Kinetics of substitution of the *cis*-bis(ethylenediamine)dichlorocobalt(III) ion with thiocyanate ion in mixed solvents

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The kinetics of substitution of the chloride ion with the thiocyanate ion in the complex ion *cis*-$[Co(en)_2Cl_2]^+$ were investigated in the medium of methyl alcohol as well as in some mixed media consisting of methyl alcohol with isopropyl alcohol, dioxan, n-hexane, cyclohexane, and benzene. The reaction is governed prevailingly by electrostatic forces only in the mixtures methyl alcohol—n-hexane and methyl alcohol—benzene. In other investigated media, specific interactions between the components of the reaction system predominate.

Исследована кинетика замещения хлорид-иона в комплексном ионе *цис*-$[Co(en)_2Cl_2]^+$ тиоцианат-ионом в метаноле, а также в смесях метанола с изопропиловым спиртом, диоксаном, н-гексаном, циклогексаном и бензолом. Реакция управляется, главным образом, электростатическими силами лишь в смесях метанол — н-гексан и метанол — бензол. В остальных использованных средах преобладают специфические взаимодействия между компонентами реакционной системы.

The substitution of the coordinatively bonded chloride ion with the thiocyanate ion in the medium of methyl alcohol was investigated in a number of reactions (*A*) by *Brown* and *Ingold* [1].

$$cis\text{-}[Co(en)_2Cl_2]^+ + X^- \rightarrow [Co(en)_2ClX]^+ + Cl^- \qquad (A)$$

$X^- = NO_3^-, Cl^-, Br^-, SCN^-, NO_2^-, N_3^-, OMe^-$

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In contrast to aqueous solution where aquation takes place in the first step even in the presence of substitution agent, the immediate substitution of the chloride ion with other anionic ligands can be followed in methyl alcohol. According to paper [1], the substitution with the thiocyanate ion proceeds *via* the S_N1 mechanism with slow dissociation of the chloride ion as rate-determining step. Reaction (*A*) can proceed in two consecutive steps, but the substitution of the second chloride ion is considerably slower so that the first step may be investigated independently [1]. Because of a lower value of the relative permittivity of methyl alcohol in comparison with water, an increased influence of electrostatic interactions between reacting particles on the course of the reaction in this medium can be expected. The aim of our study was to investigate the first step of substitution of the chloride ion with the thiocyanate ion in mixed solvents consisting of methyl alcohol with organic cosolvent (isopropyl alcohol, benzene, n-hexane, cyclohexane, dioxan) from the point of view of the influence of medium on kinetic parameters of the reaction. The composition of the reaction medium was so chosen that it was possible to alter the relative permittivity by addition of relatively small amount of cosolvent, and also from the point of view of possible interactions between the molecules of the binary mixture which can be expected in the solvents with composition methyl alcohol—isopropyl alcohol, and methyl alcohol—dioxan.

Experimental

Cis-bis(ethylenediamine)dichlorocobalt(III) chloride was prepared as described earlier [2]. Sodium thiocyanate was anal. grade chemical. Isopropyl alcohol, dioxan, n-hexane, cyclohexane, and benzene which were also anal. grade chemicals were distilled before use. Anhydrous methyl alcohol was used for preparing the mixed solvents. The relative permittivity of the mixtures methyl alcohol—organic cosolvent was measured with a universal dielectrometer OH-301 (Radelkis, Budapest). Spectrally pure absolute methyl alcohol ($\varepsilon_r = 30.6$ at 313.2 K) was used as a standard. Absorption spectra of the reaction system were taken with a recording spectrophotometer Specord UV VIS (Zeiss, Jena). For kinetic measurements a manual spectrophotometer Spektromom 202 (MOM, Budapest) was used. The reaction took place in a closed thermostated vessel ($V = 150\ \text{cm}^3$) and the temperature was held constant within ±0.05 °C. The reaction was started by mixing the thermostated solutions of the complex salt and sodium thiocyanate which was in excess in the solution with respect to the complex. In the course of reaction the absorbance increased in the region $\lambda = 310$ nm as a consequence of the formation of the bis(ethylenediamine)isothiocyanato chlorocobalt(III) ion (Fig. 1). The rate constants were calculated from the changes measured at $\lambda = 307$ nm. In contrast to paper [1] the authors of which measured the

