



## Synthesis and Characterization of Uranium(IV)-Serine Complex

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An attempt has been adopted to synthesize a complex of uranium(IV) by using serine as a ligand. For the characterization of uranium(IV)-serine complex different analytical techniques such as semi-microanalysis, UV-visible spectroscopy, infrared spectroscopy, magnetic susceptibility measurements and cyclic voltammetry were employed. The metal to ligand ratio (M:L) in this complex was found to be 1:2, while coordinating sites in the complex was found to be amino and carboxyl groups of serine. The electrochemical studies demonstrate that uranium(IV) in this coordination complex oxidized quasi reversibly to uranium(V). There was no experimental evidence that supported the adsorption of either the reactant or product at the surface of the platinum electrode. Values of thermodynamic parameters indicate that the oxidation of uranium(IV) at platinum electrode is an endothermic and a non-spontaneous process.

**Keywords:** Uranium, Serine, Spectroscopy, Electrochemistry.

### INTRODUCTION

Hydroxyl methyl moiety ( $\text{HOCH}_2^-$ ) is present as a side chain in serine and therefore it is one of the amino acid with hydroxyl group. This hydroxyl group has the ability to form hydrogen bond with the solvent water molecules; hence it is polar in nature [1-3]. The study of interaction of alkali metals with serine and other amino acids is of great interest among researchers [4]. Potentiometric methods were employed to determine the stability constants for La(III) and Y(III) L-serine complexes and thermodynamic parameters were also estimated [5]. The thermo-chemical study of complex formation between nickel(II), cobalt(II), cadmium(II) and zinc(II) ions and L-serine in aqueous medium were carried out [6]. Research of Li and Doody [7] leads to conclude that the complex of  $\text{Cu}^{2+}$  with serinate is very stable. Against that Cu(II)-serine complex, because of the presence of  $-\text{NH}_3^+$ , is not sufficiently stable to be studied potentiometrically. Similar generality can be applied to uranyl complexes. Solvent extraction method was employed to calculate the value of formation constant. The  $K_f$  value of uranyl-serine complex was estimated to be  $7.4 \pm 0.2$ . Broad and strong band at  $3400 \text{ cm}^{-1}$  specifies the formation of strong hydrogen bonding in sample of serine coordinated with  $\text{Al}_x(\text{OH})_y$ . Asymmetric and symmetric vibration bands of carboxyl group were found to be at  $1590$  and  $1410 \text{ cm}^{-1}$ , respectively. The difference between these two vibration bands ( $180 \text{ cm}^{-1}$ ) is higher than that of pure DL- $\alpha$ -serine ( $146 \text{ cm}^{-1}$ ).

The sharp and strong OH deformation band was observed at  $1250 \text{ cm}^{-1}$  both in pure serine and in complexed form with aluminum hydroxide [8]. Present study deals with the synthesis and characterization of uranium(IV)-serine complex.

### EXPERIMENTAL

Uranyl nitrate hexahydrate (BDH) was used to prepare stock solution of uranium(VI) in  $0.2 \text{ M HCl}$ . This yellow coloured solution was reduced to a leaf green coloured solution of uranium(IV) by hydrogenation process, using platinized alumina as a catalyst [9]. The complex was synthesized by adding aqueous solution of serine in uranium(IV) solution, under constant stirring. The pH of reaction mixture was adjusted to 4.5 by introducing little volume of NaOH solution. Precipitates of the synthesized complex appeared at this pH range. The precipitates were then filtered through Whatmann 542 filter paper and washed with deionized water and 99 % absolute ethanol. The residue obtained was dried by placing over silica gel in a desiccator.  $\text{U}(\text{Ser})_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  Found: C, 13.91; H, 3.44; N, 5.38; U, 46.05; .Anal. calcd. : C, 13.95; H, 3.49; N, 5.42; U, 46.11. Yield, (72.91 %).

