

SOLVATION OF THE $[\text{Cr}(\text{NCS})_4(\text{IMIDAZOLE})_2]^-$ ION IN
ETHANOL - WATER MIXTURES

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ABSTRACT

Solvation kinetics of $[\text{Cr}(\text{NCS})_4(\text{imidazole})_2]^-$ has been studied in ethanol-water mixtures at different temperatures. The first stage of the solvation consists of two competitive reactions: two NCS^- ions are exchanged, presumably, by water molecules and simultaneously an imidazole molecule by ethanol, the latter in a second-order reaction, accelerated by hydrogen ions. The exchange of the amine is followed by the substitution of the first two NCS^- ions. The third and fourth NCS^- ions are substituted only in neutral and slightly acidic solutions. Kinetic parameters have been determined for reactions (1), (2) and (4). The influence of the solvent composition and acidity is discussed.

KEYWORDS: complexes of chromium, competitive reactions, mechanism, kinetic parameters, water-ethanol solution.

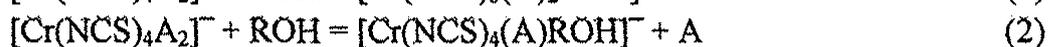
RESUMO

A cinética de solvatação do íon $[\text{Cr}(\text{NCS})_4(\text{imidazol})_2]^-$ foi estudada a várias temperaturas em soluções aquosas de etanol. A primeira etapa de solvatação consiste de duas reações competitivas: dois íons NCS^- são substituídos por moléculas de água e simultaneamente uma molécula de imidazol é substituída por etanol. A segunda reação, que é de segunda ordem, é acelerada por íons de hidrogênio. O intercâmbio da amina é seguido pela substituição dos primeiros dois íons NCS^- . O terceiro e o quarto íon NCS^- são substituídos somente em soluções neutras ou levemente ácidas. Foram determinados parâmetros cinéticos para as reações (1), (2) e (4). Os efeitos da composição do meio e da acidez do mesmo são discutidas.

INTRODUCTION

In our previous papers ¹⁻⁷ we described the solvation kinetics of some $[\text{Cr}(\text{NCS})_4(\text{amine})_2]^-$ type complexes that have been studied in ethanol-water mixtures, with the following amines: aniline, p-toluidine, p-ethylaniline, p-anisidine and p-phenetidine.

The first stage of solvation consists of two competitive reactions, viz. of the exchange of the first NCS^- ion or of an amine molecule A by the solvent molecules ROH, i.e.



Reaction (1) proceeds by a $\text{S}_{\text{N}}1$ mechanism and is followed presumably by the practically instantaneous reaction:

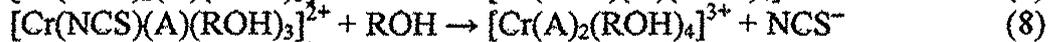
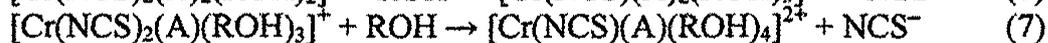


Reaction (2) seems to be of $\text{S}_{\text{N}}2$ mechanism. It is accelerated by the presence of mineral acids and is followed by the reactions:



Reaction (4) is analogous with reaction (1). Its kinetic parameters are very close to those characteristic of reaction (1) and reaction (5) is presumably also instantaneous.

In neutral solutions the third and the fourth NCS^- ions are also substituted, according to the equations:



One cannot exclude the possibility that the second amine molecule may be exchanged. Thus, other reactions may also be involved.

Kinetic parameters of reactions (1) and (4) are not influenced sensibly by the nature of the amine molecule, but the rate of reaction (2) depends on the nucleophilic character of the amine, viz. it has lower values if A is p-anisidine or p-phenetidine, when compared to the other amines studied.

EXPERIMENTAL

The synthesis of the imidazole· $\text{H}[\text{Cr}(\text{NCS})_4(\text{imidazole})_2]$ complex salt has been described in our previous paper ^{10,11}.

Kinetic measurements have been carried out in the same way as described earlier in the literature ⁵.

RESULTS AND DISCUSSION

In the present paper the solvation of the complex ion with A=imidazole has been studied at different temperatures and in ethanol-water mixtures containing 37.7, 48.5, 72.7 and 97.0 percent by volume in ethanol. The concentration of the non-transformed complex ion and the NCS^- ions liberated has been followed with time. The concentration of the non-transformed complex ion has been determined colorimetrically and since the validity of Beer's law been observed, the plot of $\log A$ versus time was used to determine the rate constants. This graphical plot gives very good straight lines, and shows the overall reaction to be of first order. Some examples are given in Figure 1.

