

Aquation of *cis*-diacetatobis(ethylenediamine)cobalt(III) ion in mixed aqueous-organic solvents

O. GRANČIČOVÁ and V. HOLBA

*Department of Physical Chemistry, Faculty of Natural Sciences,
Comenius University, CS-842 15 Bratislava*

Received 13 June 1989

Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday

Kinetics of aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion was investigated in the medium of NaCl, NaBr, and NaClO₄ as supporting electrolytes and in binary aqueous-organic solvents containing methanol, isopropyl alcohol, *tert*-butyl alcohol, acetonitrile, acetone, and dioxane as nonaqueous cosolvents. It has been found that the complex cation is associated with the Cl⁻, Br⁻, and ClO₄⁻ anions and the kinetic measurements were used for calculating the association constants. The dependence of thermodynamic transfer functions on mole fraction of the nonaqueous cosolvent was used for drawing conclusions related to the solvation of the initial and transition state of the investigated reaction.

Исследовалась кинетика аквакации иона *цис*-диацетатобис(этилендиамин)кобальта(III) в среде NaCl, NaBr и NaClO₄ как электролитов-носителей, а также в бинарных водно-органических растворителях с метиловым, изопропиловым, *трет*-бутиловым спиртами, ацетонитрилом, ацетоном и диоксаном как неводными компонентами. Было обнаружено, что происходит ассоциирование комплексного катиона с анионами Cl⁻, Br⁻ и ClO₄⁻ и на основании кинетических измерений были рассчитаны константы ассоциации. Исходя из зависимости термодинамических функций переноса от мольной доли неводного компонента смешанного растворителя сделан вывод о сольватации исходного и переходного состояния изучаемой реакции.

The ionic reactions in solution are often significantly influenced by solvent. The starting substances as well as the activated complex are solvated in the manner characteristic of reactants and used solvent of a given composition. The solvation affects the Gibbs activation energy and thus the reaction rate. The solvation, preferential solvation and some other effects in mixed solvents are in close relation with thermodynamic transfer functions, *i.e.* the Gibbs energy of transfer ΔG_i° , the transfer enthalpy ΔH_i° , the transfer entropy ΔS_i° , the transfer heat capacity ΔC_i° , and the transfer molar volume ΔV_i° [1—3]. The change in the Gibbs activation energy due to the transfer from water to a given mixture of solvents $\delta_m \Delta G^\ddagger$ may be related with the corresponding standard chemical

potentials of the activated complex, $\delta_m\mu^\ddagger$ and those of starting substances, $\delta_m\mu^0$ [4]. The dependence of these quantities on composition of the solvent enables us to come to a conclusion concerning the influence of the solvation of starting substances and activated complex on the course of an investigated reaction. This method was formerly used for examining the substitution and redox reactions of some coordination compounds [5].

The aquation of dicarboxylato complexes of the type $[\text{Co}(\text{OCOR})_2(\text{en})_2]^+$ ($\text{R} = \text{H}, \text{CH}_3, (\text{CH}_3)_3\text{CCH}_2, \text{CCl}_3, \text{C}_6\text{H}_5$) was previously studied with the aim to evaluate quantitatively the influence of polarity and steric effects of carboxylate ligands on thermodynamic and kinetic properties of complexes [6]. It has been found that the substitution of carboxylate ligands proceeds in two consecutive reactions and is catalyzed by the hydroxonium ions.

The aim of this study was to obtain experimental data relating to aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion in the medium comprising some supporting electrolytes and in mixed aqueous-organic solvents and on the basis of these data and thermodynamic transfer functions to analyze the influence of reaction medium on initial and transition state of the reaction.

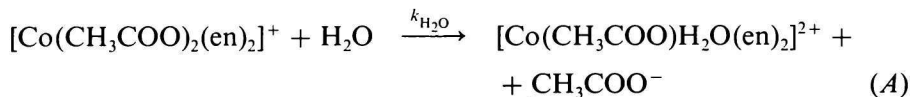
Experimental

cis-Diacetatobis(ethylenediamine)cobalt(III) perchlorate was prepared by the method described in literature [7]. The absorption spectrum of aqueous solution of the complex salt was consistent with the published data [8]. The redistilled water was used for preparing the aqueous-organic mixtures. Anal. grade chemicals, *i.e.* methyl alcohol, isopropyl alcohol, *tert*-butyl alcohol, acetone, acetonitrile, and dioxane were redistilled before use. The course of aquation was followed by measuring the change in absorbance at $\lambda = 510 \text{ nm}$ by using a colorimeter Spekol 10 which was connected with a recorder K 201 through an A. D converter TEC-1 (all instruments from Zeiss, Jena). The reaction mixture was put in a cell thermostated with precision $\pm 0.1 \text{ K}$. The rate constants were obtained by the Guggenheim method. The given values of rate constants are always the mean of four independent measurements.

