Solvent Effects on the Aquation of Chlorocobalt(III) Complexes: the Role of Nonlabile Ligand

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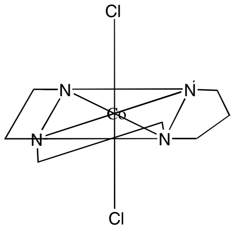
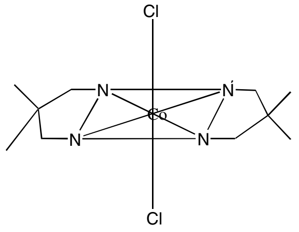
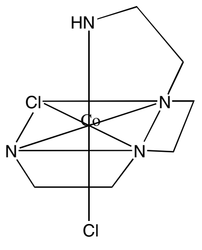
The aquation of *trans*-$[Co(me_2tn)_2Cl_2]^+$, β-*cis*-$[Co(trien)Cl_2]^+$, and *trans*-$[Co(2,2,3\text{-tet})Cl_2]^+$ has been investigated in aqueous mixtures of methanol, *tert*-butanol, acetonitrile, dimethyl sulfoxide, sulfolane, *N*-methyl-2-pyrrolidinone, ethylene carbonate, and urea, respectively, at 298.1 K. Results are discussed in terms of the importance of structure of aqueous binary mixtures in preferential solvation of complex ions and of size and hydrophobicity of the nonlabile ligands.



trans-$[Co(2,2,3\text{-tet})Cl_2]^+$



trans-$[Co(me_2tn)_2Cl_2]^+$



β-*cis*-$[Co(trien)Cl_2]^+$

Numerous papers have dealt with thermodynamic, spectroscopic, viscosimetric, dielectric, and other measurements of binary aqueous solutions with respect to the effect of cosolvents on the three-dimensional hydrogen-bonded structure of water. Cosolvent with hydrophobic and hydrophilic groups may cause: *1.* stabilization of the water structure due to the interaction between the hydrophobic groups and water (hydrophobic hydration) followed at a certain concentration by cluster forming due to hydrophobic interaction and *2.* destabilization of the water structure due to the interaction of the hydrophilic groups with the water (dipole-dipole interactions) [1]. The effect of cosolvent on the water structure should be predominantly reflected in the kinetics of aquation where one of the reactants is simultaneously a solvent. Previous studies [2, 3] of the aquation of $[CoN_4XY]^+$ ($N_4 = (NH_3)_4$, en_2; $Y = NO_2$, Cl; $X = Cl$) and of $[CoeddaCl_2]^-$ (edda = ethylenediamine-N,N'-diacetic acid, en = ethylenediamine) indicated the importance of hydrophobic effects in aqueous mixtures of alcohols but on the other hand, of ion-dipole interactions in aqueous mixtures of cosolvents having large dipole moment. The analysis of solvent effects by means of transfer Gibbs energy confirmed the decisive role of the reactant solvation on the reaction rate. In the aquation of bisethylenediamine Co(III) complex cation ion-dipole interaction resulted to some extent in preferential solvation of the complex ion by the cosolvent. This stabilization of the reactant led to the decrease in aquation rate. In the aquation of edda-Co(III) complex anion the addition of cosolvent caused the destabilization of the anion and thus consequently the increase in aquation rate (with the exception of urea). This opposite solvent effect on the aquation rate cannot be explained only by the negative charge on the edda complex ion as similar behaviour has been found in the aquation of $[Co(NH_3)_5CO_3]^+$ [4] and of *trans*-$[Copy_4Cl_2]^+$ (py = pyridine) [5—8]. It could be also accounted for by some difference in solvation of the complex ions. More information may result from investigating the aquation of complex ions solvated to various extent. The solvation of complex ion may be influenced by the large hydrophobic ligand or at least by expanding the chelate ring and by substitution of methyl groups on the carbon atoms of nonlabile multidentate ligand, *i.e.* of the ligand not involved in substitution reactions. In this work for the investigation of solvent effect on the aquation of so modified complex ions *trans*-$[Co(me_2tn)_2Cl_2]^+$, β-*cis*-$[Co(trien)Cl_2]^+$, and *trans*-$[Co(2,2,3\text{-tet})Cl_2]^+$ (me_2tn = 2,2-dimethylpropylenediamine, trien = N,N'-bis(2-aminoethyl)ethylenediamine (triethylenetetramine), 2,2,3-tet = N-(2-aminoethyl)-N'-(3-aminopropyl)ethylenediamine (1,4,7,11-tetraazaundecane)) had been chosen. The kinetics of aquation of these complex ions have been studied [9—11]. As found, the aquation of the isomers proceeds with total retention of configuration, accompanied by the loss of the chloride ligand.