**Characterization:** The synthesized complex was examined for its C, H and N contents through CHN (Carlo Erba) instrument. Quantitative analysis of uranium(IV) was carried out by volumetric titration with potassium dichromate, using barium salt of diphenylamine sulphonc acid as an indicator [9]. Shimadzu UV-160A UV-visible spectrophotometer was

utilized to study the absorption pattern of metal in the absence and presence of a ligand, within the wavelength range of 400–800 nm. Infrared spectra of complex and serine were recorded using Prestige-21 FTIR spectrophotometer. Magnetic susceptibility balance (MSB) was employed to study magnetic susceptibility value of the complex in solid state. Electrochemical Analyzer/Workstation, CHI 660C was utilized to perform cyclic voltammetric measurements under nitrogen atmosphere. The potential window in this study ranges from 0–1.5 Volts versus Ag/AgCl electrode. A platinum wire counter electrode, a platinum working electrode and a Ag/AgCl reference electrode were used in a single three electrode cell. The cyclic voltammograms at different scan rates were recorded in the temperature range of 298 to 323 K.

## RESULTS AND DISCUSSION

**UV-visible spectra:** Comparison of UV-visible absorption spectra of free uranium(IV) solution and a solution of uranium(IV)-serine complex is shown in Fig. 1. It was observed that the absorption pattern of metal after coordination with serine remains almost same but with slight bathochromic shift. However, in the presence of the ligand absorption intensity of metal enhances. Molar absorptivity coefficient values for the synthesized complex were determined by using the data of UV-visible absorption spectra (Table-1). The mole ratio plot indicates that metal to ligand ratio (M:L) in this complex is 1:2 (Fig. 2).

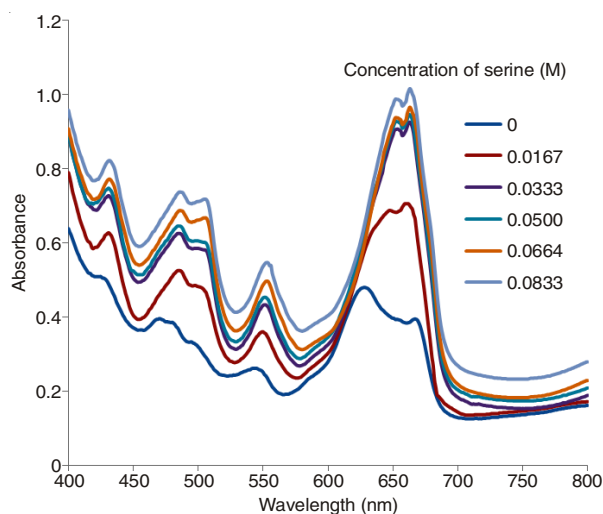


Fig. 1. Overlay of absorption spectra of uranium(IV)-serine complex with constant metal concentration of 0.0167 M and varying ligand concentration

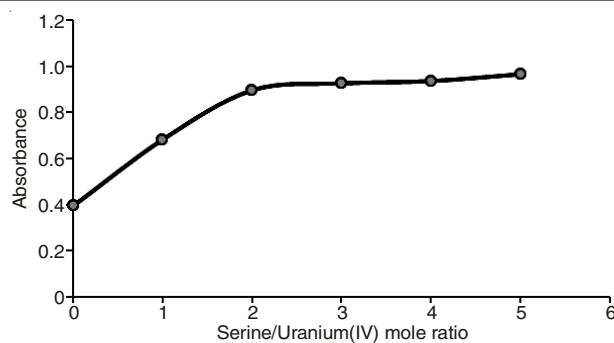


Fig. 2. Mole ratio plot of uranium(IV)-serine complex at wavelength 653 nm

Bathochromic shifts for bands at wavelengths 644.0 and 631.0 nm were found to be almost equal but the increase in intensity of 644 nm band is greater than that for 631 nm. This is an indication that in the synthesized complex the greatest decrease in transition energy occurs between the ground level  $^3H_4$  and  $^1G_4$ . The bathochromic shift and an increase in the absorption intensity specify a more uniform distribution of electronic charge over the whole compound and that around the central ion [10,11].