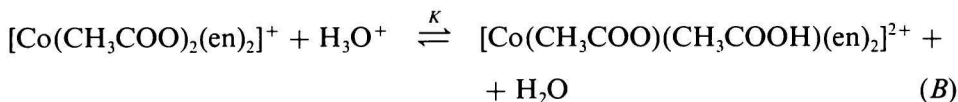
The solubility of *cis*- $[\text{Co}(\text{CH}_3\text{COO})_2(\text{en})_2]\text{ClO}_4$ at 298.1 K was determined by shaking the complex salt with solvent until the equilibrium was reached (3–4 h). Then a part of the solution was taken, centrifuged for 5 min at the number of revolutions 2000 min^{-1} , and diluted appropriately. The concentration was determined spectrophotometrically at $\lambda = 510 \text{ nm}$, the molar absorption coefficient of the complex being $12.48 \text{ m}^2 \text{ mol}^{-1}$. It was found that its value was constant for the used mixtures of solvents. The standard error of the determination of solubility was $\pm 1 \%$.

Results and discussion

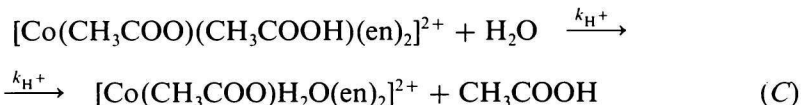
The course of the first stage of aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion in neutral medium may be described by the following scheme



At first a rapid preequilibrium is established in acid medium



Thus we may write for the reaction of the protonated form of the complex

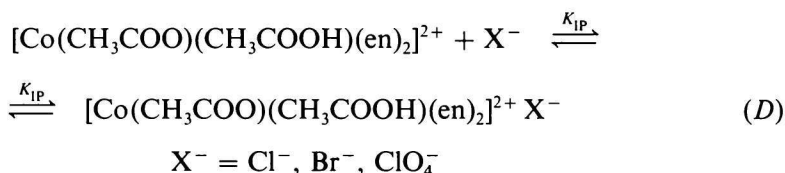


owing to which the following expression is valid for the experimental rate constant of aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion

$$k_{\text{exp}} = k_{\text{H}_2\text{O}} + k_{\text{H}^+} K [\text{H}_3\text{O}^+] \quad (\text{I})$$

The values of $k_{\text{H}_2\text{O}}$ are 100-times smaller than the values of k_{H^+} not only for water but also for the mixed media [9]. It is known that the ligands — anions of weak acids — of the Co(III) complexes are protonated in acid medium. On the basis of available data [10] we can come to the conclusion that the concentration of the non-protonated form of *cis*- $[\text{Co}(\text{CH}_3\text{COO})_2(\text{en})_2]^+$ was smaller than 1 % under our experimental conditions.

At the same time we have found that the experimental rate constant depends on concentration of the supporting electrolyte. The values of rate constant in the medium of sodium chloride, bromide, and perchlorate are given in Table 1. The rate constant increases with concentration of the supporting electrolyte, which indicates the formation of ionic pairs in the reaction system. The electrostatic reasons particularly suggest the association of the protonated form



Because of this fact, the investigated aquation involves two parallel reactions, *i.e.* reaction (C) and reaction of the ionic pair

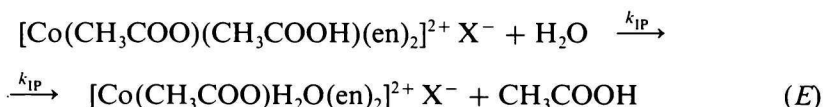


Table 1

Rate constants of aqution of $cis\text{-}[\text{Co}(\text{CH}_3\text{COO})_2(\text{en})_2]^+$ in the presence of different electrolytes
 $c(\text{complex}) = 4.16 \times 10^{-3} \text{ mol dm}^{-3}$, $c(\text{HClO}_4) = 9.9 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 298.2 \text{ K}$

c_{el} mol dm ⁻³	$10^3 \cdot k/\text{s}^{-1}$		
	NaCl	NaBr	NaClO ₄
0.1	1.61 ± 0.06	1.64 ± 0.01	1.57 ± 0.04
0.2	1.90 ± 0.03	1.92 ± 0.07	1.72 ± 0.01
0.4	2.26 ± 0.05	2.10 ± 0.05	2.08 ± 0.07
0.6	2.39 ± 0.10	2.34 ± 0.01	2.51 ± 0.11
0.8	2.76 ± 0.07	2.69 ± 0.03	2.79 ± 0.04

