KINETICS OF AQUATION OF BROMOPENTAAMMINECHROMIUM(III) AND BROMOPENTAAMMINECOBALT(III) IONS IN WATER-ALCOHOL SOLVENTS

Vladislav HOLBA and Oľga GRANČIČOVÁ
Department of Physical Chemistry,
Comenius University, 816 50 Bratislava

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The rate constants and activation parameters of aquation of bromopentaamminechromium(III) and bromopentaamminecobalt(III) ions were determined in mixtures of water with methanol, ethanol, 2-propanol, and tert-butyl alcohol. A compensation effect was observed in the first three mixtures and the isokinetic temperature was determined. The rate constants were correlated with the ionizing strength of the solvent. The influence of interactions between the water and alcohol molecules on the reaction kinetics is discussed.

In studying the reaction kinetics of coordination compounds in solution, an increasing attention has been paid in recent years to the influence of the solvent. Many useful informations have been obtained mainly by studying the reactions in mixed solvents[1]. In determining the mechanism, correlations of the rate constant with the dielectric constant of the solvent or with functions derived by linear free energy relations[2,3] are studied. The values of the rate constants and thermodynamic activation parameters can be related with quantities characterizing the structure of the mixed solvent[1,4].

The aquation of bromopentaamminechromium(III) and bromopentaamminecobalt(III) ions is among the first reactions whose kinetics has been studied in detail[5,6]. With respect to the values of the rate constants and activation parameters, these reactions can be followed by common experimental methods and confronted with physico-chemical relations that are valid for ionic reactions. The aim of the present work was to accumulate experimental data about the course of the mentioned reactions in water–alcohol mixtures and on the basis of these data to judge the role of the solvent in aquation, whose mechanism is in the cases of both mentioned complexes different.

EXPERIMENTAL

Bromopentaamminechromium(III) bromide was prepared according to Mori[7] and purified by recrystallization. The chromium content calculated for the formula $[Cr(NH_3)_5Br]Br_2$ (376·9) is 13·79%, found 14·1%. Bromopentaamminecobalt(III) bromide was prepared according to ref.[8], recrystallized and converted to perchlorate by precipitating its solution with a saturated solution of sodium perchlorate. The cobalt content calculated for the formula $[Co(NH_3)_5Br](ClO_4)_2$ (422·9) is 13·93%, found 13·9%. Perchloric acid (Merck, Darmstadt) and hydrochloric acid (Lachema, Brno) were of reagent grade. Water–alcohol mixtures were prepared from redistilled water and methanol, ethanol, 2-propanol (Lachema, Brno), tert-butyl alcohol (Reanal, Budapest) of reagent grade. The latter two alcohols were distilled prior to use.

The kinetics of aquation of the bromopentaamminechromium(III) ion was followed by measuring the transmittance at a wave length of 240 nm, at which the complex has a molar absorption coefficient of 1 403 $dm^3 mol^{-1} cm^{-1}$. The transmittance increased in the course of the reaction, which was measured directly in a tempered cuvette of a recording spectrophotometer of the type SF-8 (LOMO, Leningrad). In studying the kinetics of aquation of the $[Co(NH_3)_5Br]^{2+}$ ion, a chosen solution of perchloric acid was placed into the thermostat and after attainment of the chosen temperature a measured volume of a freshly prepared solution of the complex salt was added. Samples were taken during the reaction and after cooling their absorbancy was measured. In this case a spectrophotometer of the type MOM 202 (Budapest) was used. The absorbancy decreased in the ultraviolet region as measured at 253 nm, *i.e.*, at the maximum of the first charge transfer band with a molar absorption coefficient equal to $1·74 . 10^4 dm^3 mol^{-1} cm^{-1}$. The temperature of the reaction mixture was maintained constant with an accuracy of ±0·05°C. The rate constants were calculated from the measured changes of the absorbancy by Shank's method[9]. Their indicated values are averages from four independent measurements and their relative error did not exceed 3%.

