

EFFECT OF CONCENTRATED UNI-UNIVALENT ELECTROLYTES ON OXIDATION KINETICS OF SULFUR OF CHELATE LIGANDS IN Co(III) COMPLEXES WITH H_2O_2 , IO_4^- AND $\text{S}_2\text{O}_8^{2-}$

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The effect of concentrated uni-univalent electrolytes on the oxidation kinetics of sulfur in the chelate ligands ($-\text{SCH}_2\text{CH}_2\text{NH}_2^-$), ($-\text{SOCH}_2\text{CH}_2\text{NH}_2^-$), ($-\text{SCH}_2\text{COO}^-$)²⁻, and ($-\text{SOCH}_2\text{COO}^-$)²⁻ bound in Co(III) complexes with various oxidants (H_2O_2 , IO_4^- , $\text{S}_2\text{O}_8^{2-}$) has been studied at 298.2 K. The results show that the changes observed in the rate constants are due to interactions between the supporting electrolyte and solvent.

Key words: Kinetic salt effect; Thiolato ligands; Sulfenato ligands; Oxidation; Co(III) chelates.

The present paper is focused on a study of effect of concentration of uni-univalent electrolytes on the oxidation of chelate ligands containing nucleophilic sulfur and bound in Co(III) complexes with various oxidants. The oxidation reactions mentioned are suitable for studying the effect of medium because of their known mechanism connected with a transfer of oxygen atom from oxidant to sulfur of chelate ligand and the possibility of independent monitoring of both reaction steps¹. The various oxidants adopted, *viz.* H_2O_2 , IO_4^- and $\text{S}_2\text{O}_8^{2-}$, made it possible to vary the product of charge numbers of the reactants for seven reactions going by the same mechanism. The oxidations of the Co(III) complexes mentioned were studied in the past using H_2O_2 (refs^{2,3}), IO_4^- (refs^{4,5}) and $\text{S}_2\text{O}_8^{2-}$ (ref.⁶) in aqueous and aqueous–nonaqueous media, but little attention was paid⁷ to a systematic study of effect of concentrated electrolytes on this type of reaction. The effect of concentrated electrolytes was studied in the oxidations of various Fe(II) complexes connected with electron transfer^{8,9}. It was found that the “kinetic salt effect” observed in these reactions was due to interactions between the solvent and supporting electrolyte.

The aim of the present work is to examine the effect of concentrated electrolytes on the reactions studied, evaluate the role of specific interactions between the supporting electrolyte and solvent, and compare the effect of concentrated electrolytes on reactions of various types.

EXPERIMENTAL

The complexes examined, viz. $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]\text{ClO}_4$ (ref.¹⁰) and $[\text{Co}(\text{en})_2\text{SCH}_2\text{CH}_2\text{NH}_2](\text{ClO}_4)_2$ (ref.¹¹), were synthesized according to the literature quoted, and their purity was checked by H,C,N analysis. All the chemicals used were of p.a. purity grade. The solutions were prepared from deionized water. The concentrations of $\text{K}_2\text{S}_2\text{O}_8$ and H_2O_2 solutions were checked iodometrically. All the reactions were followed in the medium of HClO_4 of 1 mmol l^{-1} concentration. The reaction rate was followed photometrically (Specol 220, Zeiss Jena) in 1 and 5 cm cells (their temperature was kept constant with the accuracy of $\pm 0.1 \text{ K}$) at 371 nm (the region of absorption band of the oxidation products to the first step); the absorption coefficients of the respective sulfenato complexes are $\epsilon([\text{Co}(\text{en})_2\text{SOCH}_2\text{CH}_2\text{NH}_2](\text{ClO}_4)_2) = 6400$, $\epsilon([\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]\text{ClO}_4) = 5800 \text{ l mol}^{-1} \text{ cm}^{-1}$. The oxidation of sulfenato complexes produces in the second step the respective sulfinato complexes, which do not absorb at the wavelength mentioned. In the oxidations with $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 we only followed the first step: the second step is slower by a factor of 500–1000 and does not affect the monitoring of oxidation to the first step. Both reaction steps were followed in the case of the oxidation of mercaptoacetate complex with periodate, whereas in the oxidation of thiolato complex the first step was much too fast for the experimental apparatus used, hence only the second step could be followed. In the oxidation with periodate to the second step, we used a larger surplus of oxidant, and after the rapid first step was over we followed the oxidation to the second step which was slower by a factor of three orders of magnitude. The rate constants were evaluated by the Guggenheim method and the values given are mean values from 4–6 independent measurements.

