

Redox process in [N-(2-hydroxyethyl)-ethylene-diamine-N,N',N'-triacetato] uranium (IV)

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ABSTRACT

The kinetics of reduction of tris(1, 10 orthophenanthroline) iron(III) by [N-(2-hydroxyethyl)-ethylene-diamine-N,N',N'-triacetato] uranium (IV), symbolized as [U(IV) HEDTA]¹⁺, has been investigated in aqueous medium at 30 ± 0.5 °C. Measurements were recorded under pseudo first order conditions. The rate of electron transfer reaction between these reactants was measured by varying pH and ionic strength, between 2.5-3.0 and 0.01-0.05 M respectively. It was found that pH directly influenced the k₁ and values were found to be 111.8, 193.7, 344.7, 478.93 mol⁻¹ dm³s⁻¹ at pH 3.2, 3.0, 2.8, 2.5 respectively. The value of k' was evaluated as 6.35 × 10⁶ mol⁻¹ dm³s⁻¹.

Abbreviations: EDTA = Ethylene-diamine-N,N',N'-tetra acetic acid, HEDTA = [N-(2-hydroxyethyl)-]ethylene-diamine-N,N',N'-triacetic acid

Keywords: Kinetics, ionic strength, pH and HEDTA

1. INTRODUCTION

Uranium, a f block element, is found in Earth's crust at an average concentration of about 2 ppm, and is more abundant than silver or mercury. The most common uranium-containing mineral is uraninite, a complex uranium oxide. Ionic liquids replace organic liquids used in different processing operations related to f block elements¹. For example, hydrophobic ionic liquids are used in liquid/liquid f-element extraction processes, based upon electrode deposition. For f-element-catalyzed reactions, high reaction rates, enhanced selectivity, better immobilization of the catalyst and an easy product recovery has often been observed in certain ionic liquids.¹ The electro-deposition of uranium oxide (possibly UO₂) from UO₂²⁺ and its behavior in much ionic liquid has been studied in ionic liquid. At high temperatures, the cathodic peak potential shifts for the reduction of U(VI) to U(IV) towards more negative triethyloctylammonium), [N222(12)][Tf2N] (triethyldodecylammonium)^{3,4}. A review of the thermodynamic data for the different oxidation states of actinide compounds with citrate, isosaccharinate and polyaminocarboxylate complexes has underlined their importance for environmental modeling.⁵ The computational Chemistry give an insight into electronic structure of f- elements.⁶ The synthesis and reactivity behavior of uranium (IV) complexes has been described by many scientists.⁷⁻¹⁴ The substitution and redox behavior of polyamino carboxylate complexes of metal ion complexes have found increased interest from researchers in last few years.¹⁴⁻²¹

HEDTA becomes an important ligand and many studies have been made on different complexes of HEDTA and between different metals in presence of HEDTA. The interaction of [Ru(III)(HEDTA) H₂O)] with a series of selected thiols having extra functional groups was investigated potentiometrically and kinetically. The effect of dioxane on the pK(a) values [Ru(III)HEDTA (H₂O)] and the formation constants of the corresponding thiol complexes was also presented.¹⁴ Fe(II)L; L = EDTA, HEDTA, tcma (tcma = 1-acetato-1,4,7-triazacyclononane) with hydrogen peroxide in neutral and slightly acidic solutions was studied by using the beta elimination reaction as an assay for the formation of hydroxyl free radicals, OH.¹⁵ The complexation of Fe(II) with HEDTA results in the decrease of redox potential, and enhances the reducing ability of Fe(II). An important example is the use of Fe(II)-organic complexes to accelerate Cr(VI) reduction.¹⁹ The study has been made to evaluate the inhibition of Cr(III) oxidation by Mn oxide in the presence of HEDTA.²⁰ The kinetics of the oxidation of [N-(2-hydroxyethyl)-ethylene-diamine-N,N',N'-triacetato] cobalt(II), ([Co^{II}-(HEDTA)]¹⁻, by N-bromosuccinimide (NBS), has been studied in aqueous solutions and water-methanol solvent mixtures under various conditions. An inner sphere mechanism is proposed for p oxidation of both the protonated and deprotonated species of the complex, with the formation of an intermediate which slowly forms the final oxidation product, [Co^{III}(HEDTA)]¹⁻. In water-methanol solvent mixtures the reaction rate decreased as the methanol content was increased.²¹ Similarly periodate ion oxidation of varieties of [Co(III)(H₂O)]_{2-n} complexes (L = EDTA, HEDTA, NTA, DTPA, PDTA, and HPDTA) have been investigated following the inner sphere mechanism.²² A comparative study of the kinetics of the reaction of superoxide radical with Fe(III) complexes of EDTA, DETAPAC and HEDTA was also ade.²³ Uranium complex of N-hydroxyethyl-ethylenediamine-triacetic acid (HEDTA) has been prepared by Martel et al.²⁴

