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Spectrophotometric Studies on Kinetics and Mechanism of Complex Formation between Chromium(III) and EDTA in Aqueous acidic Media

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ARTICLE DETAILS

ABSTRACT

The kinetics of the formation of 1:1 complex of chromium(III) with ethylenediaminetetraacetate (EDTA) was followed spectrophotometrically at λ_{max} = 552 nm. The reaction was found to be first order in chromium(III). Increasing the EDTA concentration from 2.2×10^{-2} to 8.8 mol dm^{-3} accelerated the reaction rate. Increasing the pH from 3.3 to 4.7 also accelerate the reaction rate, while the reaction rate was retarded by increasing ionic strength and dielectric constant of the reaction medium. A mechanism was suggested to account for the results obtained which involves ion pair formation between the various species of the reactants. Value of 37.1 ± 3 kJ mol^{-1} was obtained for the energy of activation and -195.6 ± 6 K^{-1} mol^{-1} for the entropy of activation indicate an associative mechanism for the reaction. The logarithms of the formation constant of 1:1 complex formed were found to be 7.31.

1. Introduction

In ligand substitution reactions which represent a major type of inorganic processes, one or more ligands around a metal ion are replaced by other ligands [1]. Chromium(III) is classically known as a substitution-inert metal ion [2].

Aminocarboxylate chelating agents complex strongly with most metals, thus altering metal bioavailability and mobility in the environment [3]. These compounds are widely used for industrial, medical and agricultural purposes [4-12]. These compounds are used as laundry detergent builders, boiler scale inhibitors, in metal plating and cleaning operations, in textile manufacture, and in paper and cellulose industries. It is well known that EDTA is a member of the aminocarboxylate family.

Although the experimental system and reaction studied here is very simple in nature, elucidation of the mechanism in this model system has implications for a variety of more complex homogeneous and heterogeneous phenomena involving metal–organic complexes (e.g., metal ion transport, bioavailability, and toxicity).

This study deals with the kinetic of complexation of chromium(III) with EDTA in weak acid solution. The study involves factors affecting the rate of reaction. The formation constant of the studied complex is also measured.

2. Experimental Methods

All chemicals were of pure grade and were used without further purification. Stock solution of (0.1 mol/dm) of hexa-aquachromium(III) was prepared by dissolving $CrCl_3$ in bidistilled water and leaving the solution for 48 hours at 45 ^{0}C, where upon green color of $CrCl_3$ changed to blue color of aquachromium(III) [13]. All solutions were prepared using bidistilled water. The absorbance measurements were performed using thermostatted 292 Cecil spectrophotometer and pH measurements were conducted with Griffin pH meter fitted with glass-calomel electrode standardized by potassium hydrogen phthalate.

Kinetic experiments were conducted by mixing thermostatted solutions of chromium (III) with EDTA solution and adjusting hydrogen ion concentration to the required value with potassium hydroxide or perchloric acid. Ionic strength was adjusted by sodium perchlorate solution. The solution was then introduced into the reaction vessel, which was previously thermostatted to the desired temperature and the reaction was followed spectrophotometrically at λ_{max} = 552 nm for the complex formed. The reaction rate was followed under pseudo first order conditions where at least ten fold excess of the ligand concentration over the reactant chromium (III) concentration was always ensured. Values of the observed first order rate constant, k_{obs}, were determined graphically for each run by plotting log $(A_\infty - A_t)$ versus time, t, where A denotes the measured absorbance and the subscripts refer to time of reaction. The absorbance (A_∞) was obtained directly after ensuring completion of the reaction. First order plots were linear for more than 85% of the reaction progress.

3. Results and Discussion

The reaction was found to be first order in chromium(III), the observed first order rate constants, k_{obs}, did not vary with chromium(III) concentration, ensuring first order kinetics in chromium(III).