RESULTS

The effect of concentrated uni-univalent electrolytes was investigated in the following oxidation reactions:

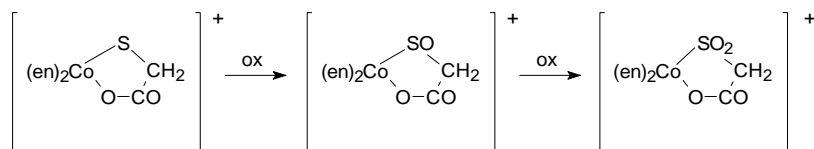
- a) $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{S}_2\text{O}_8^{2-}$
- b) $[\text{Co}(\text{en})_2\text{SCH}_2\text{CH}_2\text{NH}_2]^{2+} + \text{S}_2\text{O}_8^{2-}$
- c) $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{IO}_4^-$
- d) $[\text{Co}(\text{en})_2\text{SOCH}_2\text{COO}]^+ + \text{IO}_4^-$
- e) $[\text{Co}(\text{en})_2\text{SOCH}_2\text{CH}_2\text{NH}_2]^{2+} + \text{IO}_4^-$
- f) $[\text{Co}(\text{en})_2\text{SCH}_2\text{COO}]^+ + \text{H}_2\text{O}_2$
- g) $[\text{Co}(\text{en})_2\text{SCH}_2\text{CH}_2\text{NH}_2]^{2+} + \text{H}_2\text{O}_2$.

The two-step oxidation can be described by Scheme 1, both the steps being studied with IO_4^- , and only the first step with $\text{S}_2\text{O}_8^{2-}$ and H_2O_2 . The reaction kinetics was evaluated with the use of Eq. (1).

$$-d[[\text{Co}(\text{en})_2\text{L}]^{z+}]/dt = k [\text{Ox}][[\text{Co}(\text{en})_2\text{L}]^{z+}], \quad (1)$$

$\text{L} = (-\text{SCH}_2\text{CH}_2\text{NH}_2)^-$, $(-\text{SCH}_2\text{COO})^{2-}$, $(-\text{SOCH}_2\text{CH}_2\text{NH}_2)^-$, $(-\text{SOCH}_2\text{COO})^{2-}$;
 $z = 1, 2$; $\text{Ox} = \text{S}_2\text{O}_8^{2-}$, IO_4^- , H_2O_2 ; $[\text{Ox}]$ and $[[\text{Co}(\text{en})_2\text{L}]^{z+}]$ are total concentrations of the reactants. The excess of oxidant was large enough for the oxidation to obey the pseudo-first-order kinetics with the rate constant $k' = k [\text{Ox}]$. The rate constant values of the

reactions measured at the basic ionic strength are presented in Table I, whereas Table II gives the dependence of rate constants on concentrations of selected electrolytes.



