresponding to the peaks "C1-A1" was also checked by finding the effect of scan rate on the current-potential behavior of uranyl ion. It is obvious from the Fig. 2 that the peak potentials of the peaks "C1-A1" are not affected significantly on varying the scan rate from 100 to 1000 mV sec^{-1} and the ratio of anodic to cathodic peak current "I_{pa}/ I_{pc}" is close to unity which is a characteristic property of a reversible electron transfer process [25].

Effect of pH on the Cyclic Voltammetric Behavior of Uranyl Ion

The effect of pH on the peak current and peak potential of the peaks "C1-A1" was investigated by recording the cyclic voltammogram of 5 x 10^{-4} mol L^{-1} uranyl ions in 0.1 mol L^{-1} $NaClO_4$ solution with varying pH. The peak current and peak potential were not affected during variation of pH up to 4. Above pH 4, the hydrolysis of uranyl ions occurred due to which the peaks "C1-A1" did not appear as well defined peaks. Such observations have also been observed in polarographic studies of uranyl ion by other authors [13, 17, 26]. Due to this pH independence, the peaks "C1-A1" are assumed to arise by the following reversible one electron transfer reaction:

$$UO_2^{2+} + 1e^- \rightleftarrows UO_2^{+} \qquad (1)$$

Effect of Ionic Strength on Cyclic Voltammetric Behavior of Uranyl Ion

The effect of ionic strength on the peak current and peak potential of the UO_2^{2+}/ UO_2^{+} couple was investigated by recording the cyclic voltammogram of 5 x 10^{-4} mol L^{-1} uranyl ions in 0.1 mol L^{-1} $HClO_4$ + varying concentration of $NaClO_4$. The peak currents of the peaks "C1-A1" were not affected with variation of ionic strength of the solution. The peak potentials, however, shifted slightly towards anodic potential on making a large change in ionic strength *e.g.* the cathodic peak "C1" shifted from – 0.17 to – 0.14 V on changing the ionic strength from 0.2 to 1.5 mol L^{-1} at 25 °C.

Determination of Diffusion Co-efficient of Uranyl Ion

The diffusion co-efficient of uranyl ion was evaluated by using the Randles-Sevcik equation [27-28].

$$I_p = 2.69 \times 10^5 \, n^{3/2} \, AC \, D^{1/2} \upsilon^{1/2} \qquad (2)$$

where I_p is the peak current (in amperes), A is the surface area of the electrode (0.0115 cm^2 in this case), n is the number of electron involved in the charge transfer reaction (n =1 in this case), C is the bulk concentration of the reactant (in mol cm^{-3}), υ is the scan rate (in V sec^{-1}) and D is the diffusion coefficient (in cm^2 sec^{-1}). The value of D calculated on the basis of Eq. 2 from the slope of plot of I_{pc} vs. $\upsilon^{1/2}$ (Fig. 3) was 0.602×10^{-5} cm^2 sec^{-1}. This value is in close agreement with the reported value of 0.620×10^{-5} cm^2 sec^{-1} [13].

Determination of Heterogeneous Electron Transfer Rate Constant for Uranyl Ions

The heterogeneous electron transfer rate constant "k_s" were calculated by using the following relation developed by Klingler and Kochi [24], which is based on peak separation:

$$k_s = 2.18\left[\frac{\beta D_o nF\upsilon}{RT}\right]^{1/2} \exp\left[-\frac{\beta^2 nF}{RT}(E_{pa} - E_{pc})\right] \qquad (3)$$

where β is a dimensionless parameter known as electron transfer coefficient, n is the number of electrons transferred and D_o is the diffusion coefficient of the oxidized species in cm^2 sec^{-1} and the other parameters have their usual meanings. For a reversible reaction the value of β is taken to be 0.5. The value of heterogeneous electron transfer rate constant "k_s" was calculated at 50 mV sec^{-1} using D_o= 0.602 × 10^{-5} cm^2 sec^{-1} and found to be 2.72×10^{-3} cm sec^{-1}