Oxidation of different complexes of Uranium (IV) polyamino carboxylates with Tris 1, 10 orthophenanthroline iron (III) has been studied and reported by us previously.⁵⁻²⁷ Redox process in Uranous [N-(2-hydroxyethyl)-ethylenediamine triacetate] has been studied in the current investigations.

2. EXPERIMENTAL

Tris 1, 10 orthophenanthroline iron (III) – perchlorate was prepared by the method described by N. Sutin and B.M.Gordon²⁷ 0.1M stock solution of uranyl nitrate was prepared by dissolving an appropriate amount of uranyl nitrate (Aldrich Anal R grade) in 0.1 M HCl. Uranous solution was obtained by catalytic hydrogenation of uranyl nitrate.²⁸ Uranous solution has been standardized against potassium dichromate solution.²⁹ 0.1 M stock solution of HEDTA was prepared by trisodium salt of N-(2-hydroxyethyl)-ethylenediamine triacetate dihydrate (HEDTA). Standard U(IV) solution, warmed up to 40 – 50 °C, was mixed with HEDTA solution to get [U(IV) HEDTA 2H₂O]Cl. No precipitate appeared, as the dark leaf green solution of [U(IV) HEDTA]¹⁺ has high solubility in water. The pH of [U(IV) HEDTA]¹⁺ solution was maintained up to 3.0.

2.1 Spectrophotometric Determination of [U(IV)HEDTA]Cl

In order to determine the stability constant of [U(IV)HEDTA]¹⁺ at $\mu = 0.1\text{M}$ (NaCl) and 25 °C, a competition reaction between Th(IV), U(IV) and HEDTA was employed. The experiment was carried out at pH = 1.4-1.5. At these pH values the rate of polymerization of UOH³⁺ is slow²⁸ and it was also assumed that no hydroxo or polynuclear specie of [U(IV) HEDTA]¹⁺ are likely to be present in solution. The absorbance of a 1:1:5 U(IV) –HEDTA-Th(IV) solution was obtained at $\lambda = 659\text{ nm}$. Of the various species present in the competition reaction, U(IV), UOH³⁺, and [U(IV)HEDTA]¹⁺, Th(IV)HEDTA and Th(IV), only the UOH³⁺, [U(IV)HEDTA]¹⁺ and U(IV) absorb in the region of interest. The spectra of U(IV) UOH³⁺ had been investigated previously by Kraus and Nelson.³⁰ There is a shift of peak of U(IV) to longer wave length 659 nm after complexation. Differences in extinction coefficient at 659 and 700 nm were used for calculation rather than absolute value of extinction coefficient at one wavelength. By using the hydrolysis constant for U(IV) at 0.1M ionic strength previously determined by Kraus and Nelson²⁹ and molar extinction coefficient for three U(IV) species, it is possible to measure the concentration of each of the three U(IV) specie in solution, using the usual relationship.

$$A = \epsilon_{\text{U-HEDTA}}(1)[\text{UOH}^{3+}] + \epsilon_{\text{U}}(1)[\text{U(IV)}] + \epsilon_{\text{U-OH}}(1)[\text{U-HEDTA}]^{1+}$$

Where $\epsilon_{\text{U-HEDTA}} = 52$, $\epsilon_{\text{U}} = 22$ and $\epsilon_{\text{U-OH}} \approx 3.0$ Thus by measuring the absorbance of a 1:1:5 U(IV)-HEDTA-Th(IV) solution and knowing the stability constant of Th(IV)HEDTA previously determined it was simpler mater to determine the equilibrium constant.



The value for $K_{\text{U-HEDTA}}$ is thus obtained. The same result was obtained for equilibrium constant by changing the order of addition of the various reagents indicating that equilibrium is reached rapidly. The value of logarithm of stability constant was found to be 21.

