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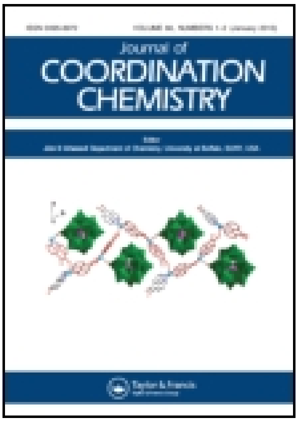

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Investigation of the kinetics of formation of 1:1 complex between chromium(III) with 1,3-propanediamine-N,N′-diacetate-N,N′-di-3-propionate ion in aqueous acidic media

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Investigation of the kinetics of formation of 1 : 1 complex between chromium(III) with 1,3-propanediamine-N,N′-diacetate-N,N′-di-3-propionate ion in aqueous acidic media

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The kinetics of formation of the 1 : 1 complex of chromium(III) with 1,3-propanediamine-N,N′-diacetate-N,N′-di-3-propionate (1,3-pddadp) were followed spectrophotometrically at $\lambda_{max} = 557$ nm. The reaction was first-order in chromium(III). Increasing the 1,3-pddadp concentration from 2.2×10^{-2} to 0.11 mol dm^{-3} accelerated the reaction rate. Increasing the hydrogen ion concentration from 1.995×10^{-5} to 6.31×10^{-4} mol dm^{-3} retarded 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 reactants. Values of 22 kJ mol^{-1} and -115 J K^{-1} mol^{-1} were obtained for the energy and the entropy of activation, respectively, which indicate an associative mechanism. The logarithm of the formation constant of the 1 : 1 complex formed was 11.3.

Keywords: Kinetics; Mechanism; Substitution; Chromium(III); 1,3-propanediamine-N; N′-diacetate-N; N′-di-3-propionate

1. Introduction

Ligand substitution reactions represent a major type of inorganic reaction [1]. Chromium (III) is a substitution-inert metal ion [2].

Aminocarboxylate chelating agents complex strongly with most metals, altering metal bioavailability and mobility in the environment [3]. These compounds are widely used for industrial, medical, and agricultural purposes, as laundry detergent builders, boiler scale inhibitors, in metal plating and cleaning operations, in textile manufacture, and in paper and cellulose production [4–12]. 1,3-Propanediamine-N,N′-diacetate-N,N′-di-3-propionate (1,3-pddadp) is a member of the aminocarboxylate family.

Although the experimental system and reaction studied here are simple, elucidation of the mechanism in this model system has implications for more complex homogeneous and heterogeneous phenomena involving metal complexes (e.g. metal ion transport, bioavailability, and toxicity) [3–12].

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The present investigation is concerned with the kinetics of complexation of chromium (III) with 1,3-pddadp in weak acidic solution, studying rate of reaction and measurement of the formation constant of the complex.

2. Experimental

All chemicals were of pure grade and used without purification. 1,3-pddadp was prepared using a previously described procedure [13]. Stock solution (0.1 mol dm^{-3}) of hexaaquachromium(III) was prepared by dissolving $CrCl_3$ (Merck) in doubly distilled water and leaving the solution for 48 h at 45 °C, where upon the green color of $CrCl_3$ changed to blue color of $Cr(H_2O)_6^{3+}$ [14]. Absorbance measurements were performed using a thermostatted 292 Cecil spectrophotometer and pH measurements were conducted with a Griffin pH meter fitted with a glass-calomel electrode standardized by potassium hydrogen phthalate.

Kinetic experiments were conducted by mixing thermostatted solutions of chromium(III) and 1,3-pddadp, and adjusting the hydrogen ion concentration to the required value with potassium hydroxide or perchloric acid. Ionic strength was adjusted by a 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 $\lambda_{max} = 557$ nm for the complex formed. The reaction rate was followed under pseudo-first-order conditions where at least 10-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 the 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 first-order in chromium(III) (table 1). The effect of varying the 1,3-pddadp 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-pddadp concentration at various pH values was nonlinear (figure 1), indicating formation of an ion-pair [15, 16].