EXPERIMENTAL

trans-[Co(me$_2$tn)$_2$Cl$_2$]Cl, *trans*-[Co(2,2,3-tet)Cl$_2$]-Cl and β-*cis*-[Co(trien)Cl$_2$]Cl were prepared as described previously [11—13] and their purities were checked by elemental analysis and electronic spectra [10, 11]. Ethylene carbonate (Merck) was purified by repeating freezing, the other solvents (Merck) were distilled before use. Urea (Merck) was used without further purification. The kinetics of aquation were followed spectrophotometrically (Specord M40, Zeiss, Jena) by measuring the absorbance at λ = 310 nm for *trans*-[Co(me$_2$tn)$_2$Cl$_2$]$^+$, λ = 250 nm for *trans*-[Co(2,2,3-tet)Cl$_2$]$^+$, and λ = 260 nm for β-*cis*-[Co(trien)Cl$_2$]$^+$.

The solubilities of *trans*-[Co(me$_2$tn)$_2$Cl$_2$]Cl and *trans*-[Co(en)$_2$Cl$_2$]ClO$_4$ in water and in 20 mass % EC were determined at 298.1 K. For rapid attainment of equilibrium between the solid phase and solution the ultrasonic generator Tesla UC 005 AJ 1 with output of 30 W at 50 kHz frequency was used. The duration of ultrasonic agitation was 300 s and after standing for 10 min the concentration was determined spectrophotometrically. The standard error in the solubility did not exceed 1 %. The estimation of transfer Gibbs energy of reactants was described earlier [14].

The rate constants were evaluated by the time lag method [15]. This method does not require the knowledge of the absorbance at the end of the reaction as the rate constant is calculated from the measured values of absorbance A_t at time t and $A_{t+\tau}$ at time $t + \tau$ as $k = -\dfrac{\ln|B|}{\tau}$ where B is the slope of the linear plot A_t *vs.* $A_{t+\tau}$ and the time interval τ is kept constant. To be sure that no reaction with cosolvent occurred, the visible spectra were also recorded throughout the reaction.

RESULTS AND DISCUSSION

The aquation of *trans*-[Co(me$_2$tn)$_2$Cl$_2$]$^+$, β-*cis*-[Co(trien)Cl$_2$]$^+$, and *trans*-[Co(2,2,3-tet)Cl$_2$]$^+$ was studied in aqueous mixtures of methanol (MeOH), *tert*-butanol (*t*-BuOH), acetonitrile (AN), dimethyl sulfoxide (DMSO), sulfolane (S), *N*-methyl-2-pyrrolidinone (NMP), ethylene carbonate (EC), and urea (U), respectively at 298.1 K. The rate constants for the studied aquation are listed in Table 1. The alcohols form typically aqueous mixtures (TA) with water ($T|S^{\mathrm{E}}| > H^{\mathrm{E}}$) and the other cosolvents used, for which $H^{\mathrm{E}} > T|S^{\mathrm{E}}|$, are classified as typically nonaqueous mixtures (TNA), *i.e.* the mixing is enthalpy-controlled [1]. Water and DMSO form typically nonaqueous mixtures (TNAN) with negative excess Gibbs energies, $G^{\mathrm{E}} < 0$, while AN, S, EC form with water typically nonaqueous mixtures (TNAP) with positive excess Gibbs energies, $G^{\mathrm{E}} > 0$. After initial strengthening of water structure in immediate vicinity of *t*-BuOH molecule due to hydrophobic hydration the formation of clusters with a micelle-like structure begins at a certain concentration. Recently the results of mass spectrometric analysis of aqueous binary mixtures provided the information on microscopic structure formed by clusters [16]. Unlike the alcohols, DMSO, S, and NMP are dipolar aprotic with large dipole moments and polarizabilities and are able to break the structure of water *via* strong dipole-dipole interactions. The urea in aqueous solutions behaves as a structure breaker.