The effect of varying EDTA concentration, at different pH values on the rate of reaction was also studied, (Table 1) and a plot of the first order rate constant, k_{obs}, against EDTA concentration was nonlinear, (Fig. 1), indicating formation of ion pair [14,15].
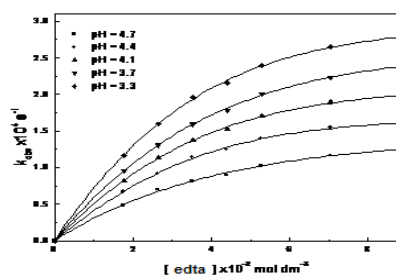

Fig. 1 Variation of k_{obs} with [EDTA] at various pH ; I = 0.6 mol/dm , t = 35 ^{0}C, [Cr(III)] = 8.8 x 10^{-3} mol/dm.

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Table 1 Values of k_{obs} under various conditions

[Cr(III)]x10³ Mol/dm	[EDTA]x10² Mol/dm	t °C	I mol/dm	ε	k_{obs} x 10⁴ / s⁻¹ pH				
					3.3	3.7	4.1	4.4	4.7
4.4	8.80	35	0.6				1.959		
6.0							1.963		
7.2							1.971		
8.8							1.969		
10.4							1.977		
12.0							1.983		
13.6							1.975		
	1.76	35	0.6		0.482	0.670	0.817	0.957	1.168
	2.64				0.699	0.920	1.135	1.308	1.595
	3.52				0.815	1.139	1.380	1.593	1.960
	4.40				0.894	1.249	1.527	1.786	2.151
	5.28				1.026	1.396	1.698	2.007	2.399
	7.04				1.163	1.551	1.895	2.236	2.648
	8.80				1.250	1.599	1.975	2.379	2.779
8.8	8.80	35	0.6				1.975		
			0.7				1.785		
			0.8				1.550		
			0.9				1.346		
			1.0				1.251		
			1.1				1.131		
			1.2				1.045		
8.8	8.80	25	0.6	78.00			1.234		
				75.32			1.287		
				72.63			1.353		
				69.95			1.433		
				67.26			1.503		
				64.58			1.591		
				61.89			1.693		
				59.21			1.819		
				56.52			1.957		

Increasing the ionic strength, I, of the reaction medium from 0.7 to 1.25 mol/dm (adjusted by sodium perchlorate) the reaction rate (Table 1). Applying Bronsted Bjerrum equation [16, 17], a linear relationship was obtained by plotting log k_{obs} versus √I, (Fig. 2) indicating that reaction involves ion pairing formation.
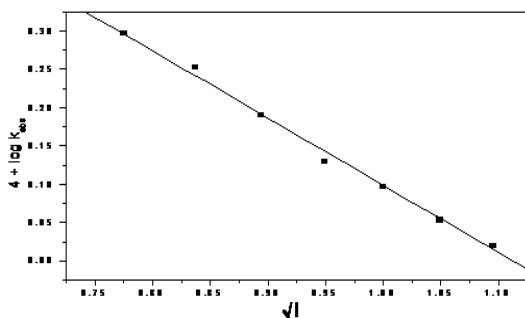
Fig. 2 Variation of log k_{obs} with √I; [EDTA] = 8.8 x10⁻² mol/dm, pH = 4.1, [Cr(III)] = 8.8 x 10⁻³ mol/dm, t = 35 °C.
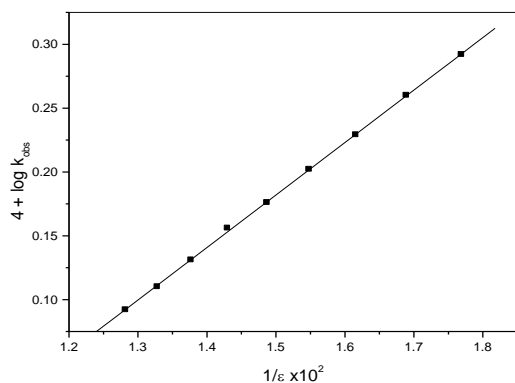
Fig. 3 Variation of log k_{obs} with 1/ε in ethanol-water mixture; t = 25 °C, pH = 4.1, [Cr(III)] = 8.8 x 10⁻³ mol/dm, I = 0.7 mol/dm , [EDTA] = 8.8x10⁻² mol/dm.
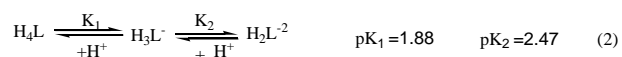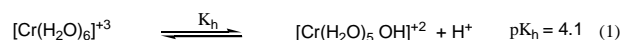
The effect of the dielectric constant on the rate of reaction was studied using different ratios of ethanol-water mixtures. The values of the observed first order rate constant, k_{obs} increased with decreasing the dielectric constant of the reaction medium, ε, (Table 1). Applying *Bjerrum's* equation [18], a plot of log k_{obs} versus 1/ε was linear with positive slopes, Fig. 3, indicating that the reaction is an ion pair type [13].

