The effect of ionic strength
on alkaline hydrolysis and on catalyzed and spontaneous aquation of pentaamminebromocobalt(III) ion

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In the present work the influence of the ionic strength on the rate and thermodynamic activation parameters of the alkaline hydrolysis, of the aquation catalyzed by mercury(II) ions and of the spontaneous aquation of the pentaamminebromocobalt(III) ion are investigated. The measured values are confronted with theoretical relations for the primary salt effect and with the results obtained in previous works.

The substitution reactions of the pentaamminebromocobalt(III) ions were investigated in several works [1—9]. Special attention was paid to the alkaline hydrolysis [4—9]

$$[CoBr(NH_3)_5]^{2+} + OH^- \rightarrow [Co(OH)(NH_3)_5]^{2+} + Br^- \qquad (A)$$

especially with regard to the ionic strength and to the effect of added electrolytes on the reaction rate [8]. As an example for a reaction between two ions with identical charge the aquation of pentaamminebromocobalt(III) ion catalyzed by mercury(II) ions was taken, for which the following stoichiometric equation is valid

$$2[CoBr(NH_3)_5]^{2+} + Hg^{2+} + 2H_2O \rightarrow 2[Co(H_2O)(NH_3)_5]^{3+} + HgBr_2. \qquad (B)$$
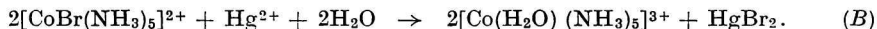
This is a second-order reaction [4]. A third, frequently described type of reaction of the pentaamminebromocobalt(III) ion is its spontaneous aquation [1—6]

$$[CoBr(NH_3)_5]^{2+} + H_2O \rightarrow [Co(H_2O)(NH_3)_5]^{3+} + Br^-. \qquad (C)$$
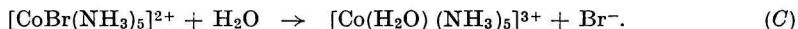
Reactions (A) and (B) were used as models for verification of the validity of the Brönsted—
—Bjerrum theory of ionic reactions [4], as well as an example for systems in which deviations from the law of ionic strength may be observed and, moreover, new interpretation of the observed phenomena was offered (*Olson—Simonson* effect) [5, 8]. Relatively little attention was devoted to the activation parameters of these reactions. The aim of the present work is the investigation of the joint effect of temperature and ionic strength on the reaction rate of the reactions (A—C).

Experimental

Pentaamminebromocobalt(III) bromide was prepared by the procedure reported in [10].

For [CoBr(NH₃)₅]Br₂ (383.83) calculated: 62.4% Br, 18.26% N, 3.94% H; found: 62.6 and 62.9% Br, 18.1 and 18.2% N, 3.9 and 4.1% H.

The bromide was transformed to perchlorate by precipitation from its saturated solution with perchloric acid and by recrystallization of the formed perchlorate.

For $[CoBr(NH_3)_5](ClO_4)_2$ (422.92) calculated: 13.93% Co; found: 13.8 and 14.1% Co.

The extinction coefficient of the aqueous salt solution at the wavelength of the peak of the first charge-transfer band (at 253 nm) was $17.4 \times 10^3 \, mol^{-1} \, cm^{-1}$. Mercury(II) perchlorate was prepared by the procedure described by [5]. Sodium perchlorate was prepared by neutralization of perchloric acid and sodium hydroxide of anal. grade and by allowing the formed salt to thicken and to crystallize. Purification was achieved by recrystallization. For the preparation of the reaction mixture carbonate-free sodium hydroxide was used. This was prepared by allowing the saturated solution of the commercially available reagent grade substance (Lachema, Brno) to boil for several hours under reflux. Redistilled water was used for the preparation of all solutions. All three reactions were investigated spectrophotometrically by recording SF-8 (USSR) spectrophotometer with which the changes of transmittance at 253 nm were recorded. Since the reactions (A) and (B) are fairly rapid under given experimental conditions, a thermostatting block to be used with the spectrophotometer was constructed and connected with an ultrathermostat into which the cell containing a part of the reaction mixture was placed and the required temperature was adjusted with the accuracy of $\pm 0.05°C$. In the second part of the apparatus the required amount of the hydroxide solution which had been injected into the cell at the beginning of the experiment, was heated to the same temperature and thus the whole reaction was started. Owing to this arrangement reactions having halftime of 15 s could be studied. A similar procedure was applied for the investigation of the reaction (B); into the cell containing the complex solution the solution of mercury(II) perchlorate was injected. In distinction to the reactions (A) and (B) the reaction (C) is considerably slower. In this case the reaction mixture was placed in an ultrathermostat, from which at appropriate time intervals samples were transmitted into a spectrophotometer cell and without delay their transmittance was measured. Sodium hydroxide, mercury(II) perchlorate, and water were in a great excess with regard to bromide and pentaamminebromocobalt(III) perchlorate; and the course of the investigated reactions was of pseudo-first order. For the calculation of the rate constants the equation [11] was used