3. RESULT AND DISCUSSION

3.1 Determination of Order of Reaction with Respect to [Fe (opt)₃]³⁺

Results of the kinetic measurements for the reduction of [Fe (opt)₃]³⁺ by [U(IV) HEDTA]¹⁺ are being reported in the Tables 1 and 2. Pseudo first order condition was applied to observe the effects. The concentration of [U(IV) HEDTA]¹⁺ was maintained at ten times excess over the corresponding [Fe (opt)₃]³⁺ concentration. Pseudo first order rate constant (k_{obs}) was obtained by plotting $\ln(A_{\infty} - A_t)$ vs. time (Figure 4), for varying concentrations of [Fe (opt)₃]³⁺ whereas other parameter have been held constant. As shown in Table 2 these values of the rate constant turn out to be reasonably constant while the concentration of [Fe (opt)₃]³⁺ is increased.

3.2 Indirect Determination of Order of Reaction with Respect to [U (IV) HEDTA]¹⁺

By varying [U (IV) HEDTA]¹⁺ concentrations the corresponding values of pseudo first order rate constant (k_{obs}) were calculated to evaluate the order of reaction with respect to [U(IV) HEDTA]¹⁺ at different pH conditions (Tables 3-7). The other parameters are kept constant. The plot of k_{obs} values against [U(IV) HEDTA]¹⁺ concentration gives a straight line passing through the origin Figure 6. Pseudo first order rate constant is linearly related to the concentration of [U(IV) HEDTA]¹⁺ and thus the order of reaction with respect to [U(IV)HEDTA]¹⁺ is also first. The second order rate constant (k_1) at different pH conditions has been found to be $k_1 = 111.85, 193.68, 344.7$ and $640.19\text{ M}^{-1}\text{s}^{-1}$ at pH 3.2, 3.0, 2.8 and 2.5.

3.3 Dependence of the Hydrogen Ion Concentration

Hydrogen ion concentration affected the concentration of protonated specie and enhanced the reaction rate as shown in Table 8 and 9 at constant temperature of (30 °C). The following equation gives the order of the reaction with respect to hydrogen ion concentration $[H^+]$

$$\text{Rate} = Kk' [H^+]^n [U(IV)HEDTA]^{1+} [Fe(opt)_3]^{3+} \quad (1) \text{ At constant pH}$$

$$k_{\text{obs}} = k_1 [U(IV)HEDTA]^{1+} \quad (2)$$

$$k_1 = Kk' [H^+]^n \quad (3)$$

K is the equilibrium constant for the protonation of $[U(IV)HEDTA]^{1+}$ and k' is the specific rate constant for the reaction between $[U(IV)HEDTA(H^+)]^{1+}$ and $[Fe(opt)_3]^{3+}$. $Kk'[H^+]^n$ is the k_1 for each experiment at constant pH. k' equals to $.35 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ evaluated from the slope of the plot of k_1 vs H^+ concentration (Figure 7). From the slope of a plot of $\log [H^+]$ against $\log k_{\text{obs}}$, at constant temperature, the value of n can therefore be concluded and it equals to 1.2. This is nearly equal to value of n being 1. The corresponding plot is shown in Figure 7-8. It is therefore suggested that the rate of oxidation of $[U(IV)HEDTA]^{1+}$ by $[Fe(opt)_3]^{3+}$ is dependent on the first power of hydrogen ion concentration.

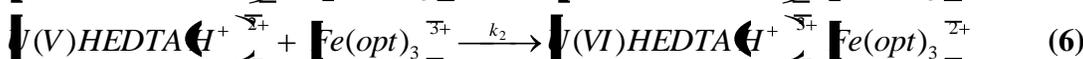
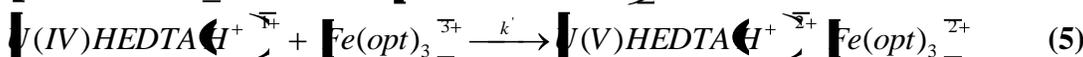
3.4 Effect of Ionic Strength on the Reaction Rate