Increasing the ionic strength, I, of the reaction medium from 0.7 to 1.8 mol dm^{-3} (adjusted by sodium perchlorate) retarded the reaction rate (table 1). Applying the *Bronsted Bjerrum* equation [17, 18], a linear relationship was obtained by plotting log k_{obs} *versus* $(I)^{1/2}$ (figure 2), indicating that the reaction involves ion-pair formation.

The effect of the dielectric constant on the rate of reaction was studied using different ratios of ethanol–water. 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 slope (figure 3), indicating that the reaction is of an ion-pair type [19].

The effect of hydrogen ion concentration on the rate of reaction was studied from 3.16×10^{-4} to 1.995×10^{-5} mol dm^{-3} at various temperatures (table 2). The results obtained show that the reaction is accelerated by lowering hydrogen ion concentration.

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

					k_{obs}/s^{-1} $[H^+] \times 10^5$ mol dm^{-3}					
$[Cr(III)] \times 10^3$ mol dm^{-3}	[1,3-pddadp]$\times 10^{-2}$ mol dm^{-3}	T (°C)	I mol dm^{-3}	ε	63.31	31.62	15.85	7.943	3.981	1.995
5.5	11	35	0.7						3.981	
7.5									4.103	
9.0									4.001	
11									4.032	
13									4.087	
15									4.113	
17									4.075	
11	2.2	35	0.7		0.481	0.797	1.107	1.350	1.581	1.946
	3.3				0.717	1.127	1.484	1.830	2.110	2.572
	4.4				0.729	1.294	1.808	2.190	2.529	3.111
	5.5				0.868	1.419	1.982	2.424	2.835	3.415
	6.6				1.022	1.629	2.216	2.696	3.185	3.808
	8.8				1.253	1.939	2.585	3.158	3.726	4.413
	11				1.417	2.119	2.71	3.347	4.032	4.875
11	11	35	0.70						4.032	
			0.85						3.611	
			0.95						3.024	
			1.10						2.866	
			1.15						2.614	
			1.20						2.341	
			1.25						2.225	
			1.40						1.897	
			1.60						1.638	
			1.80						1.373	
11	11	25	0.7	78.00					2.637	
				75.32					2.787	
				72.63					2.957	
				69.95					3.152	
				67.26					3.377	
				64.58					3.639	
				61.89					3.947	
				59.21					4.313	
				56.52					4.752	

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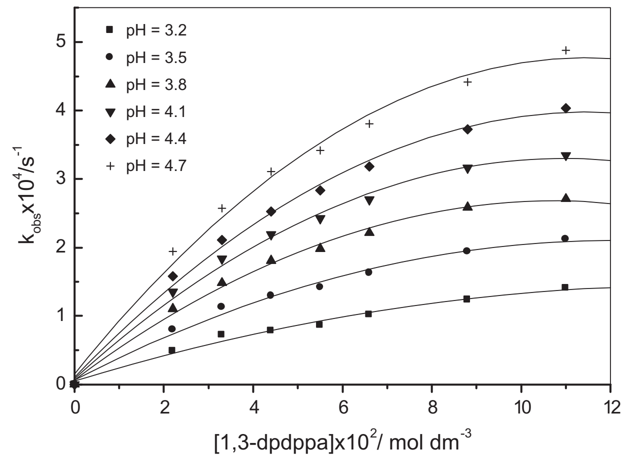

Figure 1. Variation of k_{obs} with [1,3-pddadp] at various pH; $I = 0.7\,mol\,dm^{-3}$, $[Cr(III)] = 11 \times 10^{-3}\,mol\,dm^{-3}$, $T = 35\,°C$.

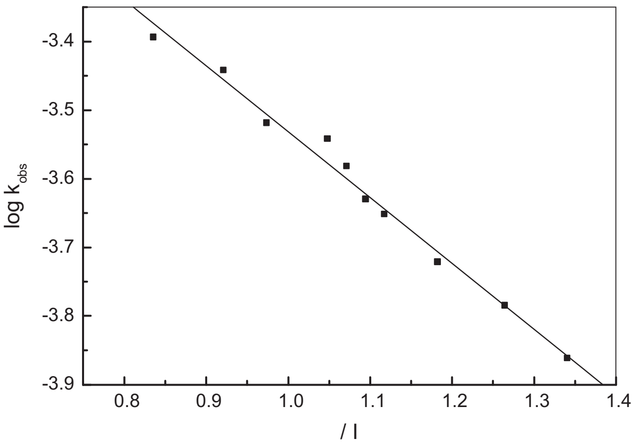

Figure 2. Variation of log k_{obs} with $(I)^{1/2}$; $[1,3\text{-pddadp}] = 11 \times 10^{-2}\,mol\,dm^{-3}$, $[Cr(III)] = 6.6 \times 10^{-3}\,mol\,dm^{-3}$, $T = 35\,°C$, $I = 0.7\,mol\,dm^{-3}$, $[H^+] = 3.981 \times 10^{-5}\,mol\,dm^{-3}$.