$$2.303 \log \Delta A = -kt + \text{const}, \qquad (1)$$

where ΔA is the difference of absorbances in the time t and t', $t - t'$ being the constant time interval. The measured time dependences obeyed very well the equation (1). The relative error of the rate constant was in most cases within the range of 0.9 to 2.6%. With regard to this accuracy and to the accuracy with which the constant temperature was maintained in the course of individual measurements, the error of the activation energy [12] can be estimated to make 2—3%.

Results and discussion

Reaction $[CoBr(NH_3)_5]^{2+} + OH^-$

The alkaline hydrolysis of the pentaamminebromocobalt(III) ion was investigated in the temperature range between 18.1 and 33.5°C and in the interval of the ionic strength of 0.0026 to 0.0126 mol l^{-1}. The results of these measurements are listed in Table 1. The constants of second order were calculated from the experimental values of the pseudo-

Table 1

Dependence of the rate constant of the alkaline hydrolysis
of pentaamminebromocobalt(III) ion on ionic strength μ and on temperature
3.78×10^{-5} M-$[CoBr(HN_3)_5](ClO_4)_2$, 2.58×10^{-3} M-NaOH

μ [mol l^{-1}]	t [°C]	k [l mol^{-1} s^{-1}]	μ [mol l^{-1}]	t [°C]	k [l mol^{-1} s^{-1}]
0.0026	18.1	2.44	0.0026	30.2	13.8
0.0046	18.1	2.35	0.0046	30.2	13.4
0.0066	18.1	2.09	0.0066	30.2	13.2
0.0086	18.1	2.07	0.0086	30.2	12.6
0.0126	18.1	1.93	0.0126	30.2	11.9
0.0026	25.0	6.66	0.0026	33.5	23.2
0.0046	25.0	6.59	0.0046	33.5	22.0
0.0066	25.0	6.27	0.0066	33.5	20.6
0.0086	25.0	5.89	0.0086	33.5	19.6
0.0126	25.0	5.54	0.0126	33.5	18.8

-first order rate constants (Table 1) by dividing the experimental values by the concentration of the hydroxide. For the calculation of constants extrapolated to zero ionic strength the quantity of log k_0', defined in [13, 14], was taken

$$\log k_0' = \log k - \frac{2Az_A z_B \mu^{1/2}}{1 + \mu^{1/2}}, \qquad (2)$$

where for the product of charges $z_A z_B$ the value -2 was substituted and for the constant A its theoretical value that results from the Debye—Hückel theory was taken [15]. Under the given experimental conditions (a mixture of electrolytes), the dependence of the experimental rate constant on the ionic strength may be expressed by the equation

$$\log k = \log k_0 + \frac{2Az_A z_B \mu^{1/2}}{1 + \mu^{1/2}} + B\mu, \qquad (3)$$

from which k_0 and B were calculated as variable parameters. Combining the equations (2) and (3) we get

$$\log k_0' = \log k_0 + B\mu. \qquad (4)$$

Table 2

Values of the activation energy E_A^0, of the frequency factor A^0, of the probability factor P^0, and of the activation entropy $\Delta S_0^{\ddagger}$ of the alkaline hydrolysis of pentaamminebromocobalt(III) ion extrapolated to zero ionic strength

E_A^0 [kcal mol^{-1}]	A^0 [s^{-1}]	P^0 [mol l^{-1}]	$\Delta S_0^{\ddagger}$ [cal mol^{-1} K^{-1}]
25.60	5.87×10^{19}	2.93×10^8	18