Rate of reaction got increased with the increase in ionic strength, which was varied between 0.01 to 0.05M Table-10. This increase in the k_{obs} may be a result of the charges on $[Fe(opt)_3]^{3+}$ and $[U(IV)HEDTA]^{1+}$ the main reacting species. By plotting a graph between $\mu^{1/2}$ and k_{obs} product of charges, $Z_A Z_B$ for the reactants, was evaluated and it equals to +3.02 (Figure 9). This ionic strength effect also confirmed that the reaction follows the outer sphere kinetics. Although the HEDTA complex has OH group for the bridge but no evidences for the bridging was found. The situation is similar to the reaction between $Co(EDTA)^{1-}$ and $Fe(CN)_6^{3-}$, where a possibility of inner sphere mechanism has been ruled out even in the presence of a bridging CN group and outer sphere mechanism has been advocated³¹⁻³² Since $[Fe(opt)_3]^{3+}$ of the two complexes is inert for substitution so the outer sphere mechanism is strongly supported for the electron transfer between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

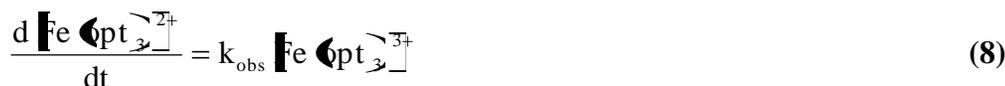
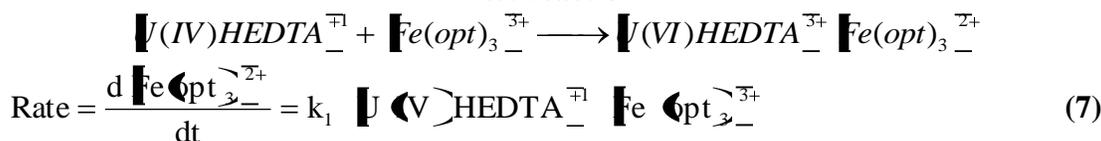
3.5 Effect of Temperature on the Reaction

Effect of temperature on the rate of a reaction is used for the determination of thermodynamic parameters. As shown in the Table 11, the rate of reaction was found to increase from 114 to 288 $M^{-1} s^{-1}$ while the temperature is increased from 10 °C to 35 °C. A plot of $\ln k_1$ against $1/T$ is linear (Figure 10). Thermodynamic parameters are listed in Table-12.

3.6 Proposed Mechanism



Net reaction



Hydrogen ion dependence is reflected in the following relationship



Expected mechanism describes that k' is specific rate constant for second order rate equation for the reaction between $[U(IV)HEDTA(H^+)]^{1+}$ and $[Fe(opt)_3]^{3+}$. K is designated as equilibrium constant for the protonation reaction $[U(IV)HEDTA]^{1+} + [H^+] = [U(IV)HEDTA(H^+)]^{1+}$. The second step which involves the reacting specie $[U(IV)$

HEDTA(H⁺)¹⁺ and [Fe (opt)₃]³⁺ will be the slowest out of the three proposed pathways, and that the steps 1 and 3 are assumed to be faster ones. Our observations are likely to support the following assumptions:

1. Mechanism involves an outer sphere pathway.
2. The over all reaction follows second order kinetics.
3. There is an equilibrium between the protonated and deprotonated forms of the [U (IV) HEDTA]¹⁺ complex. Effect of ionic strength and pH on the k_{obs} (Tables & 9) showed that the activated complex has +3 charge.
4. The equilibrium shifts towards the protonated specie with the decrease of pH (Table 5).
5. Protonation of the co-ordinated complex facilitates the unwrapping of ligand with the decrease in pH. Thus free U(IV) is made available for the redox reaction²⁵⁻²⁷. So an increase in k_{obs} is observed with the decrease of pH.

Table-1: Effect of [Fe (opt)₃]³⁺ on psuedo first order rate constant (k_{obs})

Serial No.	10 ⁵ [Fe (opt) ₃] ³⁺ / mol/dm ³	10 ² k _{obs} /s ⁻¹
1	3.0	11.20 ± 0.22
2	3.5	11.32 ± 0.21
3	4.0	11.19 ± 0.20
4	4.5	11.4 ± 0.23
5	5.0	11.31 ± 0.20

[U(IV)HEDTA]¹⁺ = 6 × 10⁻⁴ mol/dm³, pH = 3.0

Temperature = 30 °C, μ = 0.01 mol/dm³

Table-2: Effect of [U(IV) HEDTA]¹⁺ concentration on psuedo first order rate constant (k_{obs})