The dependence of k_{obs} on the hydrogen ion concentration can be explained by the following equilibria between the various species of each reactant which are present in the reaction medium [20, 21].

$$[Cr(H_2O)_6]^{+3} \overset{K_h}{\rightleftharpoons} [Cr(H_2O)_5OH]^{+2} + H^+ \quad pK_h = 4.1 \tag{1}$$

$$H_4L \underset{+H^+}{\overset{K_1}{\rightleftharpoons}} H_3L^- \underset{+H^+}{\overset{K_2}{\rightleftharpoons}} H_2L^{-2} \quad pK_1 = 2.79 \quad pK_2 = 3.75 \tag{2}$$

The pentaaquahydroxochromium(III) species is more reactive than the hexaaquachromium(III) due to the presence of OH^- that increases the water lability due to its π-bonding ability [22–30].

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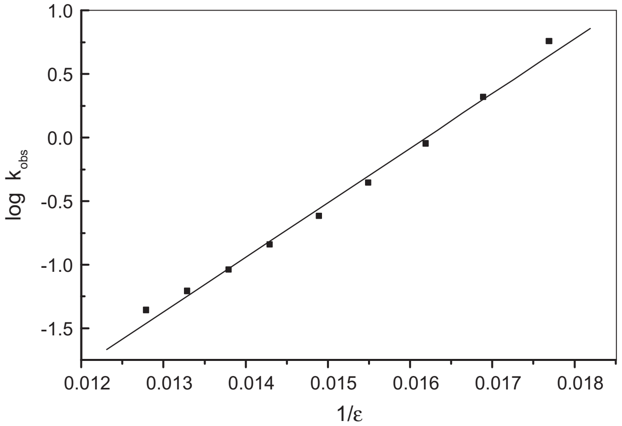

Figure 3. Variation of log k_{obs} with $1/\varepsilon$ in ethanol-water mixture; $T = 25\,°C$, $[H^+] = 3.981 \times 10^{-5}\,mol\,dm^{-3}$, [Cr (III)] $= 11 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.7\,mol\,dm^{-3}$, [1,3-pddadp] $= 11 \times 10^{-2}\,mol\,dm^{-3}$.

Table 2. Kinetic data for the interaction of Cr(III) with 1,3-pddadp at various temperature and proton concentration; [Cr(III)] $= 11 \times 10^{-3}\,mol\,dm^{-3}$, $I = 0.7\,mol\,dm^{-3}$, [1,3-pddadp] $= 11 \times 10^{-2}\,mol\,dm^{-3}$.

T/°C	$[H^+] \times 10^5/mol\,dm^{-3}$	$k_{obs} \times 10^4/s^{-1}$
25	31.62	1.599
	15.85	1.917
	7.943	2.285
	3.981	2.709
	1.995	3.193
30	31.62	2.003
	15.85	2.390
	7.943	2.836
	3.981	3.347
	1.995	3.929
35	31.62	2.633
	15.85	3.049
	7.943	3.514
	3.981	4.032
	1.995	4.606
40	31.62	3.107
	15.85	3.400
	7.943	4.558
	3.981	4.875
	1.995	5.610
45	31.62	3.346
	15.85	4.033
	7.943	4.831
	3.981	5.755
	1.995	6.818

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-pddadp in the hydrogen ion concentration range under investigation:

$$[Cr(H_2O)_6]^{+3} \overset{K_h}{\rightleftharpoons} [Cr(H_2O)_5OH]^{+2} + H^+ \quad pK_h = 4.1 \tag{3}$$