According to this expression $\log k_0'$ should be a linear function of the ionic strength. Since the measured values are in agreement with the conditions of the equation (4), it was possible to determine the values of k_0 and B at various temperatures, and on the basis of the dependence of k_0 on temperature, the extrapolated values of thermodynamic activation parameters (Table 2) could be calculated. As it was found in [8], the equation (4) holds for the reaction (A) measured at 25°C up to the relatively high concentrations of various electrolytes, the coefficient B being equal to zero, i.e. $\log k_0' \equiv \log k_0$. This was confirmed also by our measurements at lower temperatures. At the temperature of 33.5°C, however (as it may be seen from Table 1), the coefficient B diverges from zero more than an experimental error would account for. In this case the equation (4) will have the form

$$\log k_0' = 1.463 \pm 0.005 + (1.38 \pm 0.68)\,\mu. \tag{5}$$

(The regression coefficients and their errors were calculated by least-square method.) The applied experimental technique does not allow to perform the measurements at higher temperatures at which it could be proved whether, in principle, the value of coefficient B increases with temperature in perchlorate medium.

From the extrapolated values of rate constants the extrapolated values of thermodynamic activation parameters were calculated (Table 2). In the given case the relation [16] between the extrapolated value of the probability factor P^0 and the critical interionic distance r_0 is valid

$$\log P^0 = \frac{8.56}{r_0}, \tag{6}$$

according to which $r_0 = 1.01$ Å. Calculations performed by the same method yield, when the data reported in [4] and [9] are taken, the value of 1.36 Å [16] and 0.86 Å respectively. Comparison with analogous reactions justifies the conclusion that the values $r_0 \approx 1$ Å are too low for the investigated system. This may be explained by the fact that the equation (6) has only an approximative validity for more complicated ions, since, in deriving this equation, the interaction between the hydroxide ion and the dipole moments of ligands of the complex ion has not been taken into account, though this may significantly contribute to the value of P^0 [17]. From the rate constants at various temperatures and ionic strengths, the dependence of activation energy on ionic strength may be derived, for which Moelwyn—Hughes wrote the equation

$$E_A = E_A^0 + 800\,z_A z_B \mu^{1/2} \text{ cal mol}^{-1} \tag{7}$$

which is valid at temperatures round 25°C. According to the equation (7), in the investigated interval of ionic strengths the activation energy should decrease by 98 cal mol^{-1} ($z_A z_B = -2$). The values of activation energies, calculated from Table 1 lie within the range from 25.6 to 26.3 kcal mol^{-1}. This is only a slightly greater interval than the estimated error of the experimental value of E_A. In the interval under investigation, the activation energy seems to increase with the ionic strength, instead of the expected decrease. The value of the rate constant at 25°C is similar to the value reported in [4] at a comparable ionic strength (0.0026 mol l^{-1}). The difference in the extrapolated value (8.69 l mol^{-1} s^{-1} at 25°C), when compared with the values reported in some previous works (7.4 and 6.20 l mol^{-1} s^{-1} reported by [9] and [18]), can be accounted for by the fact that the above-cited authors changed the ionic strength by changing the concentration of the initial substances without adding further electrolyte. As it was shown [19],

when the dependence of log k_0' on ionic strength is used, the extrapolated value of the rate constant may depend on the electrolyte that had been added with the aim of adjusting the ionic strength. The value of the entropy of activation $\Delta S_0^{\ddagger}$ is in good agreement with conclusions of the simple electrostatic theory, according to which with the aid of the relation $\Delta S^{\ddagger} \approx -10\, z_A z_B$ the sign and a gross estimation of the numerical value of this parameter may be found [20].