S. No	[U (IV) HEDTA] ¹⁺ 10 ⁴ / mol/dm ³	10 ² k _{obs} / s ⁻¹
pH 2.5		
1	6.0	32.15 ± 0.31
2	7.0	42.34 ± 0.24
3	8.0	52.21 ± 0.25
4	9.0	59.56 ± 0.34
5	10	65.62 ± 0.42
pH 2.8		
1	6.0	19.32 ± 0.25
2	7.0	23.42 ± 0.25
3	8.0	27.25 ± 0.35
4	9.0	31.87 ± 0.33
5	10	35.34 ± 0.35
pH 3.0		
1	6.0	11.22 ± 0.23
2	7.0	13.42 ± 0.25
3	8.0	15.25 ± 0.24
4	9.0	17.87 ± 0.25
5	10	19.30 ± 0.24
pH 3.2		
1	6.0	6.82 ± 0.23
2	7.0	7.52 ± 0.32
3	8.0	8.85 ± 0.35
4	9.0	9.87 ± 0.33
5	10	11.23 ± 0.32
pH 3.5		
1	6.0	1.26 ± 0.23
2	7.0	4.31 ± 0.32
3	8.0	5.92 ± 0.25
4	9.0	6.84 ± 0.23
5	10	7.52 ± 0.24

[Fe (opt)₃]³⁺ = 3.0 × 10⁻⁵ mol/dm³, Temperature = 30 °C, μ = 0.01 mol/dm³

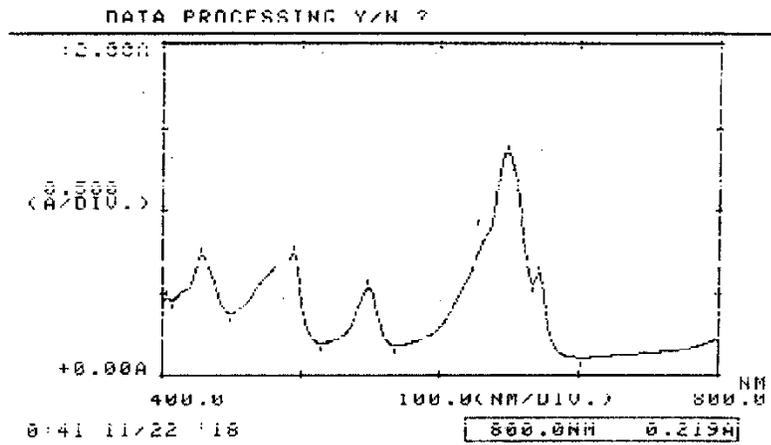


Fig-1: Spectra of 0.03 M [U(IV)HEDTA]¹⁺ at pH 3.0 and 0.1 M ionic strength.

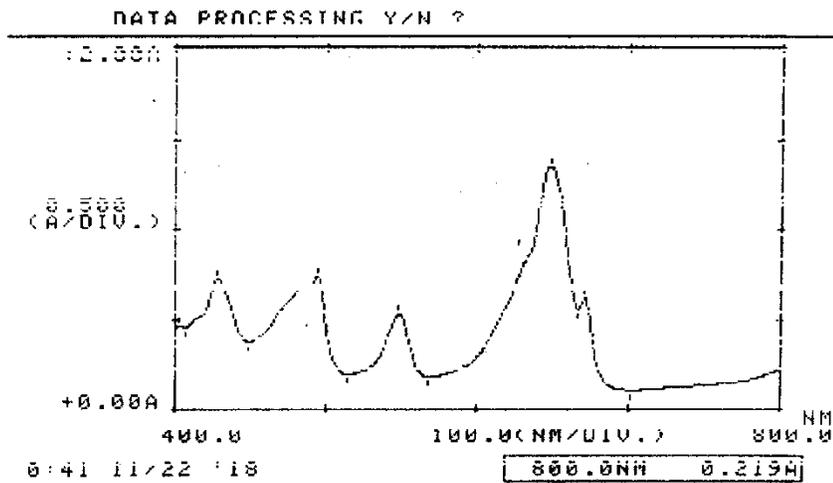


Fig-2: Spectra of 0.05 M U(IV) in 0.1 M HCl.