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$$H_4L \underset{+H^+}{\overset{K_1}{\rightleftharpoons}} H_3L^- \underset{+H^+}{\overset{K_2}{\rightleftharpoons}} H_2L^{-2} \quad pK_1 = 2.79 \quad pK_2 = 3.75 \tag{4}$$

$$[Cr(H_2O)_6]^{+3} + H_3L^- \overset{K_{IP1}}{\rightleftharpoons} IP_1 \tag{5}$$

$$[Cr(H_2O)_5OH]^{+2} + H_3L^- \overset{K_{IP2}}{\rightleftharpoons} IP_2 \tag{6}$$

$$[Cr(H_2O)_6]^{+3} + H_3L^{-2} \overset{K_{IP3}}{\rightleftharpoons} IP_3 \tag{7}$$

$$[Cr(H_2O)_5]^{+2} + H_3L^{-2} \overset{K_{IP4}}{\rightleftharpoons} IP_4 \tag{8}$$

$$IP_1 \underset{slow}{\overset{k_1}{\longrightarrow}} [Cr(H_2O)_5(H_3L)]^{+2} \overset{fast}{\longrightarrow} product \tag{9}$$

$$IP_2 \underset{slow}{\overset{k_2}{\longrightarrow}} [Cr(H_2O)_4(OH)(H_3L)]^{+} \overset{fast}{\longrightarrow} product \tag{10}$$

$$IP_3 \underset{slow}{\overset{k_3}{\longrightarrow}} [Cr(H_2O)_5(H_3L)]^{+} \overset{fast}{\longrightarrow} product \tag{11}$$

$$IP_4 \underset{slow}{\overset{k_4}{\longrightarrow}} [Cr(H_2O)_4(OH)(H_3L)]^{+} \overset{fast}{\longrightarrow} product \tag{12}$$

where $IP_1 \equiv \{[Cr(H_2O)_6]^{+3} \cdot H_3L^{-1}\}$, $IP_2 \equiv \{[Cr(H_2O)_5OH]^{+3} \cdot H_3L^{-1}\}$, $IP_3 \equiv \{[Cr(H_2O)_6]^{+3} \cdot H_2L^{-2}\}$, and $IP_4 \equiv \{[Cr(H_2O)_5OH]^{+2} \cdot H_2L^{-2}\}$. IP_1 to IP_4 are the hexaaqua and pentaaquahydroxo ion-pair complexes of chromium(III) and 1,3-pddadp.

The rate of exchange of the first water molecule in the inner coordination sphere of the metal center is slow and therefore the rate-determining equations are (7–10) [24, 25, 30]. As soon as one carboxyl of the ligand enters into the inner sphere, the electron density on the chromium center increases owing to the inductive effect, and as a result, the remaining ligands are labilized easily and their substitution is rapid. From the previous mechanism, the first-order rate constant is derived as:

$$k_{obs} = \frac{\left(k_1K_{IP_1}[H^+] + k_2K_{IP_2}K_2 + k_3K_{IP_3}K_h + k_4K_{IP_4}\frac{K_2K_h}{[H^+]}\right)[1,3\text{-pddadp}]}{\left(\frac{[H^+]^2}{K_1} + [H^+] + K_2\right)\left(1 + \frac{K_h}{[H^+]}\right) + \left(\left(K_{IP_1}[H^+] + K_{IP_2}K_2 + K_{IP_3}K_h + K_{IP_4}\frac{K_2Kh}{[H^+]}\right)[1,3\text{-pddadp}]\right)} \tag{13}$$

The inverse of equation (11) becomes

$$\frac{1}{k_{obs}} = \frac{K_{IP_1}[H^+] + K_{IP_2}K_2 + K_{IP_3}K_h + K_{IP_4}\frac{K_2K_h}{[H^+]}}{\left(k_1K_{IP_1}[H^+] + k_2K_{IP_2}K_2 + k_3K_{IP_3}K_h + k_4K_{IP_4}\frac{K_2K_h}{[H^+]}\right)} + \frac{\left(\frac{[H^+]^2}{K_1} + [H^+] + K_2\right)\left(1 + \frac{K_h}{[H^+]}\right)}{\left(k_1K_{IP_1}[H^+] + k_2K_{IP_2}K_2 + k_3K_{IP_3}K_h + k_4K_{IP_4}\frac{K_2K_h}{[H^+]}\right)[1,3\text{-pddadp}]} \tag{14}$$