SCHEME 1

DISCUSSION

The reactions studied go by the S_N2 mechanism like oxidation reactions of nucleophiles with peroxide¹. The reaction rate in water (Table I) is determined by the nucleophilic properties of sulfur of the chelate ligand in the Co(III) complexes, and it decreases in the order: $(-\text{SCH}_2\text{CH}_2\text{NH}_2)^- > (-\text{SCH}_2\text{COO})^{2-} > (-\text{SOCH}_2\text{CH}_2\text{NH}_2)^- > (-\text{SOCH}_2\text{COO})^{2-}$. For a given complex the reaction rate decreases in the series of oxidants: $\text{IO}_4^- > \text{S}_2\text{O}_8^{2-} > \text{H}_2\text{O}_2$. From the previous papers it follows that at low concentrations of electrolyte (where the Debye-Hückel theory is valid) the rate constant of reaction between two opposite ions decreases with increasing ionic strength in accordance with the Brønsted and Bjerrum theory. The slope of dependence $\log k = f(I^{1/2})$ or $\log k = f(I^{1/2}/(1 + I^{1/2}))$ for this region increases with increasing product of charge numbers of reactants *viz.* reactions *a* (ref.⁶) and *d* (ref.⁴), whereas it does not change in the region of low electrolyte concentrations in reaction *f* where the oxidant is a (uncharged) molecule³. At the electrolyte concentration $c_e > 1 \text{ mol l}^{-1}$ the specific effects clearly predominate (Fig. 1): their effect slows

TABLE I

Rate constant *k* of reactions *a* through *g* in water and intervals of k_0 values extrapolated from Eq. (2) for the electrolytes used at 298.2 K. *I* is ionic strength, $z_A z_B$ is product of ion charge numbers of reactants

$z_A z_B$	<i>I</i> , mmol l ⁻¹	$k_{\text{H}_2\text{O}}$, l mol ⁻¹ s ⁻¹	k_0 , l mol ⁻¹ s ⁻¹	$k_{\text{H}_2\text{O}}/k_0$	Reaction
-4	2.0	241 ± 6	21.8–24.6	10.4	<i>b</i>
-2	2.2	102 ± 3	27.7–33.1	3.36	<i>a</i>
-2	10.4	1.04 ± 0.03	0.383–0.409	2.63	<i>e</i>
-1	1.29	658 ± 21	351–401	1.75	<i>c</i>
-1	11.2	0.434 ± 0.006	0.248–0.288	1.62	<i>d</i>
0	1.2	0.824 ± 0.008	0.776–1.05	0.90	<i>f</i>
0	1.6	1.02 ± 0.02	0.920–1.30	0.92	<i>g</i>

down the decrease of rate constant with increasing electrolyte concentration, in some cases even the opposite effect being observed, *i.e.* an increase in the rate constant with increasing electrolyte concentration. The extent of manifestation of the specific effects for a given electrolyte depends on the nature of reactants. The rate constant values of seven oxidation-reduction reactions in the concentration interval of supporting electrolyte 1–4 mol l⁻¹ (Table II) agree with the empirical equation:

$$\ln k = \ln k_0 + S c_e, \quad (2)$$

where c_e is the concentration of added electrolyte. The slope S involves the specific interactions between electrolyte and solvent, and k_0 is the hypothetical rate constant. The linear dependences $\ln k = f(c_e)$ (Figs 2, 3) for the individual electrolytes converge in a relatively narrow interval of k_0 values, which indicates the fact that the extrapolation eliminates the specific effects of electrolytes to a considerable extent. The interval of scattering of the k_0 values of the individual reactions (Table I) is determined by experimental error and besides it can reflect some properties of electrolytes such as the nonadditivity of the contributions of cation and anion in the calculation of solvation numbers of various electrolytes due to their mutual cooperation¹². For the oxidations with H₂O₂ the rate constant of reaction in water, $k_{\text{H}_2\text{O}}$, also falls within the interval of k_0 values; for nonzero products of charge numbers $z_A z_B = -1, -2, -4$ the rate constants are $k_{\text{H}_2\text{O}} \approx 2k_0$, $k_{\text{H}_2\text{O}} \approx 3k_0$, $k_{\text{H}_2\text{O}} \approx 10k_0$, respectively. The hypothetical rate constant k_0 corresponds to the model reaction between the particles shielded by the electrical field