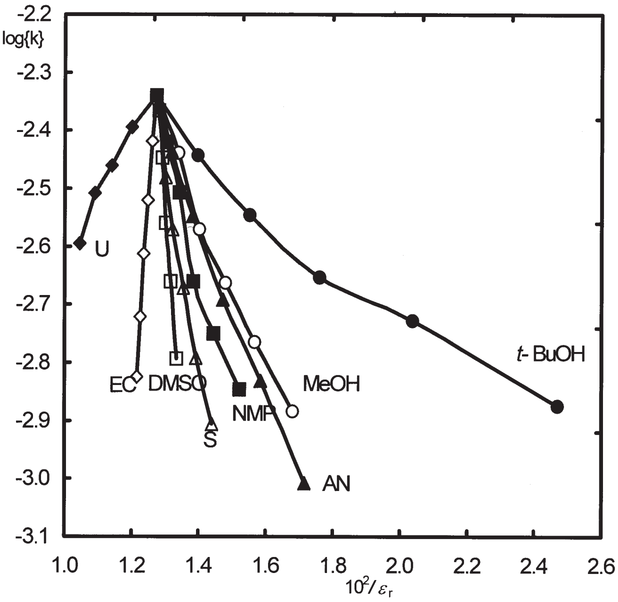


Fig. 1. Plots of log {k} *vs.* the reciprocal of the relative permittivity for the aquation of *trans*-[Co(me$_2$tn)$_2$Cl$_2$]$^+$ in mixed aqueous solvents at 298.1 K.

This different effect of solvents on the water structure seems to be reflected in the plots of $\log\{k\} = f(1/\varepsilon_{\mathrm{r}})$ for *trans*-[Co(me$_2$tn)$_2$Cl$_2$]$^+$ (Fig. 1), where $\{k\} \equiv k/\mathrm{s}^{-1}$. The reaction rate decreases with decreasing relative permittivity, ε_{r}, only in the H$_2$O—EC and H$_2$O—U mixtures the rate constants decreased with increasing ε_{r}. The effect of solvent on the aquation rate is the same in the aquation of β-*cis*-[Co(trien)Cl$_2$]$^+$ and *trans*-[Co(2,2,3-tet)Cl$_2$]$^+$ as well as of *trans*-[Co(en)$_2$Cl$_2$]$^+$ [17] and *trans*-[Co(NH$_3$)$_4$Cl$_2$]$^+$ [18]. For the series *trans*-[Co(en)$_2$-Cl$_2$]$^+$, *trans*-[Co(2,2,3-tet)Cl$_2$]$^+$, and *trans*-[Co(me$_2$tn)$_2$Cl$_2$]$^+$ the rates increased with increasing the size of the nonlabile ligands, but in spite of the expectations the exchange of ethylenediamine ligand