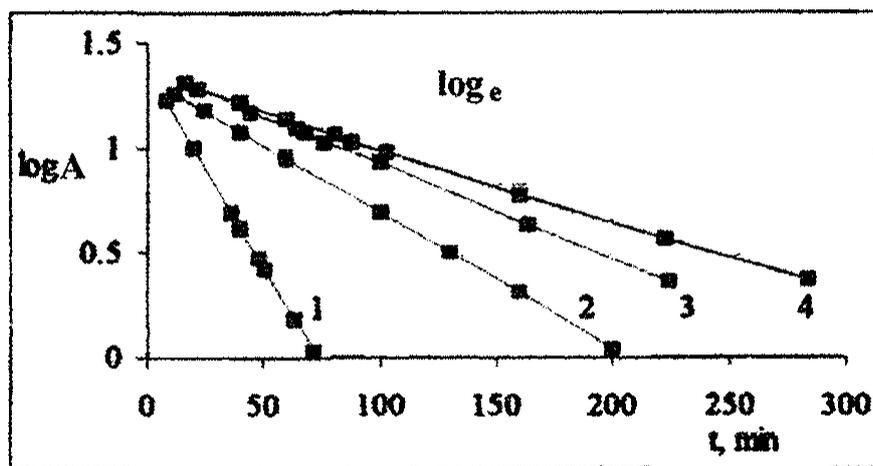


Fig.1 Determination of overall first order rate constants k 1. 48.5% EtOH, 40°C; 2. 72.7% EtOH, 40°C; 3. 97.0% EtOH, 40°C; 4. 48.5% EtOH, 40°C.

Rate constants derived from the slope of these straight lines are presented in Table 1. The graphical plot of $\log_e k/T$ values versus $1/T$ enabled us to calculate the apparent activation energy and entropy values. Both decrease systematically with increasing ethanol content of the solvent, as is seen from Table 1.

Table 1 Kinetic parameters of the overall process

EtOH content (%Vol.)	$k \cdot 10^3 \text{sec}^{-1}$				ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.
	40°C	45°C	50°C	55°C		
37.7	0.098	0.236	0.541	1.18	33.3	29.2
48.5	0.136	0.309	0.698	1.46	31.7	24.5
72.7	0.177	0.381	0.803	1.74	30.2	21.2
97.0	0.242	0.513	1.082	2.23	29.5	19.1

In order to find the fraction of reactions (1) and (2) in the overall reaction, the ratio between the concentration C_1 of NCS^- ions liberated and the complex transformed,

$r=C_1/(C_0-C)$ has been determined (C_0 and C stand for the initial and actual concentration of the complex ion studied). As in the case of the complexes investigated earlier, a finite zero-time NCS^- -ion concentration has been found and in order to estimate the concentration NCS^- liberated, C_1 -values have been corrected with the zero-time values, obtained by means of extrapolation of experimental data.

Similarly to the analogous complexes, the ratio has a practically constant value at the beginning of the solvation process and it depends only on the ethanol content of the solvent and not on the temperature. The plot of r versus transformation degree of the complex is shown in Figure 2.

