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Effect of Dipolar Aprotic Solvents on the Aquation of *cis*- and *trans*-Chloronitrobis(ethylenediamine)-cobalt(III)

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The kinetics of aquation of *cis*- and *trans*-$[Co(en)_2(NO_2)Cl]^+$ were studied in aqueous mixtures of dipolar aprotic solvents over a range of temperatures.

Previous studies[2] of the aquation of $[CoN_4XY]^+$ $[N_4 = (NH_3)_4$, en_2; $Y = NO_2$, NH_3, H_2O, Cl; X = Cl, Br] in aqueous mixtures of alcohols indicated the importance of the hydrophobic effect while in aqueous mixtures of monoalkyl ethers of ethylene glycol (alkoxyethanols) the increasing importance of water–polar-group interactions on the aquation rate of *cis*- and *trans*-$[Co(en)_2(NO_2)Cl]^+$ has been proved.[3] To obtain more detailed information on dipole–dipole interactions the aquation of *cis*- and *trans*-$[Co(en)_2(NO_2)Cl]^+$ has been investigated in aqueous mixtures of dipolar aprotic solvents where the structure-breaking ability of a hydrophilic group owing to dipole–dipole interactions could be expected.

The aquation was studied in aqueous mixtures of acetonitrile (AN), dimethyl sulfoxide (DMSO), sulfolane (S) and *N*-methylpyrrolidone (NMP) over the temperature range 298.1–322.6 K. All cosolvents used form typically non-aqueous mixtures (TNA) with water. Water and DMSO form typically non-aqueous mixtures with negative excess Gibbs energies, G^E (TNAN), while AN, S and EC form, with water, typically non-aqueous positive mixtures, TNAP ($G^E > 0$). Unlike the alcohols, these cosolvents are hydrophilic and have the ability to break the structure of water *via* dipole–dipole interactions–the water molecules exposed to these interactions cannot participate in the 3D-structure.[5c,6,7]

This different effect of solvents on the structure of water seems to be reflected in the plots of log $k = f(1/\varepsilon_r)$ (Fig. 1). While the influence of alcohols indicates the importance of the hydrophobic effect, the effect of dipolar aprotic cosolvents on the aquation rate increased with their dipole moments (with the exception of DMSO).

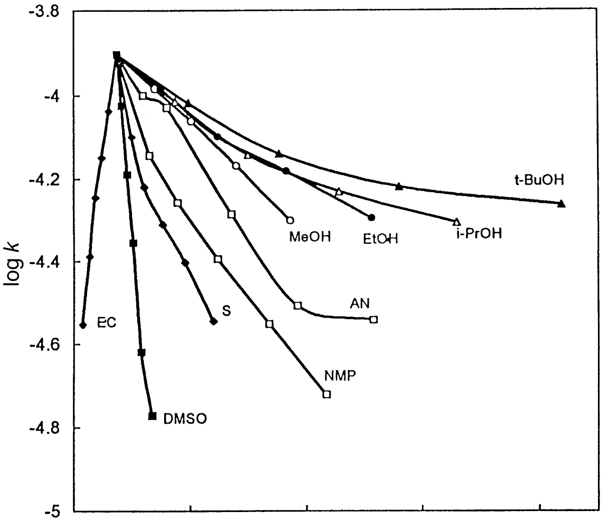

Fig. 1 Plots of log *k versus* the reciprocal of the relative permittivity for the aquation of *cis*-$[Co(en)_2(NO_2)Cl]^+$ in mixed aqueous solvents at 298.1 K

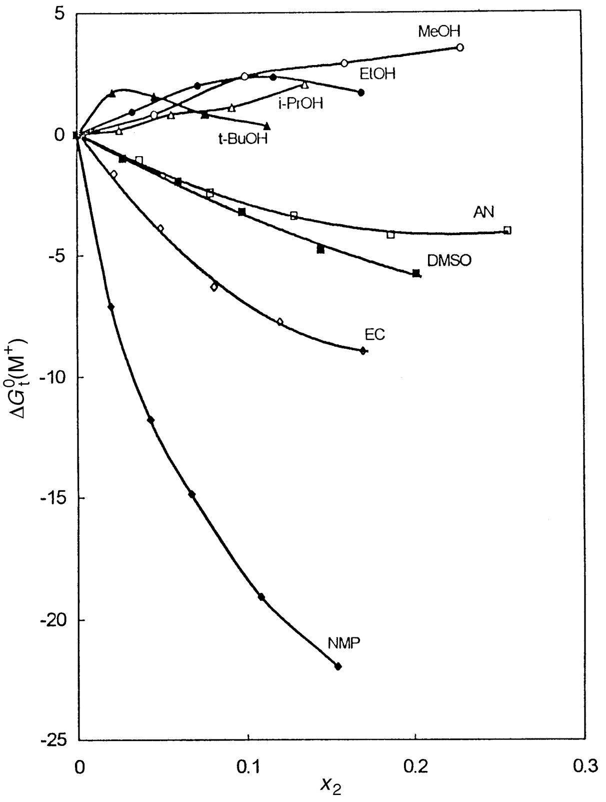

Fig. 3 Plots of the transfer Gibbs energies of *cis*-$[Co(en)_2(NO_2)Cl]^+$ *versus* mole fraction, x_2 of organic cosolvent at 298.1 K

The aquation rate is influenced not only by dipole–dipole interactions between molecules of water and cosolvent, but also by ion–dipole interactions, resulting in possible preferential solvation of the complex ion by the cosolvent. Information on solvation can be obtained from the dependence of the transfer Gibbs energy on the mole fraction of organic cosolvent (Fig. 3). The values of transfer Gibbs energy of the complex cation were estimated by the procedure reported elsewhere.[12] Chloride ion is preferentially solvated by water in aqueous mixtures of AN, DMSO, EC and NMP, the complex ions in *cis*- and *trans*-form are preferentially solvated by cosolvent, and both are stabilized to almost the same extent for a cosolvent concentration of up to 40% AN, DMSO and EC. The preferential solvation of the complex ion by cosolvent molecules influences the Co–NO_2 and Co–Cl bond polarity through strong ion–dipole interactions, and hence also affects the reaction rate.

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Techniques used: UV-VIS, spectrophotometry

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Table 1: Dependence of the rate constants on mole fraction of organic solvents and on temperature

Table 2: Dependence of activation enthalpy and activation entropy on the mole fraction of organic solvents

Table 3: Solubilities of salts in water and aqueous mixtures of organic solvents at 298.1 K

Table 4: Transfer Gibbs energies of complex ions, of transition state, of chloride and perchlorate ions

Fig. 2: Plots of log *k* *versus* the reciprocal of the relative permittivity for the aquation of *trans*-$[Co(en)_2(NO_2)Cl]^+$ in mixed aqueous solvents at 298.1 K

Fig. 4: Plots of the transfer Gibbs energies of *trans*-$[Co(en)_2(NO_2)Cl]^+$ *versus* mole fraction of organic cosolvent at 298.1 K

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