Table 1. Dependence of the Rate Constant on the Mole Fraction of Organic Solvent, x_2, for the Aquation of *a*) *trans*-$[Co(me_2tn)_2Cl_2]^+$: $c_{complex} = 5 \times 10^{-4}$ mol dm^{-3}, $c_{HClO_4} = 10^{-1}$ mol dm^{-3}, of *b*) *trans*-$[Co(2,2,3\text{-tet})Cl_2]^+$: $c_{complex} = 8 \times 10^{-4}$ mol dm^{-3}, $c_{HClO_4} = 10^{-2}$ mol dm^{-3}, and of c) *β*-*cis*-$[Co(trien)Cl_2]^+$: $c_{complex} = 6 \times 10^{-4}$ mol dm^{-3}, $c_{HClO_4} = 10^{-1}$ mol dm^{-3} in Mixed Aqueous Solvents at $T = 298.1$ K

x_2	a $10^3k/\mathrm{s}^{-1}$	b $10^3k/\mathrm{s}^{-1}$	c $10^3k/\mathrm{s}^{-1}$	x_2	a $10^3k/\mathrm{s}^{-1}$	b $10^3k/\mathrm{s}^{-1}$	c $10^3k/\mathrm{s}^{-1}$
0	4.569 ± 0.105	2.551 ± 0.050	1.383 ± 0.055				
MeOH				S			
0.046	3.642 ± 0.182	1.942 ± 0.041	1.282 ± 0.017	0.0114	3.308 ± 0.039	1.934 ± 0.012	
0.100	2.686 ± 0.053	1.557 ± 0.020	1.106 ± 0.026	0.020		1.671 ± 0.003	
0.160	2.171 ± 0.052	1.148 ± 0.033	0.926 ± 0.006	0.0253	2.688 ± 0.104	1.532 ± 0.034	
0.229	1.721 ± 0.047	0.943 ± 0.033	0.707 ± 0.019	0.0340	2.130 ± 0.038	1.148 ± 0.026	
0.306	1.306 ± 0.018			0.0519	1.617 ± 0.002	0.983 ± 0.016	
				0.0759	1.242 ± 0.004	0.848 ± 0.034	
t-BuOH				U			
0.021	3.604 ± 0.112	1.938 ± 0.040	1.278 ± 0.027	0.0323	4.033 ± 0.135	1.950 ± 0.049	1.341 ± 0.002
0.046	2.842 ± 0.076	1.502 ± 0.020	1.079 ± 0.010	0.0698	3.458 ± 0.111	1.616 ± 0.021	1.192 ± 0.010
0.076	2.218 ± 0.051	1.322 ± 0.014	0.803 ± 0.031	0.1139	3.108 ± 0.040	1.335 ± 0.031	1.067 ± 0.020
0.113	1.870 ± 0.025	1.364 ± 0.047	0.681 ± 0.015	0.1667	2.537 ± 0.042	1.052 ± 0.034	0.929 ± 0.013
0.160	1.336 ± 0.036	1.273 ± 0.057					
EC				NMP			
0.0222	3.819 ± 0.037	2.179 ± 0.066	1.349 ± 0.035	0.020	3.798 ± 0.046	1.684 ± 0.045	
0.0487	3.015 ± 0.047	1.853 ± 0.033	1.112 ± 0.024	0.043	3.116 ± 0.050	1.273 ± 0.023	
0.0806	2.439 ± 0.056	1.474 ± 0.002	0.945 ± 0.019	0.072	2.186 ± 0.064	0.956 ± 0.002	
0.120	1.901 ± 0.010	1.239 ± 0.013	0.773 ± 0.010	0.108	1.777 ± 0.074		
0.170	1.498 ± 0.012	1.095 ± 0.025		0.158	1.425 ± 0.062		
DMSO				AN			
0.0274	4.308 ± 0.074	1.859 ± 0.053	1.272 ± 0.043	0.037	3.661 ± 0.089	1.889 ± 0.015	1.385 ± 0.021
0.0596	3.568 ± 0.138	1.449 ± 0.045	1.064 ± 0.016	0.079	2.838 ± 0.069	1.492 ± 0.024	1.094 ± 0.027
0.0980	2.759 ± 0.032	1.117 ± 0.002	0.829 ± 0.023	0.129	2.032 ± 0.001	1.090 ± 0.011	0.838 ± 0.010
0.1446	2.186 ± 0.037	0.938 ± 0.027	0.645 ± 0.008	0.187	1.474 ± 0.046	0.792 ± 0.005	0.644 ± 0.018
0.2022	1.607 ± 0.036	0.591 ± 0.004		0.256	0.983 ± 0.004	0.656 ± 0.005	