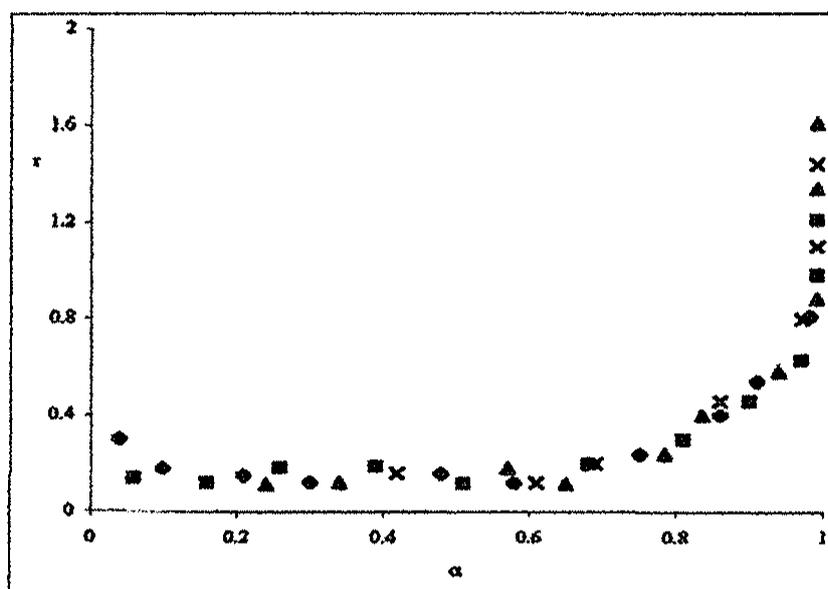


Fig.2 Ratio $r=C_1/(C_0-C)$ as function of transformation degree α . 48.5% EtOH;
 ◆ 40°C; ■ 45°C; ▲ 50°C; x 65°C.

The shape of the $r - \alpha$ curves is also similar for other ethanol concentrations. The nearly constant initial r values, which are referred to as r_0 , are the following:

Ethanol content (Vol. %)	37.7	48.5	72.7	97.0
r_0	0.26	0.17	0.091	0.052

The small r_0 values show that reaction (2) plays an important part in the overall process. By using the above given r_0 values, the rate constants k_1 and k_2 of reactions (1) and (2) can be derived from the overall first-order rate constant k . In order to diminish the influence of experimental errors, calculations have been carried out by using corrected k values, derived from ΔH^\ddagger and ΔS^\ddagger values given in Table 1, instead of the experimentally determined ones. In these calculations reaction (3) has been presumed to be instantaneous.

This presumption seems to be sound, since in the case of the Reinecke salt, with $A=NH_3$ ⁸ and also in the case of the analogous benzylamine derivative⁹, where the amine

molecules are not substituted, $r_0 \approx 2$ has been observed, which means the practically simultaneous exchange of the first two NCS^- ligands. By adopting this reaction scheme, the individual first-order rate constants k_1 and k_2 can be calculated according to the following formulae:

$$k_1 = kr_0/2 \text{ and } k_2 = k(1-r_0/2) \quad (10)$$

The results are given in Table 2.

Rate constants k_1 are a little larger than for the analogous complexes studied earlier and show a systematic decrease with increasing ethanol content. This variation is much larger than previously observed. The first order rate constants k_2 increase simultaneously with the ethanol content and the ratio k_2 to molar concentration of ethanol is practically constant for a given temperature. One may presume the amine molecules to be substituted only by ethanol by an $\text{S}_{\text{N}}2$ pathway. The corresponding second-order constants k'_2 are given in Table 2. These values are close to k'_2 obtained for the analogous complexes when A-p-toluidine and p-ethylaniline^{4,5}.

Table 2. Rate constants of reactions (1) and (2)

EtOH content (%Vol.)	Rate const.	Temperature			
		40°C	45°C	50°C	52°C
37.7	$K_1 \cdot 10^5 \text{sec}^{-1}$	1.34	3.15	7.28	16.1
48.5		1.11	2.46	5.44	11.8
72.7		0.781	1.70	3.65	7.75
97.0		0.602	1.27	2.66	5.53
37.7	$K_2 \cdot 10^4 \text{sec}^{-1}$	0.864	2.01	4.63	10.3
48.5		1.25	2.86	6.25	13.6
72.7		1.67	3.64	7.83	16.4
97.0		2.36	5.04	10.52	21.6
37.7	$K'_2 \cdot 10^4 \text{sec}^{-1}$	1.133	0.319	0.726	1.64
48.5		0.152	0.344	0.765	1.65
72.7		0.131	0.297	0.634	1.32
97.0		0.140	0.306	0.639	1.30

The influence of acidity upon the solvation kinetics has been studied in solution with 37.7 percent ethanol, by adding various amounts of perchloric acid. The results obtained are given in Table 3.

The general picture is the same as observed in our previous papers: k_1 , r_0 , ΔH^\ddagger and ΔS^\ddagger decrease with increasing in perchloric acid concentration, i.e. reaction (1) is hindered and reaction (2) is, on the contrary, enhanced. At concentration higher than 10^{-2} M, the rate constant k_1 is practically not influenced by the acidity. Generally, increasing acidity and increasing ethanol content make k_1 and k_2 vary in the some direction, but a partial reaction order can be found only in the case of k_2 and only for ethanol. The order effects involve presumably different pre-equilibria.

