Kinetics and Mechanism of Formation of 1:1 Complex Between Chromium(III) with 1,3-Propane Diaminetetraacetate in Aqueous Acidic Media

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Abstract: The kinetics of the formation of 1:1 complex of chromium(III) with 1,3-propanediamine *N, N,N′ N′*-tetraacetate (1,3-pdta) was followed spectrophotometrically at $\lambda_{max} = 552$ nm. The reaction was found to be first order in chromium(III). Increasing the 1,3-pdtp 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 accelerated the reaction rate, the reaction rate was also 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 JK^{-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 for complex formed was found 7.31.

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 in 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 production. 1,3-Propanediamine *N,N,N′N′*-tetraacetate (1,3-pdta) 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 1,3-pdta in weak acid solution. The study involves factors affecting the rate of reaction. The formation constant of the studied complex is also measured.

Experimental

All chemicals were of pure grade and were used without further purification. The 1,3 -propanediaminetetraacetic acid ($H_4$1,3- pdta) was prepared using a previously described procedure[13]. Stock solution of (0.1 mol dm^{-3}) of hexaaquachromium(III) was prepared by dissolving $CrCl_3$ in double distilled water and leaving the solution for 48 hours at 45 ^{0}C, where upon green colour of $CrCl_3$ changed to blue color of aquachromium(III)[14]. All solutions were prepared using double distilled 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) and the 1,3- pdta 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_∞-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.

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, (Table 1) ensuring first order kinetics in chromium(III).

The effect of varying 1,3-pdta 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 1,3- pdta concentration was nonlinear, (Figure 1), indicating formation of ion pair[15,16].
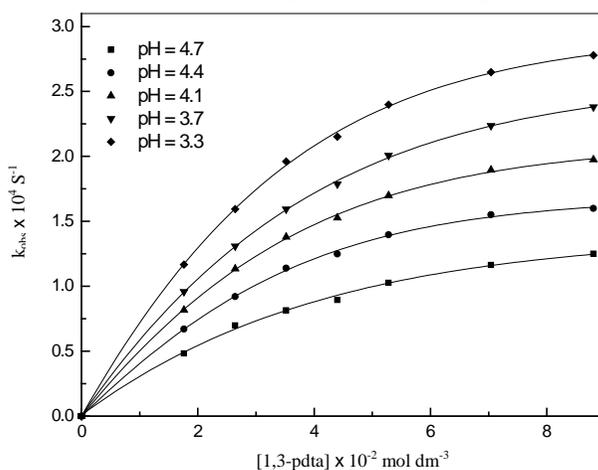
Figure 1. Variation of k_{obs} with [1,3- pdta] at various pH; I = 0.6 mol dm^{-3}, t = 35 ^{0}C, [Cr(III)] = 8.8x10^{-3} mol dm^{-3}

Increasing the ionic strength, I, of the reaction medium from 0.7 to 1.25 mol dm^{-3} (adjusted by sodium perchlorate) the reaction rate (Table 1). Applying Bronsted Bjerrum equation[17,18], a linear relationship was obtained by plotting log k_{obs} *versus* $\sqrt{I}$, (Figure 2) indicating that reaction involves ion pairing formation

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[17], a plot of log k_{obs} *versus* $1/\varepsilon$ was linear with positive slopes, (Figure 3) indicating that the reaction is an ion pair type[19].