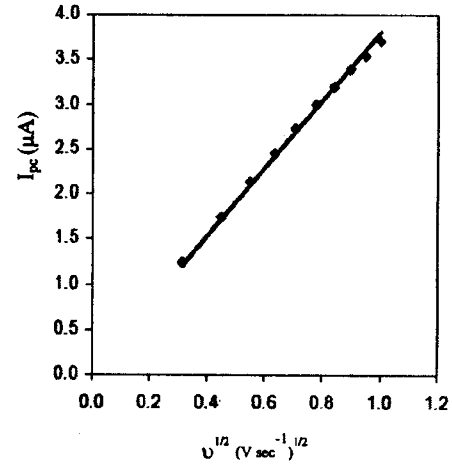

Fig. 3: Plot of variation of cathodic peak current of the simple uranyl ion "I_{pc}" versus the square root of scan rate "$V^{1/2}$".

Effect of Sulphate Ions on the Kinetic Behavior of Uranyl Ion

The effect of sulphate ions on the cyclic voltammetric behavior of UO_2^{2+}/ UO_2^{+} couple was studied at 1.5 mol L^{-1} ionic strength. The peak potential of the UO_2^{2+}/ UO_2^{+} couple shifted toward more cathodic potential side with increasing concentration of sulphate ions and at last the shift in peak potential becomes negligible above 0.4 mol L^{-1} Na_2SO_4. The cathodic shift of peak potential of uranyl ion with increasing concentration of sulphate ions is an indication of formation of a stable complex of uranyl ion with sulphate ions.

In order to find the effect of complexation of uranyl ions with sulphate ions on its kinetic behavior, we calculated the diffusion coefficient and heterogeneous electron transfer rate constants in 0.4 mol L^{-1} Na_2SO_4 solutions at 1.5 mol L^{-1} ionic strength in the same manner as for simple uranyl ions. In the presence of 0.4 mol L^{-1} Na_2SO_4 solution, the values of D_o and k_s were 0.534 x10^{-5} cm^2 sec^{-1} and 2.56 x10^{-3} cm sec^{-1} respectively, which are not significantly different from the values obtained in the absence of sulphate ions.

Thermodynamic Studies

The influence of temperature on the heterogeneous electron transfer rate constant of non-complex and complex uranyl ions was also studied from 293-318 K. In both cases the values of diffusion coefficient and the heterogeneous electron transfer rate constants increased with increasing temperature as shown by the data in Table- 1.

Table-1: Comparison of kinetics data of simple and complex uranyl ion at different temperature.

	D_o (cm^2 sec^{-1})		k_s (cm sec^{-1})	
Temp. (K)	Un-complex Uranyl ions $[SO_4^{2-}]$ = 0.0 mol L^{-1}	Complex Uranyl ions $[SO_4^{2-}]$ = 0.4 mol L^{-1}	Un-complex Uranyl ions $[SO_4^{2-}]$ = 0.0 mol L^{-1}	Complex Uranyl ions $[SO_4^{2-}]$ = 0.4 mol L^{-1}
293	0.538×10^{-5}	0.480×10^{-5}	2.62×10^{-3}	2.50×10^{-3}
298	0.602×10^{-5}	0.534×10^{-5}	2.72×10^{-3}	2.56×10^{-3}
303	0.717×10^{-5}	0.602×10^{-5}	2.95×10^{-3}	2.68×10^{-3}
308	0.799×10^{-5}	0.702×10^{-5}	3.12×10^{-3}	2.79×10^{-3}
313	0.901×10^{-5}	0.779×10^{-5}	3.29×10^{-3}	2.87×10^{-3}
318	1.06×10^{-5}	0.883×10^{-5}	3.51×10^{-3}	2.95×10^{-3}

The values of free energy of activation were calculated by using Eq. 4 proposed by Marcus [20], which can be expressed in a simpler form for one mole of a reacting species as

$$k_s = Z_{het} \exp\left[\frac{-\Delta G^*}{RT}\right] \qquad (4)$$

On rearranging we get

$$\ln\left(\frac{k_s}{Z_{het}}\right) = \frac{-\Delta G^*}{RT} \qquad (5)$$

$$\text{Since } \Delta G^* = \Delta H^* - T\Delta S^* \qquad (6)$$

Therefore, Eq. 5 can be re-written as

$$\ln\left(\frac{k_s}{Z_{het}}\right) = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \qquad (7)$$

where Z_{het} is the collision number for heterogeneous electron transfer process and its value can be calculated at given temperature by the following relation [20]:

$$Z_{het} = \left(\frac{RT}{2\pi M}\right)^{1/2} \qquad (8)$$

where R is the gas constant (8.3143 J mol^{-1} K^{-1}), T is the absolute temperature, and M is the molecular mass of the reacting species.