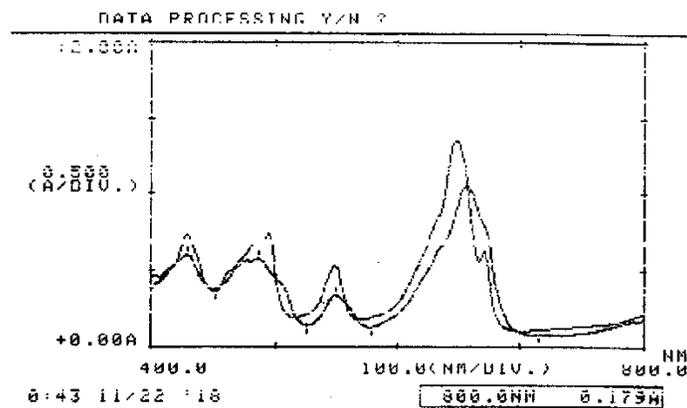


Fig-3: Spectra of 0.05 M U(IV) at in 0.1 M HCl and 0.03 M [U(IV) HEDTA]¹⁺ of at pH 3.0 and 0.1 M ionic strength.

Table-3: Effect of pH on psuedo first order rate constant k_{obs} for the reaction between $[U(IV) HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

Serial No.	pH	$10^2 k_{obs} / s^{-1}$
1	3.2	6.82 ± 0.23
2	3.0	11.21 ± 0.23
3	2.8	19.52 ± 0.24
4	2.5	32.12 ± 0.31

$[Fe(opt)_3]^{3+} = 3.0 \times 10^{-5} \text{ mol/dm}^3$, Temperature = 30 °C
 $[U(IV) HEDTA]^{1+} = 6.0 \times 10^{-4} \text{ mol/dm}^3$, $\mu = 0.01 \text{ mol/dm}^3$

Table-4: Effect of pH on second order rate constant k_1 for the reaction between $[U(IV) HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

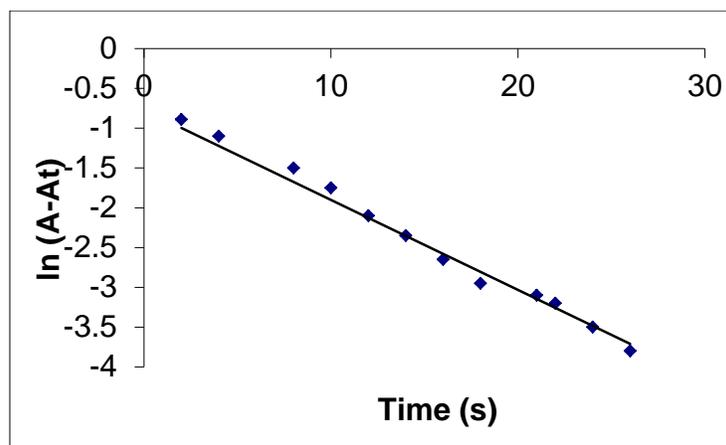
Serial No.	pH	$k_1 / \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
1	3.2	111.8 ± 3.7
2	3.0	193.7 ± 4.7
3	2.8	344.7 ± 5.2
4	2.5	478.93 ± 4.9

$[Fe(opt)_3]^{3+} = 3.0 \times 10^{-5} \text{ mol/dm}^3$, Temperature = 30 °C
 $[U(IV) HEDTA]^{1+} = 6.0 \times 10^{-4} - 11.0 \times 10^{-4} \text{ mol/dm}^3$

Table-5: Effect of ionic strength on psuedo first order rate constant k_{obs} for the reaction between $[U(IV) HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

Serial No.	Ionic strength mol/dm^3	$10^2 k_{obs} / s^{-1}$
1	0.01	11.91 ± 0.31
2	0.02	18.91 ± 0.34
3	0.03	22.48 ± 0.30
4	0.04	26.8 ± 0.33
5	0.05	30.1 ± 0.32

$[Fe(opt)_3]^{3+} = 3.0 \times 10^{-5} \text{ mol/dm}^3$, Temperature = 30 °C
 $[U(IV) HEDTA]^{1+} = 6.0 \times 10^{-4} \text{ mol/dm}^3$, pH = 3.0

**Fig-4** A typical kinetic plot for the determination of psuedo first order rate constant k_{obs} for the reaction between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$.