**Infrared spectra:** In present complex of U(IV) the  $H_2O$  and  $-NH_2$  stretching frequencies give rise to IR bands at 3469.7 and 3053.1  $cm^{-1}$ , respectively. The absorption at 2038.6  $cm^{-1}$  is assigned to deformation of O–H moiety of serine molecule. Frequencies for asymmetric and symmetric vibrations of carboxylic group are found to be at 1596.9 and 1382.9  $cm^{-1}$ , correspondingly. Peaks at 1467.7, 1126.4 and 1083.6  $cm^{-1}$  are due to bending, twisting and wagging of  $-NH_2$  group. While 800.4 and 609.5  $cm^{-1}$  frequencies are assigned to  $-COO^-$  wagging and bending modes. Infrared frequencies at 572.7 and 437.9  $cm^{-1}$  can be ascribed to  $\nu(M-N)$  and  $\nu(M-O)$ , respectively [12,13] (Fig. 3).

Additional infrared bands noticed in the spectrum are: 1413.7  $cm^{-1}$  ( $-CH_2$  bending); 1340.4 ( $-CH_2$  wagging); 1303.8  $cm^{-1}$  ( $-CH$  bending); 1220.9  $cm^{-1}$  ( $-CH_2$  twisting); 1010.8  $cm^{-1}$  (CCN asymmetric); 916.7  $cm^{-1}$  ( $-CH_2$  rocking); 850.4  $cm^{-1}$  (CCN symmetric).

**Magnetic susceptibility:** Values of magnetic susceptibility measurement were calculated by using Curie law (Table-2). The comparison of experimental and calculated values verified that magnetic moments are not isolated. These do relate with the adjacent centers as might be expected if magnetic dilutions are not adequate [14].

**Electrochemical study:** Cyclic voltammograms of uranium(IV)-serine complex (conc. =  $5 \times 10^{-3}$  M) in aqueous

TABLE-1  
ENERGY LEVELS ASSIGNED TO THE ABSORPTION SPECTRA OF FREE URANIUM(IV) AND ITS COMPLEX WITH SERINE IN AQUEOUS MEDIA

| Transitions   | Uranium(IV) solution in the absence of ligand |       |                   |              | Uranium(IV)-serine solution |       |                   |              |
|---------------|-----------------------------------------------|-------|-------------------|--------------|-----------------------------|-------|-------------------|--------------|
|               | $\lambda^a$                                   | $E^b$ | Abs. <sup>c</sup> | $\epsilon^d$ | $\lambda^a$                 | $E^b$ | Abs. <sup>c</sup> | $\epsilon^d$ |
| $^3H_4-^1G_4$ | 644.0                                         | 1.924 | 0.412             | 19.951       | 663.0                       | 1.869 | 0.925             | 55.389       |
| $^3H_4-^1D_2$ | 631.0                                         | 1.964 | 0.476             | 21.614       | 653.0                       | 1.898 | 0.896             | 53.653       |
| $^3H_4-^3P_1$ | 546.0                                         | 2.270 | 0.260             | 11.857       | 550.5                       | 2.252 | 0.433             | 25.928       |
| $^3H_4-^1I_6$ | 471.0                                         | 2.632 | 0.395             | 17.946       | 484.5                       | 2.558 | 0.625             | 37.425       |
| $^3H_4-^3P_2$ | 427.0                                         | 2.903 | 0.505             | 24.665       | 431.0                       | 2.876 | 0.727             | 43.533       |

<sup>a</sup> $\lambda$  = Wavelength in nm; <sup>b</sup> $E$  = Energy (eV/mol) associated with the radiation of specific wavelength; <sup>c</sup>Abs. = Absorbance; <sup>d</sup> $\epsilon$  = Molar absorptivity coefficient ( $M^{-1} cm^{-1}$ ).