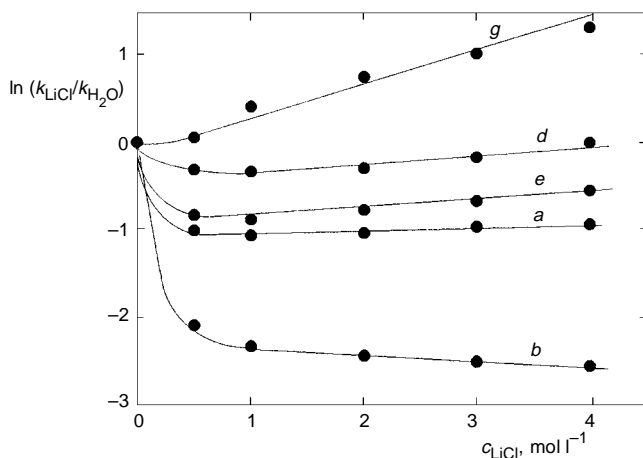


FIG. 1

Dependence of rate constant ratio $\ln(k_{\text{LiCl}}/k_{\text{H}_2\text{O}})$ on LiCl concentration in oxidations with S₂O₈²⁻ (reactions a, b), IO₄⁻ (d, e), and H₂O₂ (g). $c_{\text{HClO}_4} = 1 \text{ mmol l}^{-1}$, $T = 298.2 \text{ K}$

TABLE II
Dependence of oxidation rate constants on concentration c_e of uni-univalent electrolytes at 298.2 K

c_e , mol l ⁻¹	k , l mol ⁻¹ s ⁻¹					
	LiCl	NaCl	KCl	CsCl	NaNO ₃	NaClO ₄
Reaction <i>a</i> : [Co(en) ₂ SCH ₂ COO] ⁺ with S ₂ O ₈ ²⁻						
1	34.8 ± 0.4	28.6 ± 0.5		22.8 ± 0.5	30.7 ± 0.5	24.0 ± 0.5
2	35.6 ± 0.4	27.3 ± 0.6		14.4 ± 0.4	27.7 ± 0.4	20.3 ± 0.4
3	38.4 ± 0.4	25.7 ± 0.6		11.7 ± 0.3	25.9 ± 0.3	17.8 ± 0.4
4	38.9 ± 0.7	24.0 ± 0.4		7.8 ± 0.3	25.2 ± 0.3	15.2 ± 0.4
Reaction <i>b</i> : [Co(en) ₂ SCH ₂ CH ₂ NH ₂] ²⁺ with S ₂ O ₈ ²⁻						
1	23.2 ± 0.3	17.8 ± 0.4		14.0 ± 0.3	18.5 ± 0.5	15.3 ± 0.2
2	20.8 ± 0.5	15.2 ± 0.2		9.3 ± 0.3	15.3 ± 0.4	10.4 ± 0.2
3	19.4 ± 0.2	12.0 ± 0.2		6.9 ± 0.2	13.8 ± 0.2	7.3 ± 0.3
4	18.4 ± 0.3	10.4 ± 0.3		5.6 ± 0.2	12.0 ± 0.2	5.1 ± 0.3
Reaction <i>c</i> : [Co(en) ₂ SCH ₂ COO] ⁺ with IO ₄ ⁻						
1	433 ± 25	430 ± 8	299 ± 8		399 ± 7	339 ± 12
2	533 ± 37	442 ± 8	265 ± 9		376 ± 6	323 ± 6
3		496 ± 10	214 ± 7		387 ± 10	283 ± 11
4			371 ± 7			
Reaction <i>d</i> : [Co(en) ₂ SOCH ₂ COO] ⁺ with IO ₄ ⁻						
1	0.307 ± 0.015	0.275 ± 0.005			0.275 ± 0.005	0.275 ± 0.005
2	0.319 ± 0.004	0.282 ± 0.005			0.277 ± 0.003	0.277 ± 0.004
3	0.360 ± 0.005	0.316 ± 0.006			0.300 ± 0.005	0.251 ± 0.004
4	0.427 ± 0.012	0.345 ± 0.4			0.320 ± 0.006	0.267 ± 0.007
Reaction <i>e</i> : [Co(en) ₂ SOCH ₂ CH ₂ NH ₂] ²⁺ with IO ₄ ⁻						
1	0.427 ± 0.008	0.417 ± 0.010			0.429 ± 0.005	0.365 ± 0.010
2	0.472 ± 0.007	0.463 ± 0.006			0.449 ± 0.009	0.339 ± 0.004
3	0.521 ± 0.021	0.511 ± 0.006			0.479 ± 0.007	0.320 ± 0.011
4	0.587 ± 0.013	0.543 ± 0.007			0.493 ± 0.012	0.301 ± 0.008
Reaction <i>f</i> : [Co(en) ₂ SCH ₂ COO] ⁺ with H ₂ O ₂						
1	1.17 ± 0.01	1.10 ± 0.03		1.04 ± 0.03	1.00 ± 0.04	0.88 ± 0.02
2	1.75 ± 0.02	1.43 ± 0.03			1.18 ± 0.03	1.04 ± 0.03
3	2.36 ± 0.04	1.86 ± 0.05			1.55 ± 0.04	1.10 ± 0.02
4	3.12 ± 0.10	2.24 ± 0.06		1.00 ± 0.04	1.96 ± 0.05	1.20 ± 0.03