Table 3. Influence of perchloric acid on the kinetic parameters. (37.7% EtOH)

[HClO ₄] (mole/l)	Rate const.	Temperature				ΔH^\ddagger (kcal/mole)	ΔS^\ddagger e.u.	r_0
		40°C	45°C	50°C	55°C			
10 ⁻⁴	$k \cdot 10^3 \text{sec}^{-1}$	0.112	0.245	0.535	1.38	31.1	22.6	0.141
10 ⁻³		0.134	0.301	0.642	1.30	30.4	21.4	0.092
10 ⁻²		0.164	0.343	0.767	1.55	31.3	21.5	0.034
10 ⁻¹		0.193	0.422	0.871	1.81	29.3	18.6	0.023
10 ⁻⁴	$k_1 \cdot 10^5 \text{sec}^{-1}$	0.786	1.76	3.82	8.09			
10 ⁻³		0.601	1.31	2.87	5.97			
10 ⁻²		0.281	0.611	1.33	2.74			
10 ⁻¹		0.244	0.521	1.11	2.22			
10 ⁻⁴	$k_2 \cdot 10^4 \text{sec}^{-1}$	0.103	0.230	0.507	1.06			
10 ⁻³		0.129	0.281	0.606	1.29			
10 ⁻²		0.156	0.346	0.735	1.56			
10 ⁻¹		0.193	0.411	0.864	1.74			

The kinetic parameters ΔH^\ddagger and ΔS^\ddagger of the overall reaction decrease when the part played by reaction (2) increases. This suggests the idea, that both ΔH^\ddagger and ΔS^\ddagger of reaction (1) are higher than the same parameters for reaction (2). We could not obtain individual values, since our experimental data were too scattered to evidence the influence of temperature upon the initial ratio r_0 .

In order to obtain additional information concerning the second stage of the solvation process, i.e. reactions (4) – (9), the excess concentration C_{ex} of NCS⁻ ions has been calculated by subtracting from the experimental free NCS⁻ concentrations the theoretical C_1 , calculated from k_j values, taking also in to account the instantaneous reaction (3).

Results expressing the influence of temperature, ethanol content and of the acidity on this excess concentration are given in Figs. 3-5.

From these figures it is apparent, that the third and fourth NCS⁻ ions are also substituted in neutral and in slightly acidic solution.

However, the rate of this reaction decreases considerably with increasing ethanol content. The NCS⁻ ions are presumably exchanged by water molecules, which may be involved in the reaction mechanism too.

Fig. 5 shows reactions (6) – (7) to be entirely hindered in highly acidic solutions and the excess NCS⁻ ion concentration to be due only to reactions (4) and (5). By using a curve fitting method, described earlier^{4,7} rate constants k_4 of reaction (4) can be derived from the C_{ex} -time curves for concentration of HClO₄ = 10⁻² and 10⁻¹ M, on the presumption that reaction (5) was instantaneous. The procedure is illustrated by Fig. 6, showing several theoretical curves calculated for different k_4 values, as well as experimental data.

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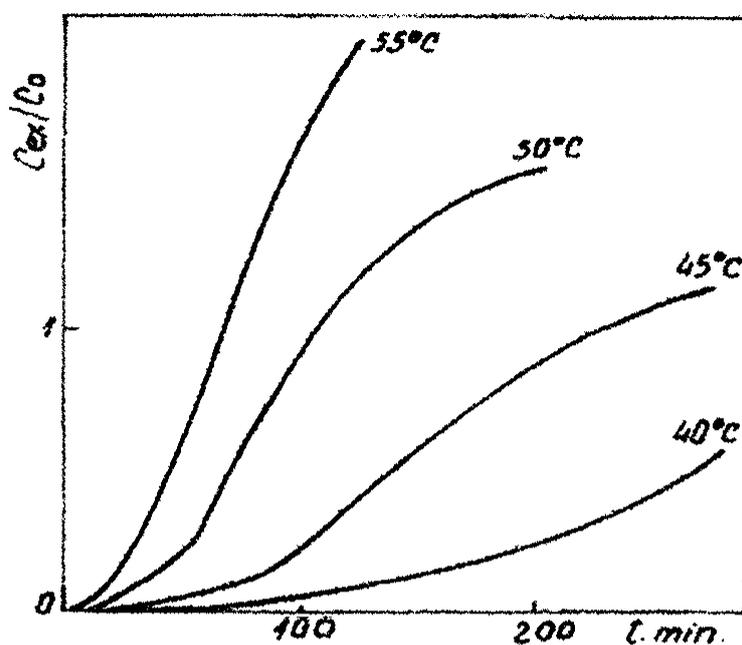