Since values of k_s and Z_{het} are known at different temperatures, therefore, the values of ΔH^* and ΔS^* can be obtained from the slope and intercept of the plot of ln (k_s/ Z_{het}) vs. 1/ T as shown in Fig. 4. The comparison of thermodynamic data for the reduction of uranyl ions in the presence and absence of sulphate ions is made in Table-2. In both cases, ΔS^* values were slightly negative while values of ΔH^* were positive which indicates that the process of reduction of uranyl ion at hanging mercury drop electrode is an endothermic and non-spontaneous process. The value of Gibbs free energy of activation at 298 K "ΔG_{298}^*" were calculated from the values of ΔH^* and ΔS^* using Eq. 6 and found to be 15.06 and 15.22 kJ mol^{-1} for simple and complex uranyl ions respectively. There was no significant difference in values of ΔG_{298}^* for simple and complex uranyl ions. The positive values of ΔG_{298}^* indicated the non-spontaneity of the reduction of uranyl ion at hanging mercury drop electrode.

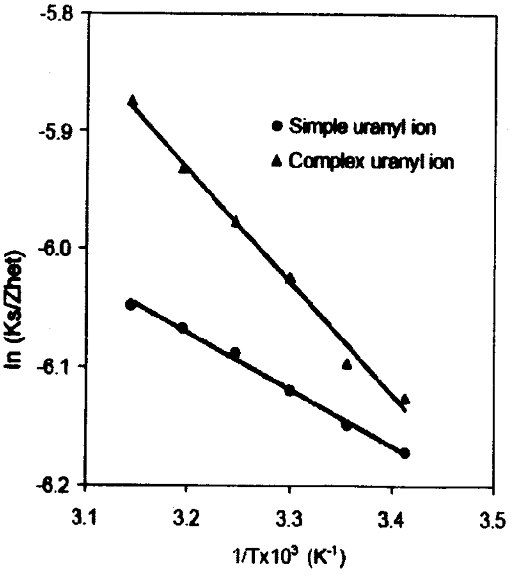

Fig. 4: Plot of ln k/ Z_{het} vs. 1/ T.

Table-2: Comparison of thermodynamic data for the reduction of UO_2^{2+} to UO_2^{+} ions at hanging mercury drop electrode in the presence and absence of sulphate ions.

Type of system	ΔH^* (kJ mole^{-1})	ΔS^* (J mole^{-1} K^{-1})	ΔG_{298}^* (kJ mole^{-1})
Un-complex Uranyl ions $[SO_4^{2-}]$=0.0 mol L^{-1}	7.97	-23.80	15.06
Complex Uranyl ions $[SO_4^{2-}]$=0.4 mol L^{-1}	3.99	-37.70	15.22

Table-3: Analysis of cathodic peak potential data of uranyl ion as a function of different concentrations of sulphate ions for evaluating the overall stability constants (scan rate = 50 mV sec^{-1}, [UO_2^{2+}] = 5 × 10^{-4} mol L^{-1}, pH = 3, μ=1.5 mol L^{-1}, Temp. = 25°C, value of (E_{pc})s for simple uranyl ions was taken to be -0.14 V).

Added [SO_4^{2-}] (mol L^{-1})	Free [SO_4^{2-}] (mol L^{-1})	(E_{pc})c (V)	(E_{pc})s - (E_{pc})c (V)	F_0(SO_4^{2-})	F_1(SO_4^{2-})	F_2(SO_4^{2-})
0.05	0.049	-0.190	0.050	6.81	118.6	-
0.10	0.099	-0.214	0.074	17.11	162.8	836
0.15	0.149	-0.23	0.090	31.62	205.5	842
0.20	0.199	-0.242	0.102	50.12	246.8	838
0.25	0.249	-0.252	0.112	73.56	291.4	849
0.30	0.299	-0.26	0.120	100.0	331.1	840
0.35	0.349	-0.267	0.127	130.8	372.0	837
0.40	0.399	-0.273	0.133	164.7	410.3	828

Determination of Stability Constants of Uranyl Sulphate Complexes from Peak Potential Data

The uranyl ions make stable complexes with the sulphate ions. Due to formation of these stable complexes, the peak potential of the UO_2^{2+}/ UO_2^{+} couple shifts toward more cathodic potential with increasing concentration of sulphate ions at a constant ionic strength as shown by the data in Table-3.