TABLE II
(Continued)

c_e , mol l ⁻¹	k , l mol ⁻¹ s ⁻¹					
	LiCl	NaCl	KCl	CsCl	NaNO ₃	NaClO ₄
Reaction g: [Co(en) ₂ SCH ₂ CH ₂ NH ₂] ²⁺ with H ₂ O ₂						
1	1.53 ± 0.02	1.46 ± 0.03	1.31 ± 0.03	1.27 ± 0.03	1.20 ± 0.04	1.02 ± 0.02
2	2.14 ± 0.04	1.78 ± 0.05	1.44 ± 0.04		1.42 ± 0.03	0.99 ± 0.02
3	2.77 ± 0.05	2.05 ± 0.03	1.61 ± 0.06		1.94 ± 0.02	1.11 ± 0.03
4	3.72 ± 0.07	2.23 ± 0.04		1.37 ± 0.04	2.50 ± 0.03	1.20 ± 0.03

Concentrations:

- a) [Co(en)₂SCH₂COO]⁺ = 5.7 μmol l⁻¹, S₂O₈²⁻ = 385 μmol l⁻¹
 b) [Co(en)₂SCH₂CH₂NH₂]²⁺ = 5.7 μmol l⁻¹, S₂O₈²⁻ = 385 μmol l⁻¹
 c) [Co(en)₂SCH₂COO]⁺ = 47 μmol l⁻¹, IO₄⁻ = 240 μmol l⁻¹
 d) [Co(en)₂SOCH₂COO]⁺ = 0.25 mmol l⁻¹, IO₄⁻ = 10 mmol l⁻¹
 e) [Co(en)₂SOCH₂CH₂NH₂]²⁺ = 0.2 mmol l⁻¹, IO₄⁻ = 8.8 mmol l⁻¹
 f) [Co(en)₂SCH₂COO]⁺ = 0.2 mmol l⁻¹, H₂O₂ = 4.93 mmol l⁻¹
 g) [Co(en)₂SCH₂CH₂NH₂]²⁺ = 0.2 mmol l⁻¹, H₂O₂ = 2.81 mmol l⁻¹,
 HClO₄ = 1 mmol l⁻¹

of ions of the supporting electrolyte. The k_{H_2O}/k_0 values correlate with the product of charge numbers, which supports the hypothesis of the role of electrostatic field of a concentrated electrolyte.