TABLE-2  
MAGNETIC PARAMETERS FOR URANIUM(IV)-SERINE COMPLEX

| $M^{\cdot} f^a$ | $\mu_{so}^c = [n(n+2)]^{1/2}$ | $\mu_{eff}^f = (8\lambda_m T)^{1/2}$ | T (K) <sup>g</sup> | $n^h$ (cal.) | n (theory) |
|-----------------|-------------------------------|--------------------------------------|--------------------|--------------|------------|
| $U^{+4} f^2$    | 2.83                          | 2.56                                 | 304                | 1.75         | 2          |

<sup>c</sup> $\mu_{so}$  is spin-only magnetic moment. <sup>f</sup> $\mu_{eff}$  is an experimental effective magnetic moment calculated assuming curie behaviour. <sup>g</sup>T is the temperature in Kelvin (K). <sup>h</sup>The number of unpair electrons per uranium ion calculated from the values of  $\mu_{eff}$  using  $\mu = [n(n+2)]^{1/2}$

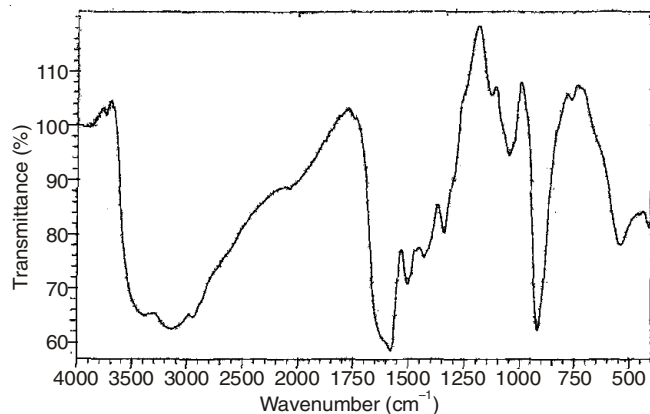


Fig. 3. Infrared spectrum of uranium(IV)-serine complex in KBr disc

media (2 M HClO<sub>4</sub>) at different scan rates were recorded (Fig. 4). The anodic and cathodic peaks at 50 mV/s scan rate appear at 1.222 and 1.044 V, respectively.

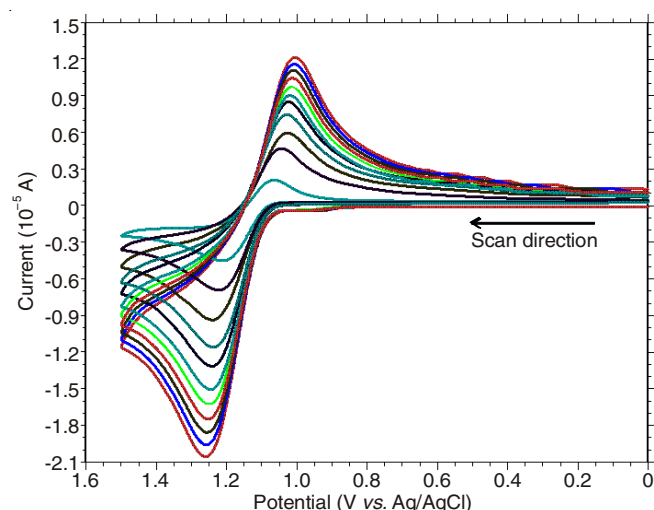


Fig. 4. Cyclic voltammograms at Pt electrode corresponding to the oxidation of uranium(IV)-serine complex (Conc. =  $5 \times 10^{-3}$  M) at scan rates from 20 mV/s to 500 mV/s in 2 M HClO<sub>4</sub> and NaClO<sub>4</sub> as an electrolyte; Temperature = 305 K

The presence of both cathodic and anodic peaks is an evidence that the oxidation of uranium(IV) is a reversible process. With the raise in scan rate (Table-3) the anodic peak moves towards positive side and cathodic peak shifts towards negative side. The difference of  $E_{pA}$  and  $E_{pC}$  is greater than the theoretical value (0.05 V) for the reversible one electron transfer process. The increase in the separation between peak potential with the increase in scan rate is the indication of charge transfer kinetics [15].

Linear variation of anodic peak current with the square root of scan rate (Fig. 5) leads to the conclusion that the oxidation of uranium(IV) to uranium(V) is a quasi-reversible process at Pt working electrode [16].