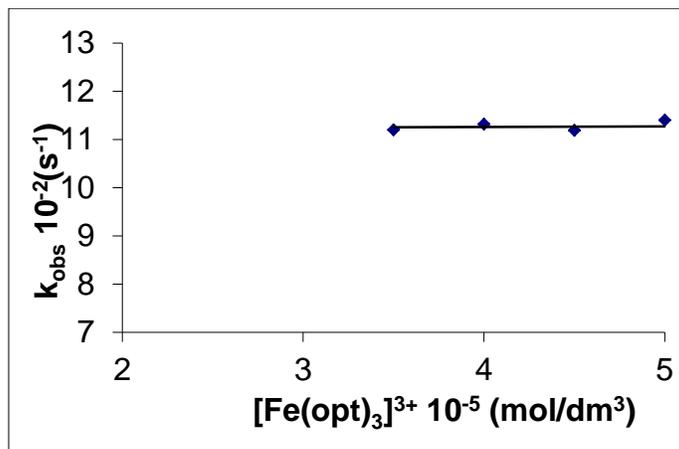


Fig-5: Effect of $[\text{Fe}(\text{opt})_3]^{3+}$ on pseudo first order rate constant k_{obs} for the reaction between $[\text{U}(\text{IV})\text{HEDTA}]^{1+}$ and $[\text{Fe}(\text{opt})_3]^{3+}$.

Table-6: Effect of temperature on second order rate constant k_1 for the reaction between $[\text{U}(\text{IV})\text{HEDTA}]^{1+}$ and $[\text{Fe}(\text{opt})_3]^{3+}$

Serial No.	Temperature / °C	Number of replicates	$10^2 k_{\text{obs}} / \text{s}^{-1}$	$k_1 / \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
1	10	3	6.84	114.1 ± 3.2
2	15	3	8.29	138.3 ± 4.1
3	20	3	9.6	160.6 ± 3.9
4	25	3	10.2	170.5 ± 4.8
5	30	3	11.2	193.1 ± 4.2
6	35	3	17.26	288.1 ± 4.7

$[\text{Fe}(\text{opt})_3]^{3+} = 3.0 \times 10^{-5} \text{ mol/dm}^3$, pH = 3.0
 $[\text{U}(\text{IV})\text{HEDTA}]^{1+} = 6.0 \times 10^{-3} \text{ mol/dm}^3$, $\mu = 0.01 \text{ mol/dm}^3$

Table-7: Thermodynamic parameters for the reaction between $[\text{U}(\text{IV})\text{HEDTA}]^{1+}$ and $[\text{Fe}(\text{opt})_3]^{3+}$

$\Delta H^\ddagger / \text{kJ/mol}$	$\Delta S^\ddagger / \text{J/mol}$	$\Delta G^\ddagger / \text{kJ/mol}$	$E_a / \text{kJ/mol}$	$\Delta G^\circ / \text{kJ/mol}$
15.3 ± 0.8	-150.6 ± 2	60.8 ± 1	19.31 ± 0.8	-30.6

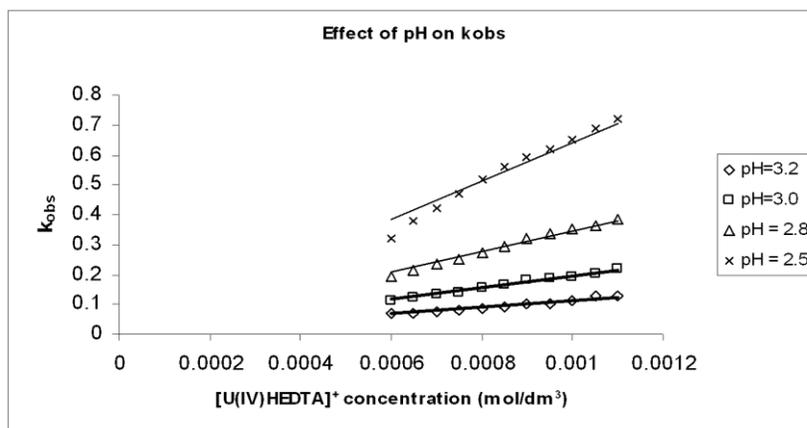


Fig-6: Effect of $[\text{U}(\text{IV})\text{HEDTA}]^{1+}$ concentration on pseudo order first rate constant k_{obs} for the reaction between $[\text{U}(\text{IV})\text{HEDTA}]^{1+}$ and $[\text{Fe}(\text{opt})_3]^{3+}$.