For calculating the stability constants from peak potential data, the basic equation used in this work is the same as initially proposed by Deford and Hume for evaluating the stability constants from polarographic half-wave potential data [29].

$$F_o(X) = \text{antilog}[\frac{nF\Delta E_{1/2}}{2.303RT} + \log(\frac{Is}{Ic})] = \sum_0^N \beta[X] \qquad (9)$$

where [X] is the free ligand ions concentration, n, F, R and T have the same meanings as in the Nernst equation, $\Delta E_{1/2}$ is the difference between polarographic half-wave potential when [X] = 0 (simple uranyl ion) and when [X] ≠ 0 (complex uranyl ion), Is and Ic are the diffusion current constants for simple and complex uranyl ion respectively, and β_j is the overall formation constant, also known as overall stability constant of a given complex. Since the value of diffusion coefficient of uranyl ion was not affected significantly during complexation with sulphate ions, therefore, the term involving diffusion current I_s and I_c in Eq. 9 may be neglected. Thus Eq. 9 becomes

$$F_0(X) = \text{antilog}[\frac{nF\Delta F_{1/2}}{2.303RT}] = \sum_0^N \beta_j [X]^{\boxed{j}} \qquad (10)$$

In order to convert Eq. 10 into a form applicable for evaluation of stability constants from peak potential data, the following relation between polarographic half-wave potential and the peak potential of a cyclic voltammogram was used [25].

$$E_{pc} = E_{1/2} - \frac{1.1RT}{nF} \qquad (11)$$

where E_{pc} is the cathodic peak potential and $E_{1/2}$ is the polarographic half-wave potential. Since both peak potential and polarographic half-wave potential shifts equally toward cathodic potential side with increasing concentration of complexing agents, therefore, at a constant temperature we may have:

$$\Delta E_{pc} = \Delta E_{1/2} \qquad (12)$$

i.e. at a constant temperature, the shift in cathodic peak potential is equal to the shift in polarographic half-wave potential. Thus the Eq. 10 in term of shift in peak potential "ΔE_{pc}" can be re-written as

$$F_0(X) = \text{antilog}[\frac{nF\Delta F_{pc}}{2.303RT}] = \sum_0^N \beta[x]^{j} \qquad \boxed{(13)}$$

Here ΔE_{pc}=(E_{pc})s - (E_{pc})c, where (E_{pc})s is the cathodic peak potential of a simple uranyl ions and (E_{pc})c is the cathodic peak potential of a complex uranyl ion. The Eq. 13 is applicable for evaluating the stability constant of uranyl-sulphate complexes from data of shift in cathodic peak potential.

The evaluation of other functions from $F_0(X)$ is described elsewhere in detail [29] and briefly they are described here for convenience:

$$F_1(X) = \frac{F_0(X) - 1}{[X]} = \beta_1 + \beta_2[X] + \beta_3[X]^2 + \qquad (14)$$

$$F_2(X)=\frac{F_1(X)-\beta_1}{[X]}=\beta_2+\beta_3[X]+\beta_4[X]^{j}+ \quad (15)$$

$$F_{N-1}(X)=\frac{F_{N-2}(X)-\beta_{N-2}}{[X]}=\beta_{N-1}+\beta_N[X] \quad (16)$$

$$F_N(X)=\frac{F_{N-1}(X)-\beta_{N-1}}{[X]}=\beta_N \quad (17)$$

The number "N" with $F_N(X)$ function shows the maximum number of ligand molecules in a given complex. Experimentally the maximum number of the ligand molecules "N" is identified by the fact that the last $F_N(X)$ function is independent of ligand concentration so that a straight line parallel to the x-axis may be obtained.