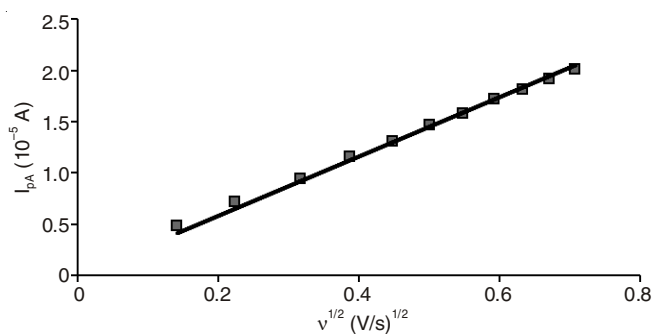


Fig. 5. Variation of anodic peak current of uranium(IV)-serine complex with the square root of scan rate

The ratio of cathodic to the anodic peak current ( $I_{pC}/I_{pA}$ ) is less than 1 and the decrease is observed in the value of  $I_{pA}/v^{1/2}$  with the raise in scan rate (Fig. 6). These results lead to an assumption of an ECE mechanism. The uranium(V) species formed by the oxidation of uranium(IV) is unstable and disproportionate into uranium(IV) and uranium(VI). No current was observed due the reduction of uranium(VI) [17].

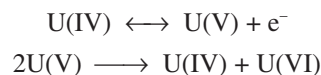


TABLE-3  
CYCLIC VOLTAMMETRIC DATA OBTAINED AT Pt ELECTRODE CORRESPONDING TO THE OXIDATION OF URANIUM(IV)-SERINE COMPLEX IN 2 M HClO<sub>4</sub> AND NaClO<sub>4</sub> AS AN ELECTROLYTE

| Scan rate (V/s) | $E_{pA}$ (V) | $E_{pC}$ (V) | $E_{pA}-E_{pC}$ (V) | $E_{pA/2}$ (V) | $E_{pA}-E_{pA/2}$ (V) | $I_{pA}$ (10 <sup>-5</sup> A) | $I_{pC}$ (10 <sup>-5</sup> A) | $I_{pC}/I_{pA}$ |
|-----------------|--------------|--------------|---------------------|----------------|-----------------------|-------------------------------|-------------------------------|-----------------|
| 0.02            | 1.212        | 1.065        | 0.147               | 1.134          | 0.078                 | 0.480                         | 0.372                         | 0.774           |
| 0.05            | 1.222        | 1.044        | 0.178               | 1.141          | 0.081                 | 0.713                         | 0.667                         | 0.935           |
| 0.10            | 1.240        | 1.026        | 0.214               | 1.151          | 0.089                 | 0.941                         | 0.938                         | 0.996           |
| 0.15            | 1.237        | 1.028        | 0.209               | 1.150          | 0.087                 | 1.161                         | 1.158                         | 0.997           |
| 0.20            | 1.242        | 1.023        | 0.219               | 1.153          | 0.089                 | 1.310                         | 1.301                         | 0.993           |
| 0.25            | 1.246        | 1.019        | 0.227               | 1.156          | 0.090                 | 1.465                         | 1.463                         | 0.998           |
| 0.30            | 1.250        | 1.015        | 0.235               | 1.158          | 0.092                 | 1.579                         | 1.577                         | 0.998           |
| 0.35            | 1.252        | 1.013        | 0.239               | 1.160          | 0.092                 | 1.717                         | 1.714                         | 0.998           |
| 0.40            | 1.255        | 1.010        | 0.245               | 1.161          | 0.094                 | 1.816                         | 1.815                         | 0.999           |
| 0.45            | 1.257        | 1.007        | 0.250               | 1.162          | 0.095                 | 1.919                         | 1.920                         | 1.000           |
| 0.50            | 1.259        | 1.005        | 0.254               | 1.164          | 0.095                 | 2.013                         | 2.012                         | 0.999           |

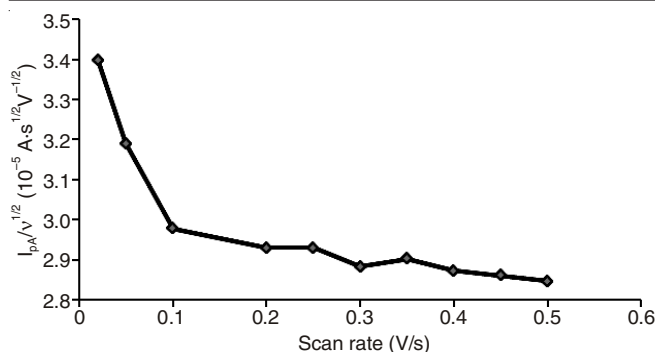


Fig. 6. Variation of peak current function of uranium(IV)-serine complex with scan rate