Table 1. Values of k_{obs} under various conditions

[Cr(III)]x10^3 mol dm^{-3}	[1,3 pdta] x10^2 mol dm^{-3}	t ^{o}C	I mol dm^{-3}	ε	k_{obs} x 10^4, s^{-1}				
					pH=3.3	3.7	4.1	4.4	4.7
4.4							41.959		
6.0							1.963		
7.2							1.971		
8.8	8.80	35	0.6				1.969		
10.4							1.977		
12.0							1.983		
13.6							1.975		
	1.76				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	35	0.6		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
			0.6				1.975		
			0.7				1.785		
			0.8				1.550		
8.8	8.80	35	0.9				1.346		
			1.0				1.251		
			1.1				1.131		
			1.2				1.045		
				78.00			1.234		
				75.32			1.287		
				72.63			1.353		
				69.95			1.433		
8.8	8.80	25	0.6	67.26			1.503		
				64.58			1.591		
				61.89			1.693		
				59.21			1.819		
				56.52			1957		
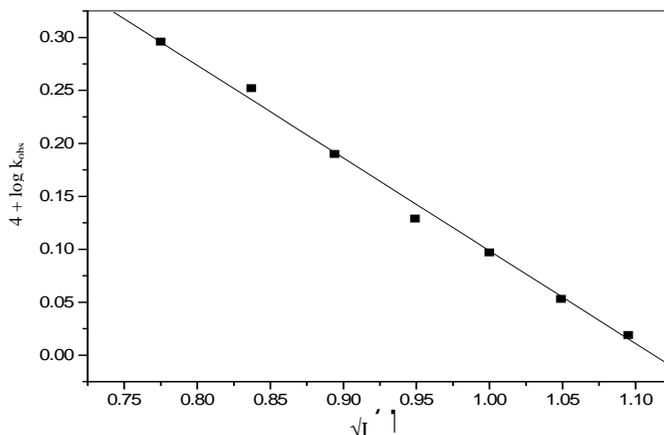
Figure 2. Variation of log k_{obs} with $\sqrt{I}$; [1,3- pdta] = 8.8×10^{-2} mol dm^{-3}, pH = 4.1, [Cr(III)] = 8.8×10^{-3} mol dm^{-3}, t = 35 ^{o}C
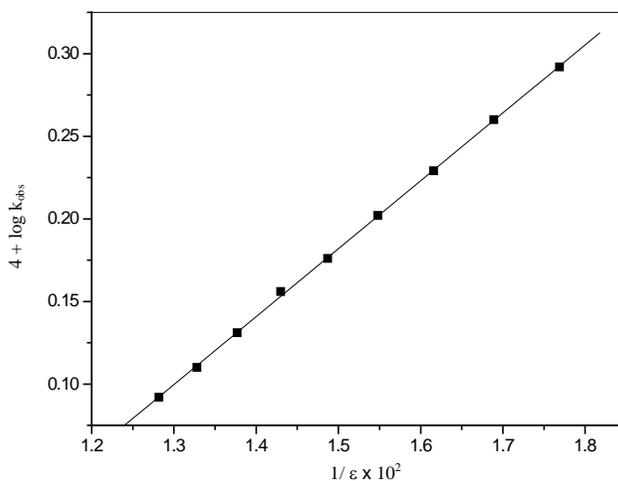
Figure 3. Variation of log k_{obs} with $1/\varepsilon$ in ethanol-water mixture; t = 25 ^{0}C, pH = 4.1, [Cr(III)] = 8.8×10^{-3} mol dm^{-3}, I = 0.7 mol dm^{-3}, [1,3- pdta] = 8.8×10^{-2} mol dm^{-3}

The effect of pH on the rate of reaction was studied in the range from 3.0 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 1,3-pdta at various temperature and proton concentration; [Cr(III)] = 8.8×10^{-3} mol.dm^{-3}, [1,3- pdta] = 11×10^{-2} mol.dm^{-3}, I = 0.6 mol.dm^{-3}

pH	$k_{obs} \times 10^4$/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[20,21]. The pentaaquahydroxochromium(III) species is more reactive than the hexaaqua-chromium(III) due to the presence of OH⁻ which causes an increase of water liabilities due to its π-bonding ability[22-30].

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 1,3- pdta in the pH range under investigation.

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

$$H_4L \underset{+H^+}{\xrightleftharpoons{K_1}} H_3L^- \underset{+\,H^+}{\xrightleftharpoons{K_2}} H_2L^{-2} \qquad pK_1 = 1.88 \qquad pK_2 = 2.47 \tag{2}$$

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

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

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

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

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

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

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

$$IP_4 \xrightarrow[slow]{k_4} [Cr(H_2O)_5(OH)\,(H_2L)] \xrightarrow{fast} product \tag{10}$$
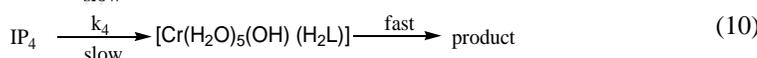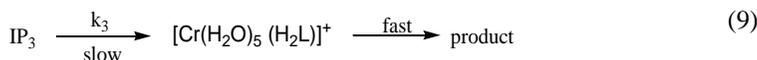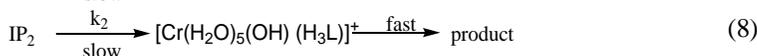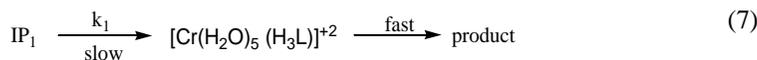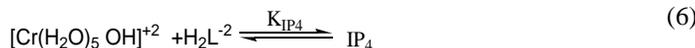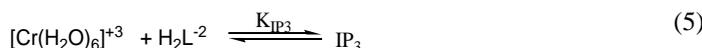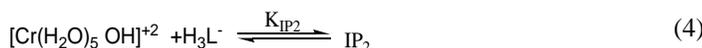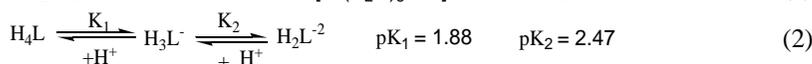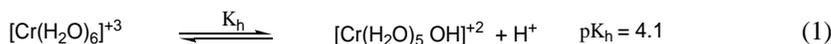
IP_1- IP_4 are the hexaaquo and pentaaquohydroxy ion pair complexes of chromium(III) and 1,3- pdta.