The effect of pH on the rate of reaction was studied in the range from 3.3 to 4.7 at various temperatures, Table 2. The results obtained show that the reaction is accelerated by lowering hydrogen ion concentration.

Table 2 Kinetic data for the interaction of Cr(III) with EDTA at various temperature and proton concentration; [Cr(III)] = 8.8 x10⁻³ mol/dm, [EDTA] = 11x10⁻² mol/dm, I = 0.6 mol/dm.

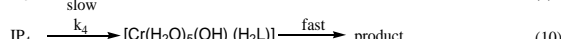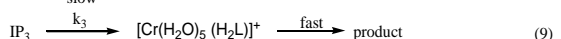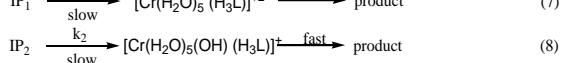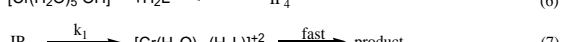| pH	k_{obs} x 10⁴ s⁻¹				
	25 °C	30 °C	35 °C	40 °C	45 °C
3.3	0.766	1.012	1.250	1.531	2.007
3.7	1.007	1.257	1.539	2.019	2.530
4.1	1.234	1.567	1.975	2.475	3.125
4.4	1.475	1.853	2.379	3.009	3.764
4.7	1.703	2.164	2.785	3.508	4.355

The dependence of k_{obs} on hydrogen ion concentration can be explained by in following equilibriums between the various species of each reactant which are present in the reaction medium[19,20].

$$[Cr(H_2O)_6]^{+3} \xrightarrow{K_h} [Cr(H_2O)_5 OH]^{+2} + H^+ \quad pK_h = 4.1 \quad (1)$$

$$H_4L \underset{+H^+}{\overset{K_1}{\rightleftharpoons}} H_3L^- \underset{+ H^+}{\overset{K_2}{\rightleftharpoons}} H_2L^{-2} \quad pK_1 = 1.88 \quad pK_2 = 2.47 \quad (2)$$

The penta-aquahydroxochromium(III) species is more reactive than the hexa-aquachromium(III) due to the presence of OH⁻ which causes an increase of water liabilities due to its π-bonding ability [21,22].