Reaction $[CoBr(NH_3)_5]^{2+} + Hg^{2+}$
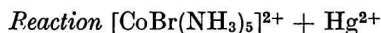
For the investigation of the catalyzed aquation of pentaamminebromocobalt(III) ion the reaction mixture was prepared from the following substances: pentaamminebromocobalt(III) bromide, mercury(II) perchlorate, and perchloric acid. The ionic strength was adjusted with sodium perchlorate. The reaction was studied in the range of 12.4 to 33.6°C and in the ionic strength interval from 0.00712 to 0.03712 mol l⁻¹. Results of these measurements are shown in Table 3. From these data the values of experimental activation energy at individual ionic strengths were calculated. These vary from 12.1 kcal mol⁻¹ ($\mu = 0.03712$ mol l⁻¹) to 13.3 kcal mol⁻¹ ($\mu = 0.00712$ mol l⁻¹); this difference (1.2 kcal) exceeds considerably the experimental error. According to the equation (7) the activation energy of the reaction (B) should increase with ionic strength, and in the given interval this increase should make 320 cal. The decrease that was actually observed may be explained by the fact that the above values represent an apparent activation energy in which the temperature dependence of the dissociation constant of mercury(II) perchlorate is included. It has been shown [21] that the mercury(II) perchlorate is a weak electrolyte and under the given conditions the $HgClO_4^+$ ion predominates in the solution. A supporting evidence for this is given also by the value of the slope of dependence $\log k_{exp} = f(\mu^{1/2})$ which is practically linear and for which at 15°C we obtain $d(\log k_{exp})/d(\mu^{1/2}) = 2.7$. This value is nearer to the product of the

Table 3

Dependence of the rate constant of the aquation of pentaamminebromocobalt(III) ion, catalyzed by mercury(II) ions, on ionic strength μ and on temperature
4.0×10^{-5} M-$[CoBr(NH_3)_5]Br_2$, 2.0×10^{-3} M-$Hg(ClO_4)_2$, 1.0×10^{-3} M-$HClO_4$

μ [mol l⁻¹]	t [°C]	$k \cdot 10^3$ [s⁻¹]	μ [mol l⁻¹]	t [°C]	$k \cdot 10^3$ [s⁻¹]
0.00712	16.2	4.24	0.01712	29.4	15.68
0.00712	18.1	5.12	0.01712	32.0	18.20
0.00712	19.6	5.32	0.02712	14.8	6.55
0.00712	20.0	5.70	0.02712	18.8	8.93
0.00712	22.0	6.85	0.02712	21.1	10.42
0.00712	24.2	8.17	0.02712	24.2	12.96
0.00712	25.9	8.87	0.02712	27.4	16.17
0.00712	28.1	9.80	0.02712	32.4	23.06
0.00712	30.0	12.37	0.03712	12.4	6.20
0.00712	33.6	16.05	0.03712	15.2	7.51
0.01712	14.7	5.34	0.03712	15.7	7.88
0.01712	18.0	6.98	0.03712	26.2	16.34
0.01712	22.0	8.87	0.03712	28.3	19.34
0.01712	26.4	12.56	0.03712	30.0	21.18

charges $z_A z_B = +2$ than to the value of $+4$ which is expected in the reaction of the complex ion with the Hg^{2+} ion. When comparing the results reported by [5] where also mercury(II) perchlorate was used, similar conclusions may be drawn.

Reaction $[CoBr(NH_3)_5]^{2+} + H_2O$

Spontaneous aquation of the pentaamminebromocobalt(III) ion was studied in 0.005 M-$HClO_4$ between $30-60°C$, in the ionic strength interval from 0.0051 to 1.0051 mol l^{-1}. The activation energy measured at various ionic strength values within this interval changed but slightly round the value of 23 kcal mol^{-1} and these changes were well within the limits of experimental error. It has been shown, however, that the reaction rate changes considerably with the ionic strength adjusted by adding sodium perchlorate. In the given interval of ionic strengths the reaction rate decreased by 25% at 60°C. This result is interesting from the viewpoint of the electrostatic theory of reactions of ion—dipole type. According to this theory [22] for the rate constant we may write

$$\log k_{\varepsilon_r,\mu} = \log k_{\varepsilon_r,0} + K \frac{z_A m_B \mu \cos \vartheta}{\varepsilon_r^2 T^2} , \qquad (8)$$