RESULTS AND DISCUSSION

The values of the rate constants of aquation of $[Cr(NH_3)_5Br]^{2+}$ and $[Co(NH_3)_5 . . Br]^{2+}$ ions at various temperatures and mole fractions of alcohols are summarized in Tables I and II. The curves illustrating the dependence of the logarithm of rate constant on the mole fraction of the alcohol (Fig. 1*a*, *b*) show mostly a discontinuity

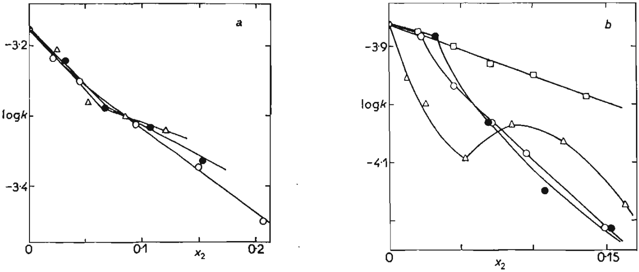

FIG. 1

Dependence of Logarithm of Rate Constant of Aquation on Mole Fraction of Alcohol

a $3·7 . 10^{-4}$M-$[Cr(NH_3)_5Br]^{2+}$, $1 . 10^{-3}$M-HCl, 40·3°C; *b* $3·9 . 10^{-5}$M-$[Co(NH_3)_5Br]^{2+}$, $5 . 10^{-3}$M-$HClO_4$, 50·1°C. ○ Methanol, ● ethanol, △ 2-propanol, □ tert-butyl alcohol, ⊗ water.

at a certain mole fraction; in the case of aquation of the cobalt complex the curve passes through a minimum and a maximum in mixtures of 2-propanol with water. The following equation was derived from the electrostatic model for the dependence of the rate constant on the dielectric constant, ε_r, of the solvent[10]:

$$\log k_{\varepsilon_r} = \log k_{\infty} + Zep/k_B T r^2 \varepsilon_r\,, \qquad (1)$$

where Ze is the charge of the reacting ion, p dipole moment, r distance ion-dipole, k_B Boltzmann's constant, T absolute temperature, k_{ε_r} rate constant, k_{∞} same at an infinitely large dielectric constant. Eq. (1), which is valid for ion-dipole reactions[10], does not fit the measured dependences. The dependence of the logarithm of the rate constant on the reciprocal value of the dielectric constant was not even in a single case linear. The studied reactions are obviously controlled by specific interactions between molecules of the solvent components. All the alcohols used have one property in common: they form with water so-called typically aqueous solvents, *i.e.*, solvents whose excess free enthalpy, ΔG^E, is given mainly by the entropic term, hence

TABLE I

Rate Constants for Aquation of Bromopentaamminechromium(III) Ion ($3{\cdot}7 \cdot 10^{-4}$M) in Water–Alcohol Medium

Mole fraction of alcohol x_2; $c_{HCl} = 1 \cdot 10^{-3}$M.

t, °C	x_2	10^4k, s^{-1}	t, °C	x_2	10^4k, s^{-1}
	methanol		40·3	0·0685	5·70
			40·3	0·1085	4·82
31·9	0·0957	1·78	40·3	0·1532	4·32
32·1	0·2068	1·39	50·0	0·0685	15·2
40·3	0·0225	6·05	50·0	0·1532	13·0
40·3	0·0449	5·61			
40·3	0·0957	4·86		2-propanol	
40·3	0·1491	4·23			
40·3	0·2068	3·55	32·3	0·0529	2·04
50·0	0·0957	13·2	32·0	0·1207	1·71
50·0	0·2068	10·1	40·0	0·0249	6·23
			40·0	0·0529	5·25
	ethanol		40·0	0·0845	4·99
			40·0	0·1207	4·78
32·0	0·0685	2·13	50·0	0·0529	15·1
32·3	0·1532	1·59	50·0	0·1207	14·4
40·3	0·0325	6·02			

$|T\Delta S^E| > |\Delta H^E|$. It is known about such mixtures that their nonaqueous component influences characteristically the degree of association of water[11]. At lower concentrations of the alcohol, its "structure making" effect comes into play, since the alcohol molecules occupy interstitial positions in the network of associated water molecules and thus stabilize the water structure. After surpassing a certain concentration, the alcohol interferes with the hydrogen bond between water molecules and a "structure

TABLE II

Rate Constants for Aquation of Bromopentaamminecobalt(III) Ion (3·9 . 10^{-5}M) in Water–Alcohol Medium