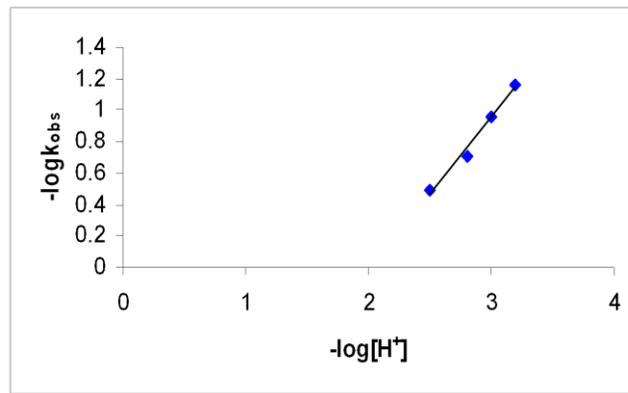


Fig-7: Effect of hydrogen ion concentration on second order rate constant k_1 for the reaction between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

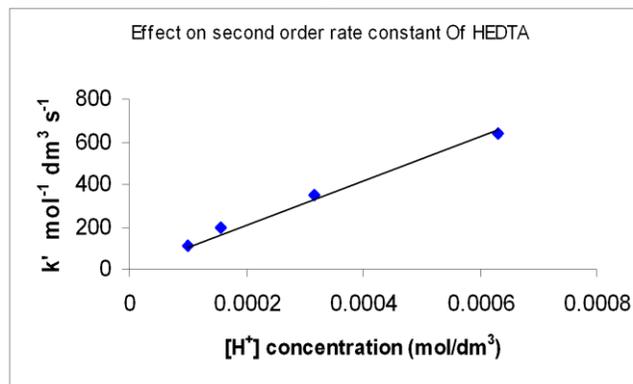


Fig-8 Effect of hydrogen ion concentration on second order rate constant k_1 for the reaction between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

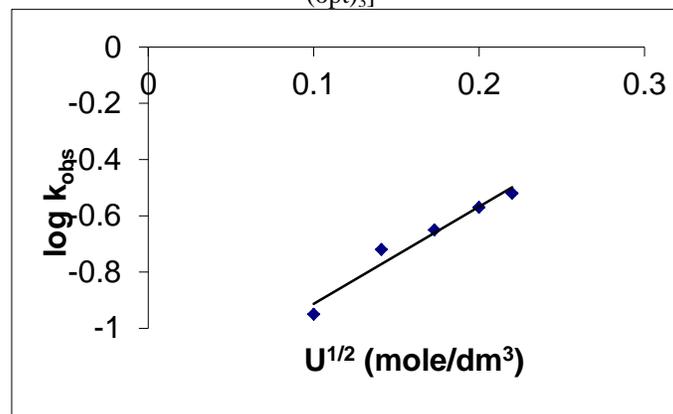


Fig-9: Effect of ionic strength on pseudo first order rate constant k_{obs} for the reaction between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$.

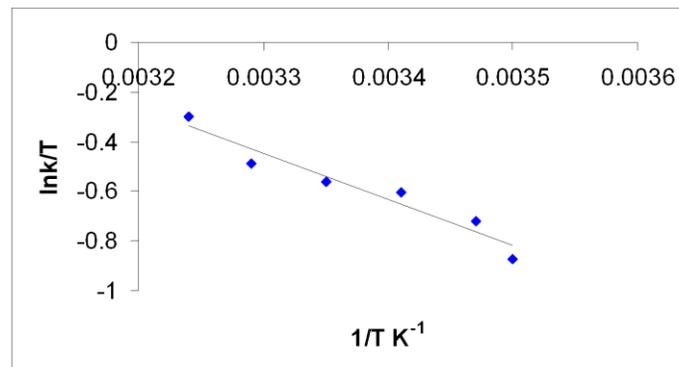


Fig-10: Effect of temperature to determine the thermodynamic parameters for the reaction between $[U(IV)HEDTA]^{1+}$ and $[Fe(opt)_3]^{3+}$

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