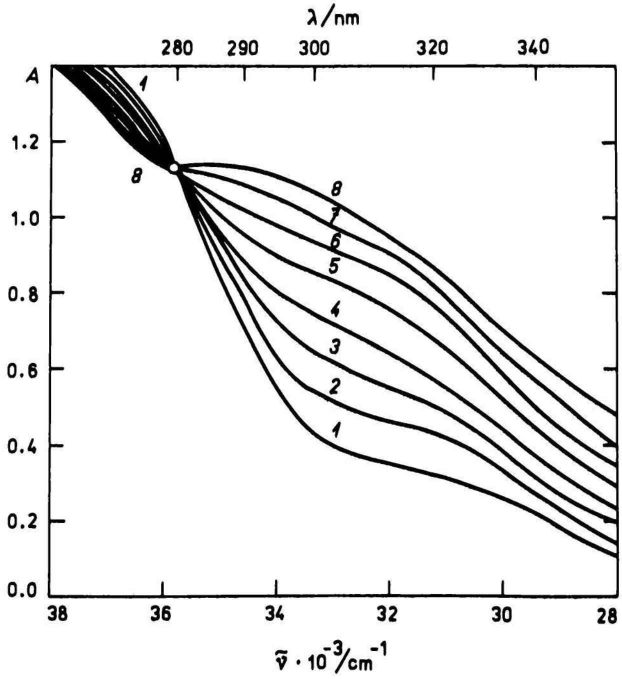

Fig. 1. Variation of absorbance with wavenumber and time for the reaction of the *cis*-$[Co(en)_2Cl_2]^+$ ion with the NCS^- ion in methyl alcohol. Concentrations of reactants as in Table 1.
1. Immediately after preparation of solution; *2.* 20 min, *3.* 40 min, *4.* 60 min, *5.* 100 min, *6.* 140 min, *7.* 200 min, *8.* 300 min after preparation of solution; temperature 40 °C, cell width 1.00 cm.

change in absorbance at $\lambda = 540$ nm where the *cis* and *trans* isomer have equal absorbance, we used for measurement the above-mentioned region of absorption of the thiocyanate ligand. This region of absorption is affected neither by configuration of the complex nor, in principle, by character of the central ion [3]. Under given experimental conditions, the reaction was of the first order and the rate constants were calculated by the *Guggenheim* method [4]. The relative error of independent measurements did not exceed 5 %.

Results and discussion

The values of experimental rate constants in the investigated mixed solvents are given in Table 1. All measurements were carried out at small values of mole fractions of cosolvents for which prevailing influence of the electrostatic effects of charged reactants and smaller influence of the specific nonelectrostatic interactions could be expected. The results of measurements, however, show that, in most cases,

Table 1

Experimental rate constants of the reaction of the *cis*-$[Co(en)_2Cl_2]^+$ ion with the thiocyanate io mixed medium methyl alcohol—organic cosolvent at 313.2 K

$c_{cis\text{-}[Co(en)_2Cl_2]Cl} = 3 \times 10^{-4}$ mol dm^{-3}, $c_{NaSCN} = 5 \times 10^{-3}$ mol dm^{-3}, x_2 = mole fraction of cosolvent

		$k\ 10^4/\mathrm{s}$	x_2		$k\ 10^4/\mathrm{s}^{-1}$
	Isopropyl alcohol			Cyclohexane	
0	30.6	1.18	0.062	27.0	1.38
0.027	29.7	1.39	0.086	25.5	1.48
0.055	28.8	1.50	0.111	23.8	1.50
0.085	27.9	1.43		n-Hexane	
0.117	27.0	1.40	0.016	29.8	1.21
0.150	26.1	1.34	0.033	28.6	1.22
	Dioxan		0.052	27.2	1.29
0.024	28.8	2.67	0.072	25.7	1.39
0.050	27.0	3.65	0.094	23.9	1.43
0.077	25.3	4.68		Benzene	
0.106	23.6	4.81	0.023	30.2	1.19
0.137	21.9	0.137	0.048	29.4	1.20
	Cyclohexane		0.074	27.9	1.26
0.019	29.6	1.20	0.102	25.5	1.39
0.040	28.4	1.37	0.131	23.4	1.43

the reaction rate significantly depends on the character of cosolvent, which is evidenced by the comparison of isodielectric mixtures (Fig. 2). Furthermore, it is obvious from Fig. 2 that the reaction is predominantly governed by electrostatic