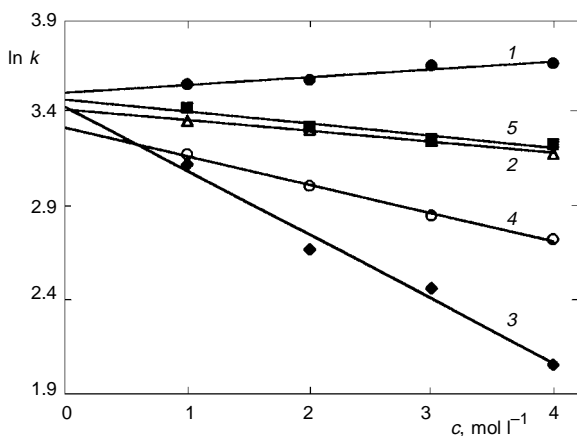


FIG. 2

Dependence of $\ln k$ on concentration of supporting electrolytes in reaction a, $c_{HClO_4} = 1$ mmol l⁻¹, $T = 298.2$ K; 1 LiCl, 2 NaCl, 3 CsCl, 4 NaClO₄, 5 NaNO₃

The effect of electrical field on a Cl^- ion surrounded by 213 water molecules was studied by the method of molecular dynamics¹³. The result of competitive action of ion field and outside field on solvent molecules is a reduction in the number of hydrogen bonds in the environment of ion, *i.e.* the number of water molecules in the primary solvation sphere of Cl^- ion is decreased to one half, and the energy of the other hy-

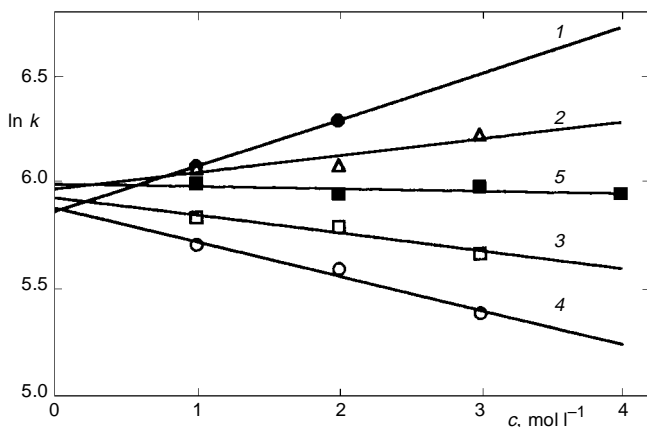


FIG. 3

Dependence of $\ln k$ on concentration of supporting electrolytes in reaction c , $c_{\text{HClO}_4} = 1 \text{ mmol l}^{-1}$, $T = 298.2 \text{ K}$; 1 LiCl, 2 NaCl, 3 KCl, 4 NaClO_4 , 5 NaNO_3