The association constant K_{IP} is given by the following expression

$$K_{\text{IP}} = \frac{[[\text{Co}(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})(\text{en})_2]^{2+} \text{X}^-]}{[[\text{Co}(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})(\text{en})_2]^{2+}][\text{X}^-] \gamma_1 \gamma_2} = K_{\text{c}}^{\text{IP}} \frac{1}{\gamma_2} \quad (2)$$

where γ_1 is activity coefficient of the complex and associate and γ_2 stands for activity coefficient of the anion of supporting electrolyte.

Thus it holds for the experimental rate constant

$$k_{\text{exp}} = \frac{k_{\text{H}^+} + k_{\text{IP}} K_{\text{IP}} \gamma_2 [\text{X}^-]}{1 + K_{\text{IP}} \gamma_2 [\text{X}^-]} \quad (3)$$

Eqn (3) enabled us to calculate the association constant K_{IP} and the rate constant k_{IP} of reaction (E). In all experiments the concentration of the complex was much lower than the concentration of the supporting electrolyte so that the difference between their analytical and equilibrium concentration was negligible. The value of the activity coefficient γ_2 was calculated from the extended Debye—Hückel relationship

$$\log \gamma_2 = - \frac{Az^2 I^{1/2}}{1 + BaI^{1/2}} + 0.1 z^2 \quad (4)$$

where I and z are the ionic strength and charge number of ion, respectively, A and B are the Debye—Hückel constants [11] and a is the contact distance for which the value of 0.4 nm [12] was used. The values of association constants are listed in Table 2 where the theoretical value of K_{IP} calculated according to the Bjerrum theory is also given [13]. In this calculation the best agreement of the theoretical value with the experimental one was achieved if the value of 0.4 nm was used as the distance of the closest approach of ions. It results from the table that the ionic pair containing the perchlorate ion is the most reactive. At the

Table 2

Association constants of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion and anions K_{IP} and rate constants of ionic pairs k_{IP} in water at 298.2 K

X^-	$10^3 \cdot k_{IP}/s^{-1}$	K_{IP}	$K_{IP}(\text{theor.})$
Cl^-	4.11	3.99	
Br^-	3.32	6.72	4.82
ClO_4^-	7.38	1.29	

Table 3

Rate constants of aquation of *cis*-[Co(CH₃COO)₂(en)₂]⁺ in mixed aqueous-organic solvents
 $c(\text{complex}) = 4.16 \times 10^{-3} \text{ mol dm}^{-3}$, $c(\text{HClO}_4) = 9.9 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 298.2 \text{ K}$

Solvent	Mole fraction $x_2(\text{solvent})$	$\frac{10^3 \cdot k}{s^{-1}}$	Solvent	Mole fraction $x_2(\text{solvent})$	$\frac{10^3 \cdot k}{s^{-1}}$
—		0.97 ± 0.01	i-PrOH	0.025	1.15 ± 0.04
				0.040	1.22 ± 0.00
MeOH	0.046	1.16 ± 0.01		0.056	1.14 ± 0.04
	0.100	1.27 ± 0.04		0.092	1.04 ± 0.04
	0.160	1.29 ± 0.06		0.136	0.99 ± 0.04
	0.229	1.32 ± 0.02		0.191	0.89 ± 0.03
Acetonitrile	0.037	1.08 ± 0.00	tert-BuOH	0.021	0.98 ± 0.03
	0.079	1.23 ± 0.04		0.046	1.04 ± 0.02
	0.128	1.21 ± 0.05		0.076	1.17 ± 0.04
	0.187	1.33 ± 0.05		0.113	0.99 ± 0.03
				0.161	0.69 ± 0.03
Dioxane	0.023	0.85 ± 0.01	Acetone	0.027	1.12 ± 0.00
	0.049	0.86 ± 0.03		0.058	1.36 ± 0.02
	0.082	1.02 ± 0.01		0.095	1.37 ± 0.03
	0.124	0.89 ± 0.01		0.134	1.32 ± 0.02
	0.174	0.63 ± 0.01			

same time, it is worth noticing that the perchlorate ion can produce changes in the hydration sphere of reactants and thus affect the rate of aquation [14]. The existence of nonelectrostatic factors is also evidenced by the fact that the kinetic method gives a greater value of the association constant for the ionic pair containing the Br^- ion than for the ionic pair containing the Cl^- ion though the associate with a smaller ion ought to be thermodynamically more stable according to the electrostatic theory.