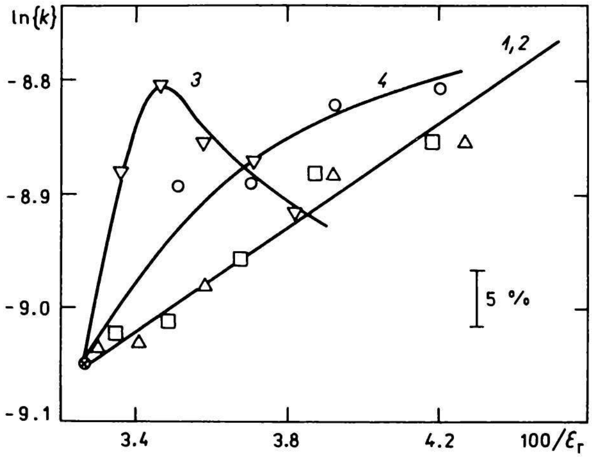

Fig. 2. Logarithm of rate constant as a function of the reciprocal value of relative permittivity of solvent. *1, 2.* Mixture methyl alcohol—n-hexane (squares) and methyl alcohol—benzene(triangles); *3.* methyl alcohol—isopropyl alcohol; *4.* methyl alcohol—cyclohexane. For other data see Table 1.

forces only in the mixtures methyl alcohol—benzene and methyl alcohol—n-hexane where eqn (*1*) expressing the dependence of the rate constant of ionic reaction on the relative permittivity of medium is fulfilled in the limits of experimental error, *i.e.* the relationship $\ln \{k\} = f(1/\varepsilon_r)$ is linear.

$$\ln \{k\} = \ln \{k_{\varepsilon_r=\infty}\} - \frac{z_A z_B e^2}{4\pi\varepsilon_0\varepsilon_r kTr_0} \qquad (1)$$

The symbols z_A, z_B, e, ε_0, k, T, and r_0 stand for charge numbers of reacting ions, electron charge, permittivity of vacuum, the Boltzmann constant, absolute temperature, and critical interionic distance of reacting ions, respectively. In harmony with electrostatic model, the experimental rate constant increases with decreasing relative permittivity because the ions with opposite electric charge react in the rate-determining step. The critical interionic distance calculated for the above-mentioned linear dependence by the method of least squares is 2.5 nm. This value is too high with respect to radii of the reacting ions. One of possible explanations of this fact is the assumption of the existence of anomalous saturation in strong electric fields of the reacting ions owing to which the value of relative permittivity increases [5]. In calculating the critical interionic distance, we inserted in eqn (*1*) the macroscopic values of ε_r. In the medium of isopropyl alcohol, a maximum appears on the plot $\ln \{k\} = f(1/\varepsilon_r)$ in the region of the mole fraction of cosolvent equal to 0.05 (Fig. 2). An addition of dioxan brought about the most pronounced increase in reaction rate (Table 1), while the experimental rate constant monotonously increased with the concentration of dioxan but the relation $\ln \{k\} = f(1/\varepsilon_r)$ was not linear even in this case. The molecules of the last two cosolvents are able to interact with the molecules of methyl alcohol not only in the solvate shell of the reactants and activated complex but also in the bulk of solution. The essence of this interaction is the intermolecular hydrogen bond. It is known that there are only few free nonassociated OH groups of methyl alcohol at the temperature of our experiments [6]. An addition of nonaqueous solvent can influence the degree of association and thus the ability of a solvent to solvate the reactants and activated complex. The relation between solvation and reactivity of ionic reactants in substitution reactions may be considered to be proved [7]. The cosolvents which are not able to form hydrogen bonds with methyl alcohol do not disturb the solvate shell of reactants and affect the reaction mainly by changing the relative permittivity of solvent.

By measuring the reaction rate in the temperature interval 308.2—328.2 K in the medium of methyl alcohol, we obtained the following values of thermodynamic activation parameters: $\Delta H^{\neq} = 110.4\ \text{kJ mol}^{-1}$ and $\Delta S^{\neq} = 44\ \text{J mol}^{-1}\ \text{K}^{-1}$. The value of activation energy corresponds to the values usually found for the substitution reactions of octahedral complexes involving the rupture of the bond between central atom and ligand [8]. The value of activation entropy is positive in agreement with electrostatic theory because it relates to a reaction between ions with opposite electric charges [9].

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