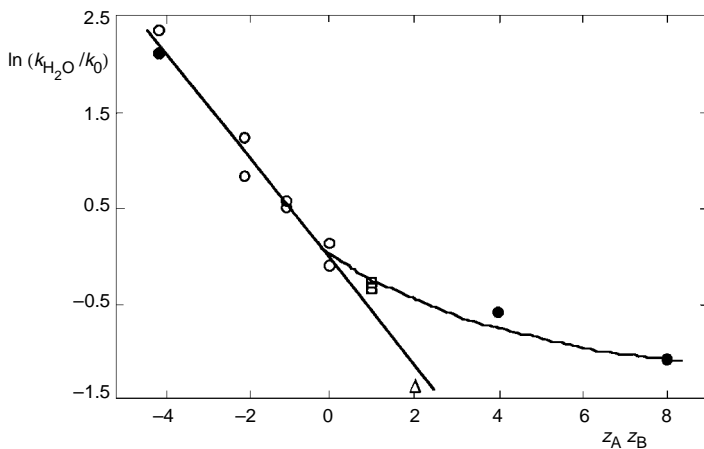


FIG. 4

Dependence of $\ln(k_{\text{H}_2\text{O}}/k_0)$ on product of charge numbers of reactants $z_A z_B$ at 298.2 K. ● oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ with $\text{S}_2\text{O}_8^{2-}$ ($z_A z_B = 8$) (ref.⁹), $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ with $\text{S}_2\text{O}_8^{2-}$ ($z_A z_B = 4$) (ref.⁸), $[\text{Fe}(\text{bipy})_3]^{2+}$ with $\text{S}_2\text{O}_8^{2-}$ ($z_A z_B = -4$) (ref.⁸); □ alkaline hydrolysis of methyl hydrogenphthalate and methyl hydrogenterephthalate ($z_A z_B = 1$) (ref.¹⁶); Δ $[\text{Ir}(\text{Cl})_6]^{2-}$ with Γ^- ($z_A z_B = 2$) (ref.¹⁵); ○ reactions: b ($z_A z_B = -4$), a , e ($z_A z_B = -2$), c , d ($z_A z_B = -1$), and f , g ($z_A z_B = 0$)

drogen bonds is increased, which leads to strengthening of the water structure as compared with the water structure in the absence of an outside electrical field. It is interesting to compare the manifestation of shielding effect of electrical field of ions of the supporting electrolyte in the reactions studied with that in reactions going by another mechanism. The k_0 values were calculated from Eq. (2) for the oxidation reactions of Fe(II) complexes with a charge of -4 (ref.⁹), -2 (ref.⁸) and $+2$ (ref.⁸) with $S_2O_8^{2-}$ (where the central atom is oxidized with concomitant electron transfer⁸), oxidation of I^- with $[Ir(Cl)_6]^{2-}$ (refs^{14,15}), as well as for alkaline hydrolyses of methyl hydrogenphthalate and methyl hydrogenterephthalate¹⁶ (which go by the B_{AC2} mechanism¹⁷). From the dependences $\ln(k_{H_2O}/k_0) = f(z_A z_B)$ (Fig. 4) it follows that the operation of shielding effect particularly depends on the charge of reactants, the specific effects being more significant in the reactions between ions of the same sign and greater value of product of charge numbers. Equation (2), which represents a first approximation to expressing the effect of concentrated solution of electrolyte on reaction rate, seems satisfactory in a number of reaction systems.

The manifestation of specific effects can be seen in Figs 2 and 3 where the slope S in Eq. (2) depends on the electrolyte used. Similar effects were observed also with other reactions studied (Table II). In the oxidations with H_2O_2 we observed an increase in the rate constant for all the electrolytes used (reactions f and g), in the oxidations with IO_4^- the rate constant only increased in the media of LiCl and NaCl (reactions c , d , e), and with $S_2O_8^{2-}$ only in LiCl (reaction a). The value of slope S decreased in the following series of alkali metal chlorides: $LiCl > NaCl > KCl > CsCl$. This order is identical with that of the Gibbs solvation energies of cations¹⁸ and that of viscosity coefficients B (refs^{19,20}) of the respective solutions (Fig. 5). The B coefficient reflects the extent of

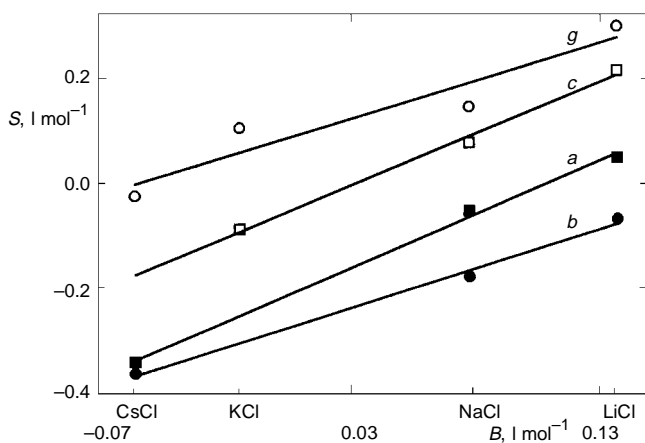


FIG. 5

Dependence of slope S on the Jones-Dole viscosity coefficient B for reactions a , b , c , g in media of concentrated solutions of alkali metal chlorides, $T = 298.2$ K