Mole fraction of alcohol x_2; c_{HClO_4} = 5 . 10^{-3}M.

t, °C	x_2	10^5k, s^{-1}	t, °C	x_2	10^5k, s^{-1}
	methanol			2-propanol	
40·5	0·0705	3·32	40·3	0·0529	3·02
40·5	0·2068	2·07	40·5	0·1207	2·90
44·8	0·0705	5·56	44·8	0·0529	4·75
44·9	0·2068	3·53	44·9	0·1207	4·42
50·1	0·0225	13·1	50·1	0·0121	11·0
50·1	0·0449	10·7	50·1	0·0249	9·98
50·1	0·0705	9·3	50·1	0·0529	8·04
50·1	0·0957	8·2	50·1	0·0845	9·21
50·1	0·1491	6·1	50·1	0·1207	8·64
50·1	0·2068	5·9	50·1	0·1623	6·70
55·0	0·0705	17·0	55·1	0·0529	17·4
55·0	0·2068	10·0			
	ethanol			2-propanol	
40·5	0·0685	3·78	55·0	0·1207	15·2
40·5	0·1532	2·31	60·2	0·0529	30·2
45·2	0·0685	6·66	60·2	0·1207	29·4
44·9	0·2068	3·96			
50·1	0·0325	13·1			
50·1	0·0685	9·3		tert-butyl alcohol	
50·1	0·1085	7·1			
50·1	0·1532	6·0	50·0	0·0201	1·33
55·2	0·0685	16·5	50·0	0·0435	1·25
55·0	0·2068	11·6	50·0	0·0695	1·18
60·1	0·0685	24·8	50·0	0·1002	1·12
60·1	0·2068	20·1	50·0	0·1358	1·03

breaking" effect takes place. The critical concentration, x_2^*, at which the influence of the alcohol on the water structure changes, is known for many alcohols[12]. For alcohols used in the present work, x_2^* is roughly given by the mole fraction of 0·05 (at 298 K). It is seen from Fig. 1*a*, *b* that characteristic changes on the function $\log \boldsymbol{k} = f(x_2)$ occur just close to the mentioned value. An exception is tert-butyl alcohol (Fig. 1*b*), for which the dependence of the log $\boldsymbol{k}$ value of $[Co(NH_3)_5Br]^{2+}$ is monotonous in the whole concentration range under study. Thus, this ion differs from some other Co(III) ions, whose aquation in water–alcohol media was studied earlier[4,13]. It follows by comparison of Figs 1*a* and *b* that with the aquation of $[Cr(NH_3)_5Br]^{2+}$ the function $\log \boldsymbol{k} = f(x_2)$ differs much less from a linear one than with the aquation of the other complex. This fact may be related to a different mechanism of the spontaneous aquation of the Cr(III) and Co(III) complexes. From the results of several authors we can conclude that the prevailing mechanism of aquation of Cr(III) complexes is the associative exchange of the ligand, whereas the aquation mechanism of Co(III) complexes is prevailingly dissociative[14]. Based on known facts about the aquation mechanism of transition metal complexes in mixed aqueous

TABLE III

Thermodynamic Activation Parameters for Aquation of Bromopentaamminechromium(III) and Bromopentaamminecobalt(III) Ions at Various Mole Fractions of Alcohol, x_2

Alcohol	x_2	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
		$[Cr(NH_3)_5Br]^{2+} + H_2O$		
Methanol	0·0957	97·1	88·8	−25·5
	0·2068	98·0	87·9	−30·5
Ethanol	0·0685	96·7	87·1	−29·7
	0·1532	97·1	95·0	− 6·3
2-Propanol	0·0529	96·7	90·4	−19·3
	0·1207	96·7	96·7	− 0·4
		$[Co(NH_3)_5Br]^{2+} + H_2O$		
Methanol	0·0705	104·2	90·0	−43·1
	0·2068	105·5	86·7	−57·8
Ethanol	0·0685	104·7	80·4	−72·8
	0·1532	105·1	89·6	−47·7
2-Propanol	0·0529	104·2	94·6	−28·9
	0·1207	104·7	97·5	−21·3

solvents, it is not possible to express the influence of the nonaqueous component on the elementary reaction step quantitatively.