and a plot of $1/k_{obs}$ *versus* 1/[1,3-pddadp] gave straight lines with slopes

$$S = \frac{\left(\frac{[H^+]^2}{K_1} + [H^+] + K_2\right)\left(1 + \frac{K_h}{[H^+]}\right)}{\left(k_1 K_{IP_1}[H^+] + k_2 K_{IP_2} K_2 + k_3 K_{IP_3} K_h + k_4 K_{IP_4} \frac{K_2 K_h}{[H^+]}\right)} \tag{15}$$

and intercepts

$$I = \frac{K_{IP_1}[H^+] + K_{IP_2} K_2 + K_{IP_3} K_h + K_{IP_4} \frac{K_2 K_h}{[H^+]}}{\left(k_1 K_{IP_1}[H^+] + k_2 K_{IP_2} K_2 + k_3 K_{IP_3} K_h + k_4 K_{IP_4} \frac{K_2 K_h}{[H^+]}\right)} \tag{16}$$

and

$$\frac{I}{S} = \frac{K_{IP_1}[H^+] + K_{IP_2} K_2 + K_{IP_3} K_h + K_{IP_4} \frac{K_2 K_h}{[H^+]}}{\left(\frac{[H^+]^2}{K_1} + [H^+] + K_2\right)\left(1 + \frac{K_h}{[H^+]}\right)} \tag{17}$$

The ion-pair formation constants, K_{IP}, and the rate constants of the rate-determining steps, k, were calculated by plotting $1/k_{obs}$ *versus* 1/[1,3-pddadp] at different hydrogen ion concentrations (Figure 4). The values 9.91, 13.95, 12.48, and 15.7 $mol^{-1} dm^3$ for the ion-pair formation constants K_{IP}, and 2.03, 3.78, 2.85, and $4.27 \times 10^{-3} s^{-1}$ for the rate-determining steps k, respectively, were calculated by applying equations (13–15) at different hydrogen ion concentrations and taking the values of K_1, K_2, and K_h from equations (1) and (2). The unexpected values of ion-pair formation constants, K_{IP} ($K_{IP_2} > K_{IP_3}$), indicate that the mechanism not only is via electrostatic attraction but also include hydrogen bonding between acetates and the first coordination sphere waters.

The effect of temperature on the reaction rate was also studied at different hydrogen ion concentrations (table 2). The activation parameters were calculated using *Arrhenius* plots

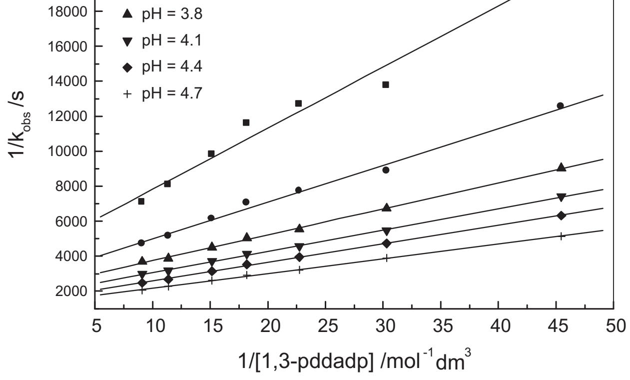

Figure 4. Variation of $1/k_{obs}$ with 1/[1,3-pddadp]; $[Cr(III)] = 11 \times 10^{-3}$ mol dm^{-3}, $T = 35$ °C, $I = 0.7$ mol dm^{-3}, $[H^+] = 3.981 \times 10^{-5}$ mol dm^{-3}.

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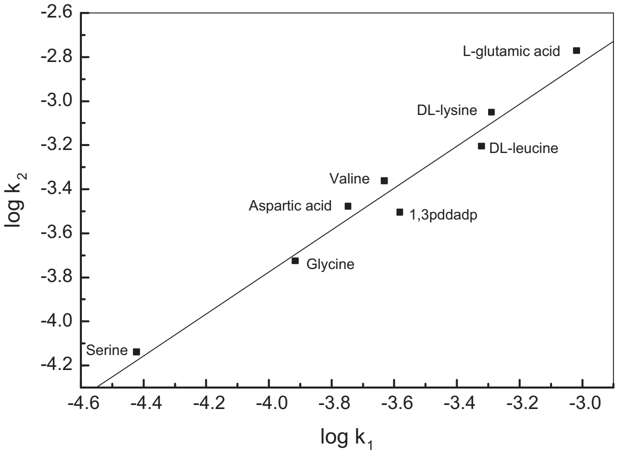