interactions between an electrolyte and solvent. The specific effect is the highest for the strongly solvated LiCl. The presence of ions in water results in its molecules being exposed to two competitive influences: first, the mutual influence of water molecules, and second, the influence of sterically symmetrical ion field, which is mainly significant with small ions or ions of higher charges²¹. Increasing concentration of electrolyte results in a considerable part of water molecules being engaged in the formation of solvation spheres of ions of the electrolyte, the concentration of free water molecules being decreased²². These changes bring about changes in solvations spheres of reactants and the activated complex, which influences the reaction rate. Other effects which can be expected in a concentrated electrolyte include the change in local acidity in the vicinity of ions due to polarization of water, the higher mobility of water molecules near K^+ and Cs^+ ions as compared with that near Na^+ due to increased population of bifurcated hydrogen bonds in the vicinity of large univalent ions²³. No correlation was found between $\Delta G_{\text{sol}}^{\ddagger}$ and B for the anions Cl^- , NO_3^- and ClO_4^- of the respective sodium salts. The anions differ in their numbers of atoms and geometries, which plays a decisive role in the interactions between the ion and solvent molecules.

The results found in the study of the effect of electrolytes in the concentration interval of 1–4 mol l⁻¹ have shown that the shielding effect of field of electrolytes as well as the structure of solvent modified by the supporting electrolyte bring about a change in kinetic behaviour of the reactants. At the electrolyte concentration of $c_{\text{LiCl}} > 4$ mol l⁻¹ the rate constant values do not obey Eq. (2), e.g. for reactions d and e the following values were measured: for $c_{\text{LiCl}} = 5$ mol l⁻¹ it was $k_d = 0.483 \pm 0.020$, $k_e = 0.938 \pm 0.016$ l mol⁻¹ s⁻¹; for $c_{\text{LiCl}} = 6$ mol l⁻¹ it was $k_d = 0.581 \pm 0.011$, $k_e = 1.41 \pm 0.05$ l mol⁻¹ s⁻¹. The effect of temperature on the reactions taking place in the presence and in the absence of electrolyte supports the idea about the role of solvent structure. In reactions f and g decreasing temperature increased the ratio of rate constants in 4 mol l⁻¹ LiCl and in water: $k_g(\text{LiCl})/k_g(\text{H}_2\text{O}) = 3.98_{298.2\text{K}}; 3.37_{308.8\text{K}}$; $k_f(\text{LiCl})/k_f(\text{H}_2\text{O}) = 3.84_{298.2\text{K}}; 3.47_{308.8\text{K}}$. Increasing temperature deteriorates the solvent structure due to increased thermal movements of water molecules and the effect of supporting electrolyte on solvent structure will be relatively smaller as compared with that at the lower temperature. This fact was also reflected in the change of the activation parameters upon transferring the reacting system from water to 4 mol l⁻¹ LiCl: $\Delta H_g^{\ddagger}(\text{H}_2\text{O}) = 36.5$, $\Delta H_g^{\ddagger}(\text{LiCl}) = 30.5$ kJ mol⁻¹, $\Delta S_g^{\ddagger}(\text{H}_2\text{O}) = -118$, $\Delta S_g^{\ddagger}(\text{LiCl}) = -131$ J K⁻¹ mol⁻¹, $\Delta H_f^{\ddagger}(\text{H}_2\text{O}) = 40.2$, $\Delta H_f^{\ddagger}(\text{LiCl}) = 36.0$ kJ mol⁻¹, $\Delta S_f^{\ddagger}(\text{H}_2\text{O}) = -111$, $\Delta S_f^{\ddagger}(\text{LiCl}) = -116$ J K⁻¹ mol⁻¹.

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