The data of shift in cathodic peak potential "ΔE_{pc}" along with calculated values of different F (SO_4^{2-}) functions at different concentration of sulphate ions at a constant ionic strength of 1.5 mol L^{-1} are given in Table 3. The slight change in pH did not affect the values of ΔE_{pc}. The pH of the solution was, however, maintained at pH 3. The amount of sulphate ions added was corrected for the amount present in complexed form which is assumed to be equal to $2\times[UO_2^{2+}] = 0.001$ mol L^{-1}.

The values of $F_o(SO_4^{2-})$ were evaluated from Eq. 13 using ΔE_{pc} values. The values of $F_1(SO_4^{2-})$ were evaluated from values of $F_o(SO_4^{2-})$ using Eq. 14. The values of $F_2(SO_4^{2-})$ were evaluated from Eq. 15 using value of β_1 that was obtained by extrapolating $F_1(SO_4^{2-})$ to $[SO_4^{2-}] = 0$.

The plot of values of different functions $F(SO_4^{2-})$ vs. $[SO_4^{2-}]$ is shown in Fig. 5. It is clear from Fig. 5 that values of $F_2(SO_4^{2-})$ are almost constants. It indicates that there may be maximum of two ligand molecules in a uranyl sulphate complex. In other words, it indicates the formation of complexes of the types $UO_2(SO_4)$ and $UO_2(SO_4)_2^{2-}$ in sulphate medium which may be formed according to the following equations:

$$UO_2^{2+}+SO_4^{2-} \rightleftarrows UO_2SO_4 \quad (18)$$

$$\beta_1=\frac{[UO_2SO_4]}{[UO_2^{2+}][SO_4^{2-}]}=79\ (\text{mol L}^{-1})^{-1}$$

$$UO_2^{2+}+2SO_4^{2-} \rightleftarrows UO_2(SO_4)_2^{2-} \quad (19)$$

$$\beta_2=\frac{[UO_2(SO_4)_2^{2-}]}{[UO_2^{2+}][SO_4^{2-}]^2}=832\ (\text{mol L}^{-1})^{-2}$$

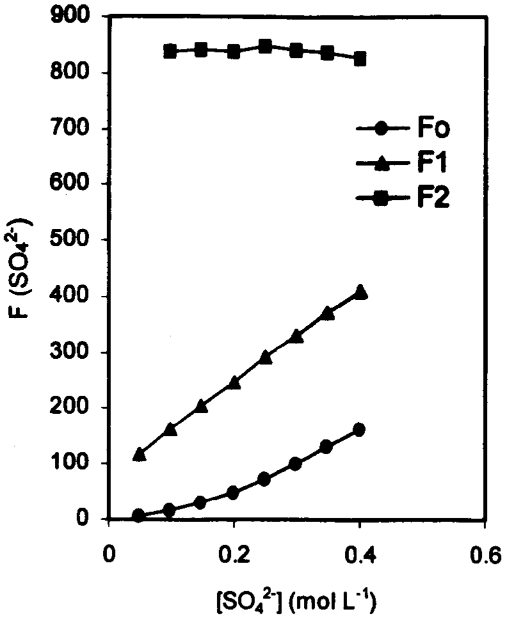

Fig. 5: Plot of $F(SO_4^{2-})$ vs. $[SO_4^{2-}]$.

Due to existence of maximum of two SO_4^{2-} molecules in uranyl sulphate complex, the corresponding values of overall stability constants, β_1 and β_2 were evaluated by using Eq. 14, which may be re-written as

$$F_1(SO_4^{2-})=\beta_1+\beta_2[SO_4^{2-}] \quad (20)$$

This is a linear straight-line equation, hence the value of β_2 may be evaluated from the slope while the value of β_1 may be evaluated from the intercept of the plot of $F_1(SO_4^{2-})$ vs. $[SO_4^{2-}]$ as shown in Fig. 5.

In order to check the consistency between experimental and calculated values of $F_o(SO_4^{2-})$, the experimental values of β_1 and β_2 were used to re-calculate the values of $F_o(SO_4^{2-})$ by using the following equation:

$$F_0(SO_4^{2-})=1+\beta_1[SO_4^{2-}]+\beta_2[SO_4^{2-}]^2 \quad (21)$$

The data in Table 4 show that the calculated values of $F_o(SO_4^{2-})$ are in close agreement with the experimental values of $F_o(SO_4^{2-})$, which indicates the accuracy of the experimental values of β_1 and β_2.