Besides in aqueous medium, the aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion was also investigated in mixed aqueous-organic solvents; methyl alcohol, isopropyl alcohol, *tert*-butyl alcohol, acetone, acetonitrile, and dioxane being the nonaqueous components. The rate constants found in these media are given in Table 3. The nonmonotonous course of the plot of the logarithm of rate constant against mole fraction x_2 of the nonaqueous cosolvent (Fig. 1) and in some cases the different values, of rate constant in isodielectric mixtures indicate that the effect of the nonaqueous cosolvent is more complicated and cannot be interpreted only on the basis of a change in relative permittivity of medium. From the viewpoint of classification of solvents in typical aqueous and typical nonaqueous solvents [15], it is interesting that the relationship $\log k = f(x_2)$ exhibits practically identical course for water—methanol and water—acetonitrile solvents though these mixtures belong to different classes of solvents.

The influence of solvent on the initial and transition state was analyzed by means of the thermodynamic transfer functions $\delta_m\mu^\circ$ and $\delta_m\mu^\ddagger$. The change in the Gibbs activation energy due to the transfer from water into a mixed aqueous-organic solvent is given by the expression

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - \delta_m\mu^\circ(M^{2+}) \quad (5)$$

where $\delta_m\mu^\circ(M^{2+})$ is the transfer function of the protonated form of the complex $[\text{Co}(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})(\text{en})_2]^{2+}$ ion which prevails under given experimental conditions. The values of $\delta_m\mu^\circ(M^{2+})$ in the mixtures of water with methyl alcohol, *tert*-butyl alcohol, and acetone were obtained by combining the values

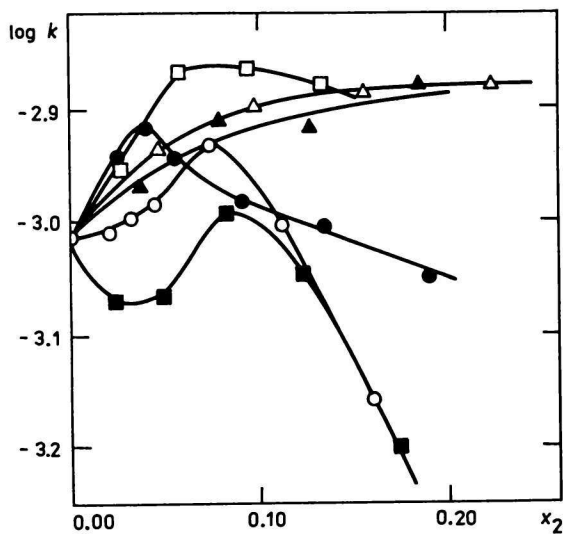


Fig. 1. Variation of $\log k$ with mole fraction x_2 of the nonaqueous cosolvent for aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion. $c(\text{complex}) = 4.16 \times 10^{-3} \text{ mol dm}^{-3}$, $c(\text{HClO}_4) = 9.9 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 298.2 \text{ K}$.

△ Methyl alcohol, ● isopropyl alcohol, ○ *tert*-butyl alcohol, □ acetone, ▲ acetonitrile, ■ dioxane.