Fig. 3 Influence of temperature on the excess NCS^- concentration. (37.7% ethanol by volume)

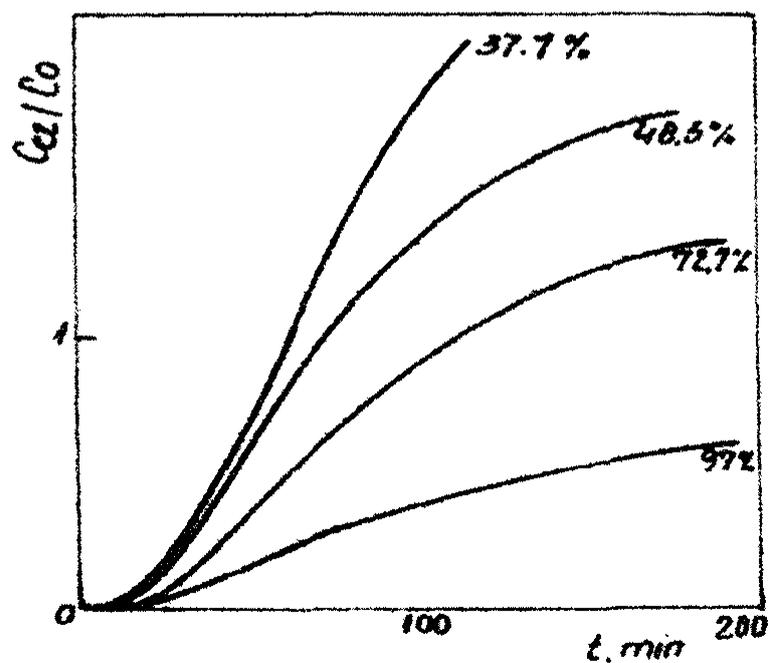


Fig. 4 Influence of the ethanol content on the excess NCS^- concentration. 55°C

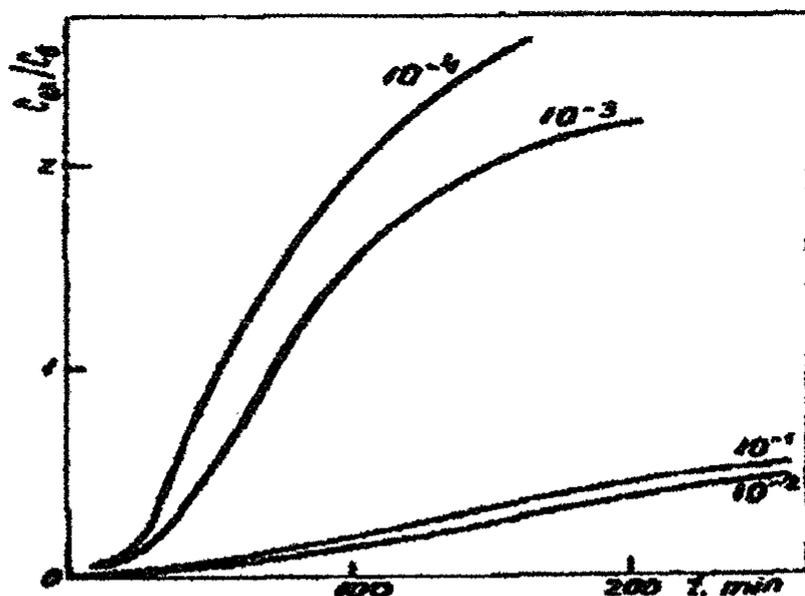


Fig. 5 Influence of perchloric acid concentration (in mole/l) on the excess NCS^- concentration. (37.7% EtOH, 55°C.)