Table 2. Rate Constants, k_{H_2O}, Solubilities, S, of Complexes in Water at 298.1 K, Transfer Gibbs Energies of Complex Ions, $\Delta G_t^o(M^+)$ into 20 mass % of EC and the Slope of $\log\{k\}$ *vs.* $(1/\varepsilon_r)$

	$10^4k/\mathrm{s}^{-1}$	$S/(\mathrm{mol\ dm}^{-3})$	$\Delta G_t^o(M^+)/(\mathrm{kJ\ mol}^{-1})$	$10^{-2}\ \mathrm{d}\log\{k\}/\mathrm{d}(1/\varepsilon_r)$
trans-$[Co(en)_2Cl_2]ClO_4$ [16]	0.377	0.0118	−4.31	6.0
trans-$[Co(2,2,3\text{-tet})Cl_2]Cl$	25.5			6.6
trans-$[Co(me_2tn)_2Cl_2]Cl$	45.7	0.2015	−4.60	8.4
trans-$[Co(NH_3)_4Cl_2]ClO_4$ [17]	21.4			6.3
α-*cis*-$[Co(trien)Cl_2]ClO_4$ [3]	1.64	0.066	−5.03	4.8
β-*cis*-$[Co(trien)Cl_2]ClO_4$	13.8			5.8
cis-$[Co(en)_2Cl_2]ClO_4$ [16]	2.50			5.7

for larger ligand did not influence the sequence of the curves $\log\{k\}$ *vs.* $(1/\varepsilon_r)$. The increased hydrophobicity of ligand is reflected only at higher concentration of such a hydrophobic cosolvent as *e.g.* *t*-BuOH. In aqueous mixtures of EC, DMSO, and U, respectively, the ligand exchange results only in slight change of the slope of the plots. As shown recently [16], the microheterogeneity (molecular clustering) of DMSO—H_2O and AN—H_2O binary mixtures affects the preferential solvation of some hydrophobic solutes. The preferential solvation of complex ions by cosolvent and thus their stabilization are determining in the aquation rate of Co(III) complexes [1] but the modification of the nonlabile ligand in complex ions *trans*-$[CoN_4Cl_2]^+$ ($N_4 = (NH_3)_4$, en_2, 2,2,3-tet, $(me_2tn)_2$,) had not been sufficient to change the solvation. It is well-demonstrated by the aquation of complex ions in quasi-isodielectric H_2O—EC mixtures, where the electrostatic effects arising from the difference of relative permittivity of solvents may be negligible, that the transfer Gibbs energy $\Delta G_t^o(M^+)$ may result only from the ion-dipole and dispersion interactions as well as from the cavity formation. Negative values of $\Delta G_t^o(M^+)$ for the transfer into 20 mass % EC reflect the stabilization of the reactant due to preferential solvation by the cosolvent. Unfortunately the solubility of *trans*-$[Co(2,2,3\text{-tet})Cl_2]Cl$ and *β*-*cis*-$[Co(trien)Cl_2]Cl$ could not be determined due to rapid aquation, so the comparison of preferential solvation of both studied complex ions was impossible. The complexes with various nonlabile ligands differ much in solubilities (Table 2), yet the values of transfer Gibbs energy, $\Delta G_{\mathrm{t}}^{\mathrm{o}}$, differ slightly and therefore cannot affect to greater extent the plots of $\log\{k\}$ *vs.* $(1/\varepsilon_{\mathrm{r}})$. Probably only much more bulkier hydrophobic ligands could have greater effect on the plots.

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