Table 4

Solubilities S , Gibbs energy (kJ mol^{-1}) of transfer of complex ion $\delta_m\mu^\circ(\text{M}^{2+})$ and of transition state $\delta_m\mu^\ddagger$, and Gibbs activation energy $\delta_m\Delta G^\ddagger$ for aquation of $\text{cis}[\text{Co}(\text{CH}_3\text{COO})_2(\text{en})_2]^+$ in mixed aqueous-organic solvents at 298.2 K

$x_2(\text{solvent})$	$\frac{S}{\text{mol dm}^{-3}}$	$\delta_m\mu^\circ(\text{M}^+)$	$\delta_m\mu^\circ(\text{H}^+)$	$\delta_m\mu^\circ(\text{M}^{2+})$	$\delta_m\Delta G^\ddagger$	$\delta_m\mu^\ddagger$
0	1.700					
MeOH						
0.046	1.578	0.42	0.27	0.69	-0.44	0.25
0.098	1.506	0.55	0.41	0.96	-0.67	0.29
0.160	1.384	0.92	0.44	1.36	-0.71	0.65
0.229	1.312	1.38	0.35	1.73	-0.76	0.97
<i>tert</i> -BuOH						
0.021	1.732	0.27	1.15	1.42	-0.03	1.39
0.046	1.575	0.07	0.35	0.42	-0.17	0.25
0.076	1.406	-0.71	-1.45	-2.16	-0.46	-2.62
0.113	1.257	-1.37	-2.85	-4.22	-0.05	-4.27
Acetone						
0.027	1.750	-0.54	-1.48	-2.02	-0.36	-2.38
0.058	1.785	-1.14	-3.23	-4.37	-0.84	-5.21
0.095	1.711	-1.63	-5.34	-6.97	-0.86	-7.83
0.134	1.651	-2.25	-7.45	-9.71	-0.76	-10.47

of the transfer functions of ClO_4^- , H^+ , and Cl^- calculated from the published data [16—21] with the values of the transfer function of *cis*-diacetatobis(ethylenediamine)cobalt(III) perchlorate ($\delta_m\mu^\circ(\text{complex})$)

$$\delta_m\mu^\circ(\text{M}^{2+}) = \delta_m\mu^\circ(\text{complex}) - \delta_m\mu^\circ(\text{ClO}_4^-) + \delta_m\mu^\circ(\text{H}^+) \quad (6)$$

The value of $\delta_m\mu^\circ(\text{complex})$ was calculated from the measured solubilities of $[\text{Co}(\text{CH}_3\text{COO})_2(\text{en})_2]\text{ClO}_4$ (Table 4) by using the equation

$$\delta_m\mu^\circ(\text{complex}) = 2RT \ln \frac{S_0}{S_{x_2}} \quad (7)$$

where S_0 and S_{x_2} are solubilities of the complex salt in water and in a given mixed solvent, respectively. Eqn (7) is valid on the assumption that the ratio of activity coefficients of the complex salt in the used solvents is equal to one. The values of the transfer functions are given in Table 4. It results from this table that the influence of methanol on solvation of the reactant and of the activated complex

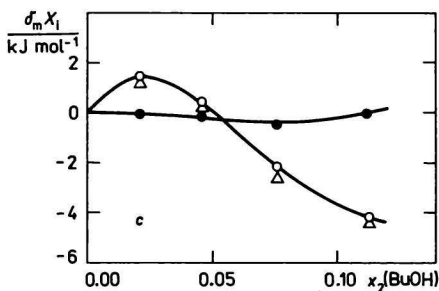
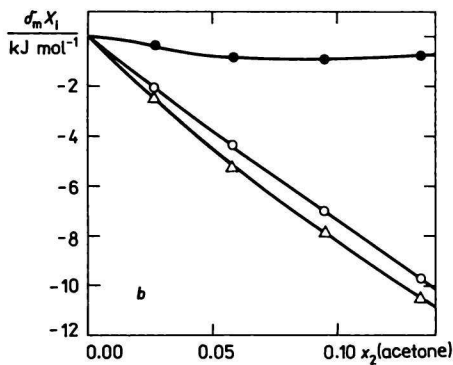
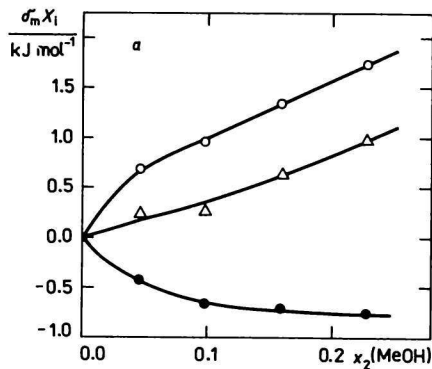


Fig. 2. Aquation of the *cis*-diacetatobis(ethylenediamine)cobalt(III) ion in mixtures: water—methyl alcohol (a), water—acetone (b), water—*tert*-butyl alcohol (c) at 298.2 K. Dependence of the transfer parameters on solvent composition x_2 .