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)[24,25,30]. 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;

$$k_{obs} = \cfrac{(k_1 K_{IP1}[H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})[1,3-\mathrm{pdta}]}{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]}) + ((K_{IP1}[H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4}\frac{K_2 Kh}{[H^+]})[1,3-\mathrm{pdta}]\,)} \tag{11}$$

by inversing equation (11) we get equation

$$\frac{1}{k_{obs}} = \cfrac{K_{IP1}[H^+] + K_{IP2} K_2 + K_{IP3} K_h + K_{IP4}\frac{K_2 K_h}{[H^+]}}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})} + \cfrac{(\frac{[H^+]^2}{K_1} + [H^+] + K_2)(1 + \frac{K_h}{[H^+]})}{(k_1 K_{IP1}[H^+] + k_2 K_{IP2} K_2 + k_3 K_{IP3} K_h + k_4 K_{IP4}\frac{K_2 K_h}{[H^+]})[1,3-\mathrm{pdta}]} \tag{12}$$

and a plot of $1/k_{obs}$ *versus* $1/[1,3\text{- pdta}]$ gave straight line with slopes

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

and intercepts, I

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

and

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

The values of the ion pair formation constants, K_{IP} and the rate constants of the rate determining steps, k, were calculating by plotting $1/k_{obs}$ *versus* $1/[1,3\text{- pdta}]$ at pH, (Figure 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 5.23x10^{-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).
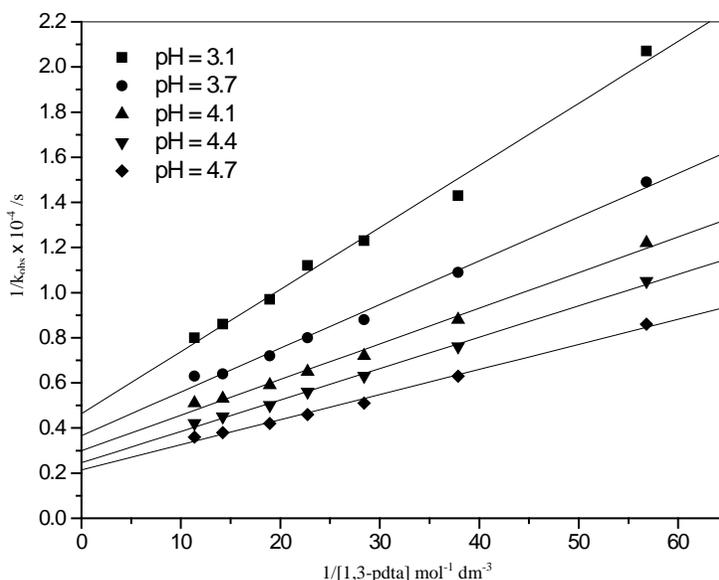
Figure 4. Variation of $1/k_{obs}$ with $1/[1,3\text{- pdta}]$; $[Cr(III)] = 8.8$x10^{-3} mol dm^{-3}, $t = 35$ ^{0}C, $I = 0.6$ mol dm^{-3}, pH = 4.1

The effect of temperature on the rate reaction was also studied at different hydrogen ion concentrations (Table 2). The activation parameters were calculating using Arrhenius plots values and the Eyring equation and were found to be 37.1±3 kJ mol^{-1} for the energy of activation and -195.6±6 J K^{-1} mol^{-1} for the entropy of activation.

It is well known that substitution reactions of hexaaquachromium(III) with a variety of ligands proceed by associative[19,31,32] and dissociative[33,34] mechanisms. Swaddle[35,36] and Lincoln[37] have reviewed that the activation parameters and mechanism of octahedral substitution and concluded that an associative mechanism is operative for octahedral cationic complexes of trivalent metal ions except for Co(III) with ionic radii greater than 60 pm, which demand associative character for substitution reaction of $[Cr(H_2O)_6]^{+3}$.