**Determination of diffusion coefficient:** Randles-Sevcik equation was used to determine the value of diffusion coefficient of the synthesized complex [18].

$$I_p = 0.4463 (nF)^{3/2} (RT)^{-1/2} ACD_0^{1/2} v^{1/2} \quad (1)$$

where  $I_p$  is the peak current (in amperes),  $n$  is the number of electrons transferred in the redox reaction,  $F$ ,  $R$  and  $T$  are Faraday constant, general gas constant and temperature in Kelvin, respectively,  $A$  is the surface area of the electrode ( $0.0314 \text{ cm}^2$  in this case),  $C$  is the concentration (in mole/ $\text{cm}^3$ ),  $D_0$  is the diffusion coefficient (in  $\text{cm}^2/\text{s}$ ) and  $v$  is the scan rate (in  $\text{V/s}$ ).

Eqn. 1 is verified in Fig. 5. It is concluded that the system is not completely reversible but quasi-reversible. The value of  $D_0$  calculated from the slope of plot  $I_{pA}$  vs.  $v^{1/2}$  (Fig. 5) is equal to  $2.5790 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

**Determination of heterogeneous electron transfer rate constant:** Heterogeneous electron transfer rate constant ( $k_s$ ) value was calculated by the following equation [19].

$$k_s = 2.18 \left( \frac{\beta D_0 n F v}{RT} \right)^{1/2} \exp \left( \frac{-\beta^2 n F}{RT} (E_{pA} - E_{pC}) \right) \quad (2)$$

where  $\beta$  is the dimensionless parameter known as electron transfer coefficient,  $D_0$  is the diffusion coefficient of the oxidized species in  $\text{cm}^2/\text{s}$ ,  $n$  is the number of electrons transferred,  $v$  is the scan rate,  $(E_{pA} - E_{pC})$  is the peak separation and  $F$  is the Faraday's constant,  $R$  is the general gas constant and  $T$  is the temperature in Kelvin. Assuming the value of 0.5 for  $\beta$  heterogeneous electron transfer rate constant ' $k_s$ ', at scan rate  $50 \text{ mV/s}$ , was calculated to be  $6.2790 \times 10^{-4} \text{ cm s}^{-1}$ .

**Study of adsorption process:** Interfacial behaviour of the complex was also examined by cyclic voltammetry. Forty repetitive cyclic voltammograms, at platinum working electrode, signify no alteration in the intensities of anodic and cathodic peak currents (Fig. 7). In addition to that neither pre nor any post-peak was noticed. These observations reveal that both the reactant and the product of this redox process do not involve in adsorption-desorption process at the surface of platinum electrode [20,21].

**Assessment of thermodynamic parameters:** The values of heterogeneous rate constants ( $k_s$ ) were calculated at different temperatures and thermodynamic parameters were estimated with the help of these values (Table-4).

With the increase in the temperature, the value of heterogeneous rate constant increases, this specifies that the oxidation

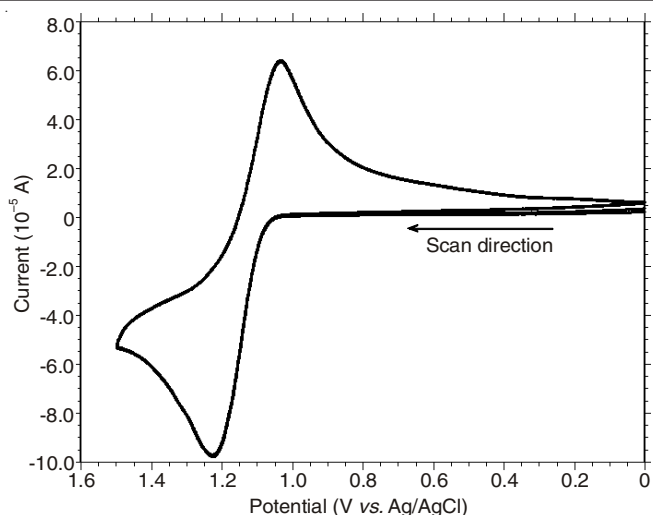


Fig. 7. Repetitive cyclic voltammograms at Pt electrode corresponding to the oxidation of uranium(IV)-serine complex (Conc. =  $5 \times 10^{-3} \text{ M}$ ) at scan rate  $50 \text{ mV/s}$  in  $2 \text{ M HClO}_4$  and  $\text{NaClO}_4$  as an electrolyte; Temperature =  $305 \text{ K}$