Figure 5. Plot of log k_1 with log k_2 for the substitution of water in $[Cr(H_2O)_6]^{3+}$ by different ligands at temperatures 35 and 40 °C, respectively.

and the *Eyring* equation, as $22 \pm 3\,kJ\,mol^{-1}$ for the energy of activation, E_a, and $-115 \pm 20\,J\,K^{-1}\,mol^{-1}$ for entropy of activation, ΔS^*.

Substitution reactions of hexaaqua-chromium(III) with a variety of ligands were proceed by associative [19, 31, 32] and dissociative [33, 34] mechanisms. Swaddle [35, 36] and Lincoln [37] have reviewed 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 an associative character for the substitution reaction of $[Cr(H_2O)_6]^{+3}$.

The associative mechanism is further supported by (1) lowering of the enthalpy and large negative entropy of activation for substitution of water by the ligand compared to water exchange (for water exchange $\Delta H^* = 109.6\,kJ\,mol^{-1}$ and $\Delta S^* = +12\,JK^{-1}\,mol^{-1}$ [38]); (2) the straight line obtained from plotting log k_1 *versus* log k_2 [39] (figure 5) (where k_1 and k_2 are the first-order rate constants at different temperature) for the substitu-

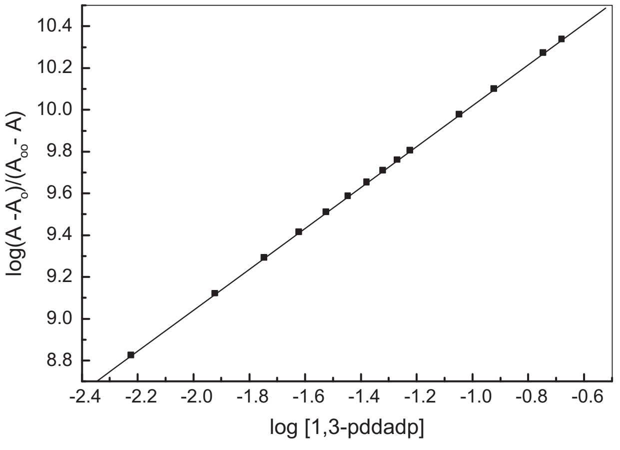

Figure 6. Plot of log $(A-A_0)/(A_\infty-A)$ *vs.* log [1,3-pddadp]; $I = 0.7\,mol\,dm^{-3}$, $[Cr(III)] = 11 \times 10^{-3}\,mol\,dm^{-3}$, $T = 35\,°C$, $[H^+] = 3.981 \times 10^{-5}\,mol\,dm^{-3}$.

tion of water in $[Cr(H_2O)_6]^{3+}$ by glycine [27], serine [28], valine [26], DL-leucine [32], L-glutamic acid [31], DL-lysine [32], aspartic acid [29], and 1,3-pddadp (this work).

The composition and formation constants of the complexes between chromium(III) and 1,3-pddadp were determined using *Hill's* equation (16) [40]:

$$log(A - A_o)/(A_\infty - A) = \log K + n \log[1,3\text{-pddadp}] \tag{18}$$

where A is the absorbance reached at the end of the reaction, A_0 is the absorbance at zero 1,3-pddadp concentration, and A_∞ is the equilibrium absorbance for the highest concentration of 1,3-pddadp. Plots of log $(A - A_0)/(A_\infty - A)$ *versus* log [1,3-pddadp], where [1,3-pddadp] is the total concentration used, yield a straight line with slope = 1 (number of ligand molecules attached to one chromium) and intercept of log $K = 11.3$ (figure 6).

4. Conclusions

The kinetics of the reaction between chromium(III) and 1,3-pddadp in weak acidic aqueous solutions were investigated. The reaction was first-order in chromium(III), accelerated with increasing 1,3-pddadp concentration, pH, temperature, decreasing 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 the complex was 11.3.

Acknowledgment

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