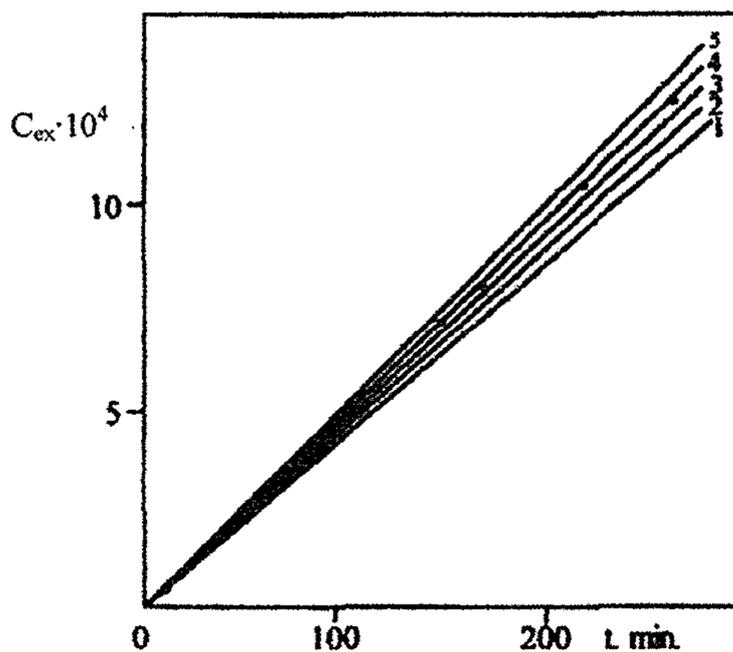


Fig. 6 Determination of k_4 by means of the curve fitting method. (37.7% EtOH, 55°C.)
 Conc. of $\text{HClO}_4 = 10^{-1}$ M. Presumed $k_4 \cdot 10^5$ values:
 1 and 2.0; 2 and 2.1; 3 and 2.2; 4 and 2.3; 5 and 2.4

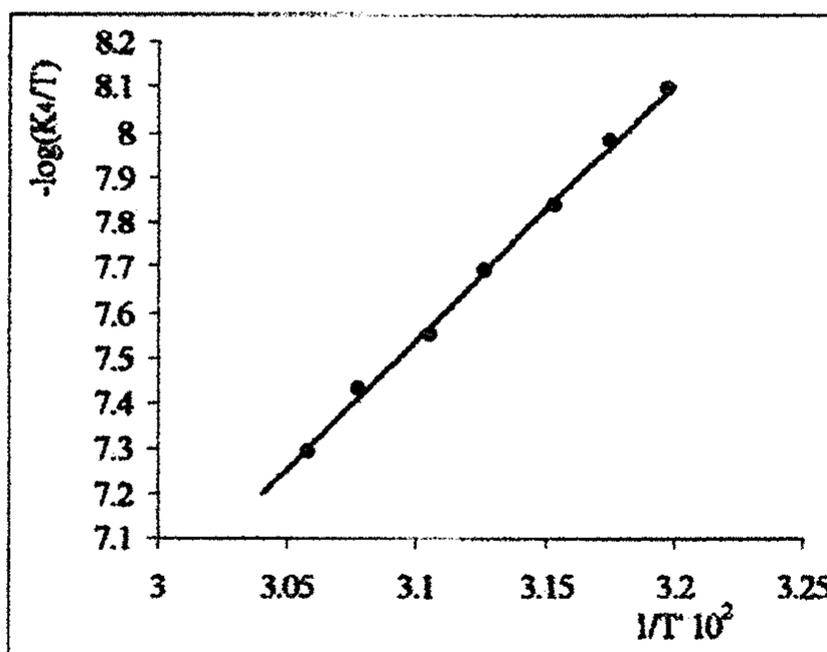
Rate constants k_4 determined by means of this procedure are presented in Table 4.

Table 4. Rate constants of reaction (4) in acid solutions $k_4 \cdot 10^5 \text{sec}^{-1}$, (37.7% ethanol by volume)

t°C	[HClO ₄], (mole/l)	
	10 ⁻¹	10 ⁻²
40	0.28	0.29
45	0.58	0.58
50	1.17	1.13
55	2.28	2.32

Values obtained are very close to k_d values for analogous complexes studied earlier⁴⁻⁷.

The plot of $\log(k_4/T)$ versus $1/T$, given in Fig.7, shows a good linearity and enabled us to calculate, by means of the least square method, the following kinetic parameters of reaction (4). $\Delta H^\ddagger = 27.6 \pm 0.6 \text{ kcal/mole}$, $\Delta S^\ddagger = 3.6 \pm 2.0 \text{ e.u.}$

Fig.7 Determination of ΔH^\ddagger and ΔS^\ddagger in acid solution.(37.7% ethanol by volume)

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