The dependence of the logarithm of the rate constant of aquation for both studied complexes on the ionizing power of the solvent, Y, in water–methanol and water–ethanol mixtures is not even in a single case linear; only for the chromium complex at lower values of Y the dependence approaches somewhat to a linear course. This enables to estimate the slope, which is 0·2 in methanol and 0·1 in ethanol. This result agrees to some extent with ref.[15,16] according to which the dependence $\log k = f(Y)$ is nonlinear if the reaction proceeds by an S_N2 mechanism, while the tangents of the curve have slopes in the interval 0·2–0·5. Accordingly, the dependence for the aquation of the Co(III) complex should be linear similarly to solvolytic reactions of organic compounds, which proceed by a S_N1 mechanism[17]. However, the dependence is curved and the slope of the tangents lies in the interval 0·1–0·6.

The dependence of the rate constant on the temperature was studied in both cases at two molar fractions of the nonaqueous component: The first one corresponded to the break on the curve $\log k = f(x_2)$ (in the case of aquation of the Co(III) complex in the presence of 2-propanol, a minimum), the second one was higher (Table III). The maximum error of the $\Delta H^{\neq}$ value is ± 2 kJ/mol. It is seen from the table that the nonaqueous component has a larger influence on the activation entropy than on the activation enthalpy. The latter has values only little different from $\Delta H^{\neq}$ for the reaction of the studied complexes in a purely aqueous medium[18]; the smallest difference between the values of $\Delta H^{\neq}$ in water and in water–alcohol mixtures is in aqueous 2-propanol. However, the values of $\Delta S^{\neq}$ for both reactions in water–alcohol mixtures are considerably different from analogous values in water. It can be also seen from Table III that the activation free enthalpy $\Delta G^{\neq}$ is in the used solvents for both studied reactions constant within the limits of the experimental errors, *i.e.*, the compensation effect comes into play. The dependence of $\Delta H^{\neq}$ on $\Delta S^{\neq}$ is in both cases linear; the correlation coefficient and the isokinetic temperature is 0·996 and 303 K for aquation of $[Cr(NH_3)_5Br]^{2+}$, 0·995 and 312 K for $[Co(NH_3)_5Br]^{2+}$. The existence of the compensation effect with these isokinetic temperatures may be also related to changes in the water structure caused by the addition of the nonaqueous component[19,20].

In reactions of more complicated polyatomic reactants, vibrations of parts of the molecule (complex ion) can contribute to the activation. The theory according to which the molecule is considered as an ensemble of classical coupled oscillators gives their number, s, as defined by the equation

$$k = (k_B T/h) \exp(-E/RT) \left[(E/RT)^{s-1}/(s-1)!\right], \qquad (2)$$

where the symbols have their usual significance. After introducing the proper values we obtain for the aquation of both complexes in all the studied media $s = 1$ in accord with the data for aquation of other chromium(III) and cobalt(III) complexes[21].

According to Tables I and II, additions of methanol and ethanol into the reaction system have a different influence on the studied reactions. At lower alcohol concentrations, the influence of methanol and ethanol is larger with the Co(III) complex while at higher concentrations their influence is small in both cases. This suggests that the bromopentaamminechromium(III) ion is hydrated preferentially[14]. It is notable that the activation entropy is in both cases negative similarly as with aquation of other Cr(III) and Co(III) complexes[18]. By comparison of the values of $\Delta S^{\neq}$ for both studied reactions it follows that the activation entropy of aquation of the $[Co(NH_3)_5Br]^{2+}$ ion is in all studied media smaller than that for the other complex. This is in accord with the concept according to which the activation entropy is a measure of the change in the degree of ordering during transition from the starting compound to the activated complex. If the aquation of the cobalt complex proceeds by a dissociative mechanism, an intermediate complex $[Co(NH_3)_5]^{3+}$ is formed, which bears a higher charge than the original complex. In the vicinity of a particle with a higher charge the electrostatic field is stronger and exerts a stronger orienting force on the polar solvent molecules. Their degree of ordering (orientation around the solvated ion) is hence higher than in the vicinity of the original complex $[Co(NH_3)_5Br]^{2+}$.

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