TABLE-4  
KINETIC DATA FOR URANIUM(IV) ION AT DIFFERENT TEMPERATURES WHEN FORM COMPLEX WITH SERINE

| Temperature (K) | Heterogeneous rate constants ( $k_s \times 10^4 \text{ cm s}^{-1}$ ) |
|-----------------|----------------------------------------------------------------------|
| 298             | 5.33                                                                 |
| 303             | 6.08                                                                 |
| 308             | 6.65                                                                 |
| 313             | 7.80                                                                 |
| 318             | 8.78                                                                 |
| 323             | 9.60                                                                 |

of uranium(IV)-serine complex at Pt working electrode is an endothermic process.

Following equations were used to find out thermodynamic parameters:

$$k_s = Z_{\text{het}} \exp \left( \frac{-\Delta G^*}{RT} \right) \quad (3)$$

By the rearrangement of the above expression eqn. 4 can be obtained.

$$\ln \left( \frac{k_s}{Z_{\text{het}}} \right) = \frac{-\Delta G^*}{RT} \quad (4)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

Therefore, the eqn. 4 can be rewritten as:

$$\ln \left( \frac{k_s}{Z_{\text{het}}} \right) = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \quad (6)$$

where  $Z_{\text{het}}$  is the collision number for the heterogeneous electron transfer process and at any specific temperature its value can be calculated by using the following equation.

$$Z_{\text{het}} = \left( \frac{RT}{2\pi M} \right)^{1/2} \quad (7)$$

where  $M$  is the molecular weight of the reacting species,  $R$  is the gas constant and  $T$  is the temperature in Kelvin and the value of  $\pi$  is 3.14.

The value of  $\Delta G_{298}^*$ , an apparent free energy of activation, at 298 K was computed using the equation.

$$\Delta G_{298}^* = \Delta H^* - 298\Delta S^* \quad (8)$$

The values of  $\Delta H^*$  (enthalpy change) and  $\Delta S^*$  (entropy change) for the synthesized complex were evaluated from the slope and intercept of the plots of  $\ln(k_s/Z_{het})$  versus  $1/T$  (Fig. 8).

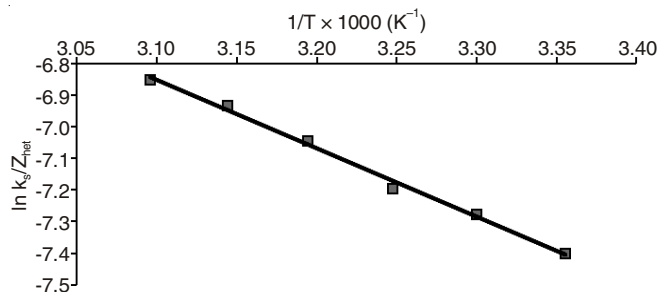


Fig. 8. Plot of  $\ln(k_s/Z_{het})$  vs.  $1/T$  for the evaluation of thermodynamic parameters for the oxidation of uranium(IV)-serine complex at Pt electrode

The values of thermodynamic parameters *i.e.*  $\Delta H^*$  and  $\Delta G_{298}^*$  are found to be 17.93 and 34.66 kJ mol<sup>-1</sup>, respectively. The value of  $\Delta S^*$  was calculated to be -56.12 J mol<sup>-1</sup> K<sup>-1</sup>.

The positive values of  $\Delta H^*$  and  $\Delta G_{298}^*$  show that the oxidation of uranium(IV) ion at Pt electrode is an endothermic and a non-spontaneous process [22-24].

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