where ε_r is the relative dielectric permittivity of the medium, z_A is the charge of the reacting ion, m_B is the dipole moment of the second reacting component, ϑ is the angle between the vector of the dipole moment and the line connecting the centre of the dipole and the ion, T is the absolute temperature, K is a constant. According to the relation (8) there is a linear dependence of the logarithm of the rate constant of the reaction ion— dipole on ionic strength. As it may be seen from Fig. 1, the dependence of the experimental rate constant on the ionic strength is actually linear. A prediction of the orientation of the dipole with regard to the ion, and consequently a prediction of the sign of the dependence, is extremely difficult in the given case, since, as the reacting dipoles there are the molecules of the solvent by which the reacting ion is solvated. The reacting ion itself consists of an ionic part (central ion) and of dipoles (ligands). Electrolytes, as it is well known, affect the structure of the solvent (water) which is caused by the existence of hydrogen bonds and thus they may influence the orientation of molecules of the solvent with regard to the reacting ions. Especially perchlorate, which was used in the discussed case, is known for its considerable influence on the structure of water [23, 24].
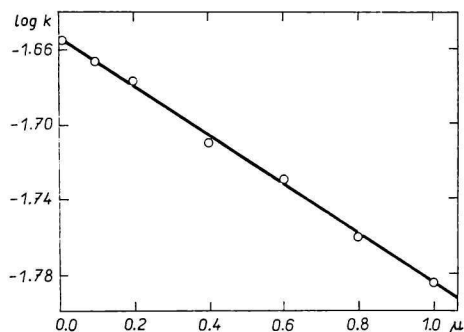

Fig. 1. Dependence of the experimental rate constant of the spontaneous aquation of the pentaamminebromocobalt(III) ion on ionic strength.
4.26×10^{-5} M-$[CoBr(NH_3)_5]Br_2$,
5.0×10^{-3} M-$HClO_4$, 60.0°C.
Ionic strength was adjusted by additions of sodium perchlorate.

References

1. Lamb, A. B. and Marden, J. W., *J. Amer. Chem. Soc. 33*, 1873 (1911).
2. Lamb, A. B. and Fairhall, L. T., *J. Amer. Chem. Soc. 45*, 378 (1923).
3. Freundlich, H. and Bartels, R., *Z. Phys. Chem. 101*, 177 (1922).
4. Brönsted, J. N. and Livingston, R., *J. Amer. Chem. Soc. 49*, 435 (1927).
5. Olson, A. R. and Simonson, T. R. *J. Chem. Phys. 17*, 1167 (1949).
6. Adamson, A. W. and Basolo, F., *Acta Chem. Scand. 9*, 1261 (1955).
7. Davies, C. W. and Williams, I. W., *Trans. Faraday Soc. 54*, 1547 (1958).
8. Perlmutter-Hayman, B. and Weissman, Y., *J. Phys. Chem. 68*, 3307 (1964).
9. Davies, M. B. and Lalor, G. C., *J. Inorg. Nucl. Chem. 31*, 799 (1969).
10. *Inorganic Synthesis*, I. (Booth, H. S., Editor.) P. 186. McGraw-Hill, New York, 1939.
11. Guggenheim, E. A., *Phil. Mag. 2*, 538 (1926).
12. Benson, S. W., *The Foundations of Chemical Kinetics*, p. 59. (Russian translation.) Mir, Moscow, 1964.
13. Bell, F., Gill, R., Holden, D., and Wynne-Jones, W. F. K., *J. Phys. Colloid Chem. 55*, 874 (1951).
14. Guggenheim, E. A. and Prue, J. E., *Physicochemical Calculations*, p. 450. (Russian translation.) Izd. inostrannoi literatury, Moscow, 1958.
15. Robinson, E. A. and Stokes, R. H., *Electrolyte Solutions*, p. 541. (Russian translation.) Izd. inostrannoi literatury, Moscow, 1963.
16. Moelwyn-Hughes, E. A., *The Kinetics of Reactions in Solution*, p. 90. Clarendon Press, Oxford, 1947.
17. Lalor, G. C. and Moelwyn-Hughes, E. A., *J. Chem. Soc. 1963*, 1560.
18. Chan, S. C., Hui, K. Y., Miller, J., and Tsang, W. S., *J. Chem. Soc. 1965*, 3207.
19. Indelli, A., *Israel J. Chem. 9*, 301 (1971).
20. Laidler, K. J., *Chemical Kinetics*, p. 134, McGraw-Hill, New York, 1950.
21. Davies, C. W., *Progress in Reaction Kinetics*, I. (G. Porter, Editor.) P. 161. Pergamon Press, Oxford, 1961.
22. Jungers, J. C., *Chemická kinetika*. (Chemical Kinetics.) P. 358. Publishing House of the Czechoslovak Academy of Sciences, Prague, 1963.
23. Walrafen, G. E., *J. Chem. Phys. 52*, 4176 (1970).
24. Subramanian, S. and Fisher, H. F., *J. Phys. Chem. 76*, 84 (1972).

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