Comparison of Stability Constants of Uranyl Sulphate Complexes with the Reported Data

The experimental values of $\log\beta_1$ and $\log\beta_2$ of sulphate complexes are presented in Table- 5

Table-4: Comparison of experimental values of function $F_0(SO_4{}^{2-})$ with those calculated from Eq. 21 taking β_1=79 (mol $L^{-1})^{-1}$ and β_2=832 (mol $L^{-1})^{-2}$.

Free $[SO_4{}^{2-}]$ (mol L^{-1})	Experimental value of $F_0(SO_4{}^{2-})$	Calculated value of $F_0(SO_4{}^{2-})$
0.049	6.81	6.87
0.099	17.11	170
0.149	31.62	31.2
0.199	50.12	49.7
0.249	73.56	72.3
0.299	100.0	99.0
0.349	130.8	130

Table-5: Comparison of observed and reported values of stability constants of uranyl sulphate complexes at 25 °C.

Stability constants	Observed values	Reported values with references
log β_1	1.90 ± 0.01	1.75 [7, 30] 1.92 [31]
log β_2	2.92 ± 0.02	2.54 [7, 30] 2.90 [31]

alongwith their estimated uncertainties and comparison with the reported data. The values of logβ_1 and logβ_2 are in close agreement with the reported data [7, 30-31]. This close agreement between observed and reported data is an important result, which shows the applicability of cyclic voltammetry for complexation studies.

Experimental

A model 175 universal programmer, model 173 potentiostat/galvanostat equipped with model 179 digital coulometer, model 303A SMDE and model 306 interface, all from EG&G Princeton Applied Research (PAR), New Jersey, USA, were used for cyclic voltammetric measurements. The cyclic voltammograms were recorded with model RE 0089 x-y recorder from Houston instrument. A three-electrode system was used with hanging mercury drop electrode (HMDE) as working electrode, Ag/ AgCl (sat. KCl) as reference electrode and Pt-wire as counter electrode. All potentials within this paper are quoted with respect to Ag/ AgCl (sat. KCl) reference electrode

All experiments were carried out in double-walled jacketed cell where temperature was controlled with circulating water. All experiments were carried out at 25 °C except when measuring the thermodynamic parameters.

The stock solution of uranyl perchlorate was prepared by dissolving accurately weighed amount of UO_2 in concentrated HNO_3 and then the resulting uranyl nitrate was evaporated with conc. $HClO_4$. All solutions were prepared in deionized water. The 2.0 mol L^{-1} $NaClO_4$ solution was used to adjust the ionic strength of the working solution. The pH of the working solution was adjusted with 0.1 mol L^{-1} $HClO_4$ or 0.1 mol L^{-1} NaOH solutions and measured with Metrohm 605 pH meter. Before each measurement, the working solution was purged with nitrogen gas to avoid the interference due to the dissolved oxygen.

Conclusion

The uranyl ion gives one electron reversible cyclic voltammetric peaks for $UO_2{}^{2+}/UO_2{}^{+}$ couple in aqueous perchlorate media. The kinetic behavior of the uranyl ions was not affected significantly in the presence of sulphate ions. The thermodynamic parameters, ΔH^*, ΔS^* and $\Delta G_{298}{}^*$ were calculated from the effect of temperature on values of heterogeneous electron transfer rate constants "k_s" for simple uranyl ions as well as uranyl-sulphate complex and found to be 7.97 kJ mol^{-1}, -23.80 J mol^{-1}. K^{-1} and 15.06 kJ mol^{-1} in simple perchlorate medium and 3.99 kJ mol^{-1}, -37.70 J mol^{-1} K^{-1}, and 15.22 kJ mol^{-1} in sulphate medium. The stability constants of uranyl-sulphate complexes were calculated from the analysis of data of shift in peak potential with increasing concentration of sulphate ions at 1.5 mol L^{-1} ionic strength. The values of logβ_1 and logβ_2 for 1:1 and 1:2 uranyl sulphate complexes were found to be 1.90 ± 0.01 and 2.92 ± 0.02 respectively, which were in close agreement with the reported values.

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