The results obtained can be explained by the following mechanism for the interaction between the predominant species of chromium (III) with the predominant species of EDTA in the pH range under investigation.

$$[Cr(H_2O)_6]^{+3} \xrightleftharpoons{K_h} [Cr(H_2O)_5 OH]^{+2} + H^+ \qquad pK_h = 4.1 \quad (1)$$

$$H_4L \xrightleftharpoons[+H^+]{K_1} H_3L^- \xrightleftharpoons[+H^+]{K_2} H_2L^{-2} \qquad pK_1 = 1.88 \qquad pK_2 = 2.47 \quad (2)$$

$$[Cr(H_2O)_6]^{+3} + H_3L^- \xrightarrow{K_{IP1}} IP_1 \qquad (3)$$

$$[Cr(H_2O)_5 OH]^{+2} + H_3L^- \xrightarrow{K_{IP2}} IP_2 \qquad (4)$$

$$[Cr(H_2O)_6]^{+3} + H_2L^{-2} \xrightarrow{K_{IP3}} IP_3 \qquad (5)$$

$$[Cr(H_2O)_5 OH]^{+2} + H_2L^{-2} \xrightarrow{K_{IP4}} IP_4 \qquad (6)$$

$$IP_1 \xrightarrow[slow]{k_1} [Cr(H_2O)_5 (H_3L)]^{+2} \xrightarrow{fast} product \qquad (7)$$

$$IP_2 \xrightarrow[slow]{k_2} [Cr(H_2O)_5(OH) (H_3L)]^{+} \xrightarrow{fast} product \qquad (8)$$

$$IP_3 \xrightarrow[slow]{k_3} [Cr(H_2O)_5 (H_2L)]^{+} \xrightarrow{fast} product \qquad (9)$$

$$IP_4 \xrightarrow[slow]{k_4} [Cr(H_2O)_5(OH) (H_2L)] \xrightarrow{fast} product \qquad (10)$$
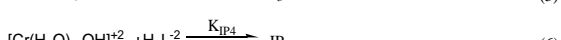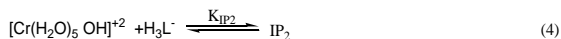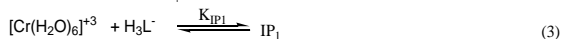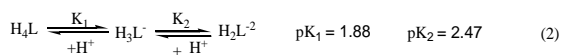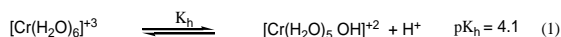
Where $IP_1 \equiv \{[Cr(H_2O)_6]^{+3}.H_3L^{-1}\}$, $IP_2 \equiv \{[Cr(H_2O)_5 OH]^{+3}.H_3L^{-1}\}$, $IP_3 \equiv \{[Cr(H_2O)_6]^{+3}.H_2L^{-2}\}$ $IP_4 \equiv \{[Cr(H_2O)_5 OH]^{+2}.H_2L^{-2}\}$

IP_1- IP_4 are the hexa-aquo and penta-aquohydroxy ion pair complexes of chromium (III) and EDTA.

The rate of exchange of the first ligand molecule, in the inner coordination sphere of the metal center is slow and therefore the rate determining equations (7-10) [21]. As soon as one carboxyl group of the ligand enters into the inner sphere, the electron density on the chromium center increases owing to the inductive effect and as results the remaining ligands are labilized easily and its substitution is rapid. From the previous mechanism, the first order rate constant is derived as

$$k_{obs} = \frac{(k_1 K_{IP1}[H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})[edta]}{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]}) + ((K_{IP1}[H^+] + K_{IP2}K_2 + K_{IP3}K_h + K_{IP4}\frac{K_2 K_h}{[H^+]})[edta]} \qquad (11)$$

by inversing equation (11) we get equation

$$\frac{1}{k_{obs}} = \frac{K_{IP1}[H^+] + K_{IP2}K_2 + K_{IP3}K_h + K_{IP4}\frac{K_2 K_h}{[H^+]}}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2}K_2 + k_3 K_{IP3}K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})} + \frac{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2}K_2 + k_3 K_{IP3}K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})[edta]} \qquad (12)$$

and a plot of $1/k_{obs}$ versus $1/[EDTA]$ gave straight line with slopes

$$S = \frac{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2}K_2 + k_3 K_{IP3}K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})} \qquad (13)$$

and intercepts, I

$$I = \frac{K_{IP1}[H^+] + K_{IP2}K_2 + K_{IP3}K_h + K_{IP4}\frac{K_2 K_h}{[H^+]}}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2}K_2 + k_3 K_{IP3}K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})} \qquad (14)$$

and

$$\frac{I}{S} = \frac{K_{IP1}[H^+] + K_{IP2}K_2 + K_{IP3}K_h + K_{IP4}\frac{K_2 K_h}{[H^+]}}{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})} \qquad (15)$$