○ $\delta_m \mu^{\circ}(\text{M}^{2+})$, △ $\delta_m \mu^{\ddagger}$, ● $\delta_m \Delta G^{\ddagger}$.

in the investigated concentration interval is much smaller than the influence of *tert*-butyl alcohol and acetone. In addition, the investigated cosolvents differ from each other in their stabilizing or destabilizing effect on the initial and transition state. In the mixture water—methanol the starting complex ion as well as the activated complex is destabilized (the corresponding transfer functions in Fig. 2a are positive) and the increase in rate constant accompanying the increase in mole fraction of methanol is a consequence of a greater destabilization of the complex ion when compared with the activated complex. In the water—acetone mixture the complex ion as well as the activated complex is stabilized and the change in rate constant results from a greater stabilization of the activated complex (Fig. 2b). The transfer functions $\delta_m \mu^{\circ}(\text{M}^{2+})$ and $\delta_m \mu^{\ddagger}$ for the mixture water—*tert*-butyl alcohol exhibit a maximum (Fig. 2c). If the content of the nonaqueous component is low, a destabilization of the complex ion as well as of the activated complex appears while both species are stable at higher content of that component. However, the differences are too small and do not allow interpreting the change in rate constant.

The use of thermodynamic transfer functions gives a more detailed information about the influence of medium on the investigated reaction. As far as the

ionic reactants are concerned, the result, to a great extent, depends on extrathermodynamic assumptions. It appears that the assumption of equal value of the contribution of cation and anion to the Gibbs transfer energy of tetraphenylarsonium tetraphenylborate (assumption TATB) is a good basis for obtaining correct values of the transfer functions of individual ions.

References

1. Arnett, E. M., Bentrude, W. G., Burke, J. J., and McDuggleby, P. C., *J. Am. Chem. Soc.* **87**, 1541 (1965).
2. Golivkin, H. S., Lee, I., and Hynes, J. B., *J. Am. Chem. Soc.* **89**, 1307 (1967).
3. Menninga, L. and Engberts, J. B. F., *J. Org. Chem.* **41**, 3101 (1976).
4. Blandamer, M. J. and Burgess, J., *Coord. Chem. Rev.* **31**, 93 (1980).
5. Holba, V. and Grančičová, O., *Chem. Listy* **79**, 449 (1985).
6. Carunchio, V., Messina, A., and Ortaggi, G., *Ann. Chim.* **64**, 111 (1974).
7. Linhard, M. and Stirn, G., *Z. Anorg. Allg. Chem.* **268**, 105 (1952).
8. Carunchio, V., Illuminati, G., and Ortaggi, G., *Inorg. Chem.* **6**, 2168 (1967).
9. Grančičová, O., unpublished results.
10. Laird, J. L. and Jordan, R. B., *Inorg. Chem.* **21**, 855 (1982).
11. Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions*, p. 468. Butterworths, London, 1970.
12. Nightingale, E. R., *J. Phys. Chem.* **63**, 1381 (1959).
13. Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry*, p. 257. Plenum Press, New York, 1970.
14. Arnett, E. M., in *Physico-Chemical Processes in Mixed Aqueous Solvents*. (Franks, F., Editor.) P. 105. Heinemann, London, 1967.
15. Franks, F., in *Hydrogen Bonded Solvent System*. (Covington, A. K. and Jones, P., Editors.) P. 31. Taylor and Francis, London, 1968.
16. Abraham, M. H., Hill, T., Ling, H. C., Schulz, R. A., and Watt, R. A. C., *J. Chem. Soc., Faraday Trans. 1* **80**, 489 (1984).
17. Smits, R., Massart, D. L., Juillard, J., and Morel, J.-P., *Electrochim. Acta* **21**, 431 (1976).
18. Basu Mullick, I. N. and Kundu, K. K., *Indian J. Chem., A* **23**, 812 (1984).
19. Vollárová, O. and Benko, J., *J. Chem. Soc., Dalton Trans.* **1983**, 2359.
20. Feakins, D., Hickey, B. E., Knox, M., McCarthy, P. J., Waghorne, E., and Clune, T. A., *J. Chem. Soc., Faraday Trans. 1* **84**, 4219 (1988).
21. Blandamer, M. J., Briggs, B., Burgess, J., Guardado, P., Radulović, S., and Hubbard, C. D., *J. Chem. Soc., Faraday Trans. 1* **84**, 1243 (1988).

Translated by R. Domanský