The associative mechanism is further supported by i-lowering of enthalpy and large negative entropy for substitution of water by ligand compare to water exchange (for water[38] exchange $\Delta H^* =109.6$ kJ mol^{-1} and $\Delta S^*= +12$ JK[-1] mol^{-1}) ii-the straight line obtained from plotting of log k_1 with log k_2[39], (Figure 5) (where k_1 and k_2 are the first order rate constants at different temperature) for the substitution of water in $[Cr(H_2O)_6]^{3+}$ by valine[26], glycine[27], serine[28], DL- leucine[32], L-glutamic acid[30], DL-lysine[32], aspartic acid[29] and 1,3-pdta (this work).
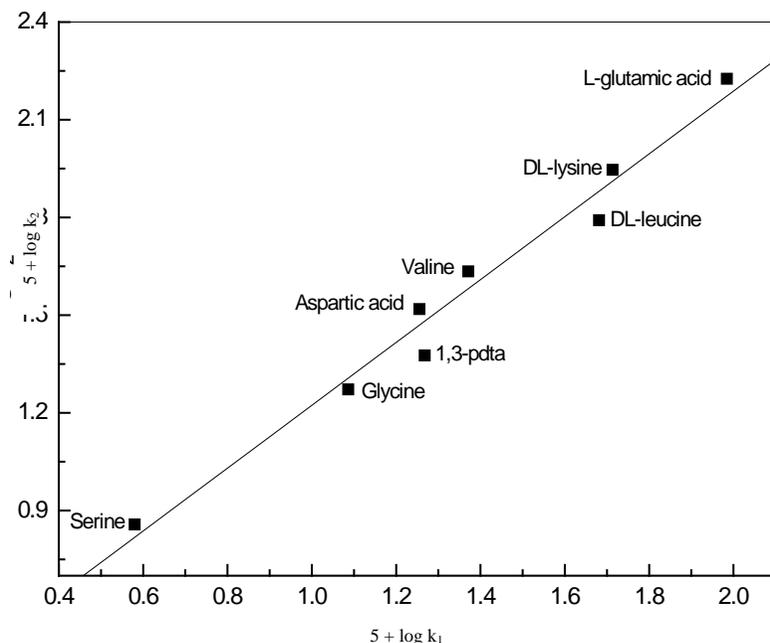
Figure 5. Plot of log k_1 with log k_2 for the substitution of water in $[Cr(H_2O)_6]^{3+}$ by different ligands

The composition and formation constants of the complexes between chromium(III) and 1,3- pdta were determined using Hills equation (eq.16)[40].

$$\log (A-A_o)/(A_\infty-A) = \log K + n \log [1,3\text{- pdta}] \qquad (16)$$

Where A is the absorbance reached at the end of the reaction, A_0 is the absorbance at zero 1,3- pdta concentration and A_∞ is the equilibrium absorbance for highest concentration of 1,3-pdta. Plots of log $(A- A_0)/ (A_\infty-A)$ *vs*. log [1,3- pdta], where [1,3- pdta] 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 (Figure 6).
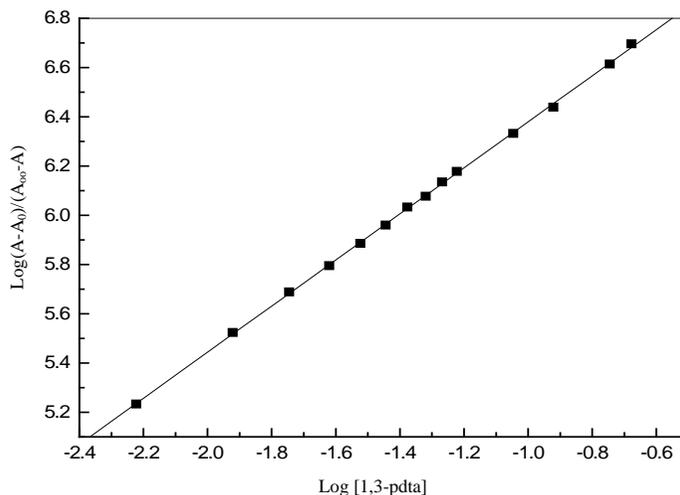
Figure 6. Plot of log (A −A$_0$) / (A$_\infty$ − A) *vs.* log [1,3- pdta]; I = 0.6 mol dm^{-3}, pH = 4.1, [Cr(III)] = 8.8x10^{-3} mol dm^{-3}, t = 35 ^{0}C

Conclusion

In the present study, the kinetics of the reaction between chromium(III) and 1,3-pdta in weak acid aqueous solutions was investigated. The reaction was found to be first order in chromium(III). The reaction rate accelerated with increasing the 1,3-pdtp concentration, pH, temperature, ionic strength and dielectric constant of the reaction medium. An associative mechanism was suggested to account for the results obtained. The logarithm of the formation constant of complex formed was found 7.31.

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