The values of the ion pair formation constants, KIP and the rate constants of the rate determining steps, k, were calculating by plotting $1/k_{obs}$ versus $1/[EDTA]$ at pH, 4.1 (Fig. 4). Values 7.11, 14.78, 10.15 and 16.81 mol^{-1} dm^3 for the ion pair formation constants, K_{IP} and 1.83, 4.81, 2.97 and 5.23×10^{-3} s^{-1} for the rate determining steps, k, respectively were calculating by applying equation (13-15) at different hydrogen ion concentrations and taking the values of K_1, K_2 and K_h from equations (1,2).

The composition and formation constants of the complexes between chromium(III) and EDTA were determined using *Hills* equation (eq.16) [22]

$$\log(A-A_0)/(A_\infty-A) = \log K + n \log [EDTA] \qquad (16)$$

Where A is the absorbance reached at the end of the reaction, A_0 is the absorbance at zero EDTA concentration, and A_∞ is the equilibrium

absorbance for highest concentration of EDTA. Plots of log $(A- A_0)/ (A_\infty-A)$ vs. log [EDTA], where [EDTA] is total concentration used, yield a straight line of slope = 1 (number of ligand molecules attached to one chromium atom) and intercept of log K = 11.3 (Fig. 5).
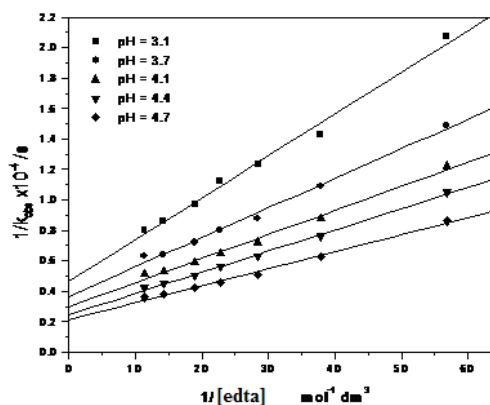

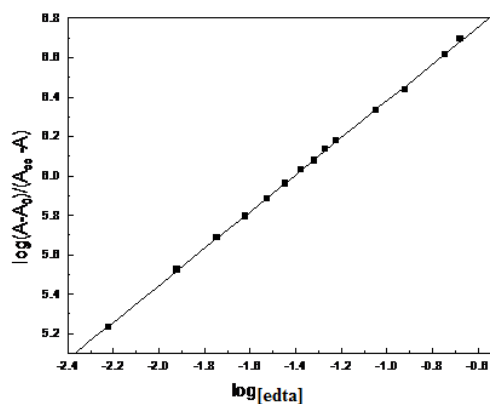**Fig. 4** Variation of $1/k_{obs}$ with $1/[EDTA]$; [Cr(III)] = 8.8×10^{-3} mol/dm, $t = 35\,^\circ$C, $I = 0.6$ mol/dm, pH = 4.1

Fig.5 Plot of log $(A - A_0)/ (A_\infty - A)$ vs log [EDTA]; $I = 0.6$ mol/dm, pH = 4.1, [Cr(III)] = 8.8×10^{-3} mol/dm, $t = 35^0$C

4. Conclusion

As it is very well known that chromium is one of the dangerous and poisonous element which can harm and effect the environment, therefore and in this article we hope that we can participate in minimizing the danger of this element by removing it through complexation with a ligand which is quite available and inexpensive and study the kinetic and the mechanism of its removal in moderately dilute acidic media.

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