Kinetics of the solvolysis of chloropenta-amminecobalt(III) ions in mixtures of water with *t*-butyl alcohol or with 2-methoxyethanol

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Summary

As the transition state for the solvolysis of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ ions is known to have $\mathrm{Cl^-}$ ions in a situation closely similar to that in the bulk solvent, the kinetics of this solvolysis have been investigated for comparison in H_2O with added cosolvents of low and high hydrophobicities. A linear variation of log(rate constant) with the reciprocal of the dielectric constant is found with the former, but not with the latter cosolvent. Maxima in the enthalpies and entropies of activation found using the more hydrophobic cosolvent appear at solvent compositions where extrema occur in the physical properties influenced by structural changes in the solvent. The application of a free energy cycle to the solvolysis in H_2O and in the mixtures shows that the emergent solvated cobalt(III) ion in the transition state is more stabilised in the latter than $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ with both cosolvents. The application of such a cycle to cases where the initial state is destabilised in the mixture is discussed.

Introduction

The kinetics of solvolysis of the $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ ion have been investigated in mixtures of H_2O with a hydrophobic alcohol, propan-2-ol(1), and with a hydrophilic additive, glucose(2). Despite the difference in the effects of the two additives on the properties of H_2O(1,2), they produced similar changes in the kinetics of the solvolysis of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$. Both investigations found nonlinear variations for log(rate constant) with the reciprocal of the dielectric constant D_s(1,2). An analysis of the volumes of activation for the solvolysis of complexes $[\mathrm{Co(NH_3)_5X}]^{3-x}$ in H_2O with various anions X^{x-} has shown(2) for this I_d mechanism that X^{x-} in the transition state probably corresponds closely with X^{x-} in the bulk solvent. Movement of solvent molecules can be accounted for by changes in the solvation of species in the reaction

$$\underset{\text{initial state}}{\mathrm{Co(NH_3)_5X^{(3-x)+}}} \longrightarrow \underset{\text{transition state}}{\mathrm{Co(NH_3)_5^{3+}\cdots X^{x-}}} \qquad (1)$$

with a very long extension of the $\mathrm{Co^{3+}\cdots X^{x-}}$ bond in the transition state: the Laidler-Landskroener equation(3) would require log(rate constant) for such a reaction in an unstructured solvent to vary linearly with D_s^{-1}. Both investigations found extrema in the variations of the enthalpy of activation, ΔH^*, and the entropy of activation, ΔS^*, with solvent composition. The solvolysis in H_2O + propan-2-ol showed twin peaks(1), one at mole fraction of cosolvent $x_2 \simeq 0.04$, close to the minimum in $(\bar{V}_2 - V_2^0)$ (the partial molar volume of the cosolvent relative to that of the pure cosolvent) in H_2O + propan-2-ol(4), and the other at $x_2 \simeq 0.07$, close to the maximum in the ultrasonic absorption of the mixtures(5). However, the solvolysis in H_2O + glucose showed a single broad extremum in both ΔH^* and ΔS^* at $x_2 \simeq 0.02$–0.04, although no minimum in $(\bar{V}_2 - V_2^0)$ has been found in the H_2O + glucose mixtures(2). As it has been found, for example, in the solvolysis of $[\mathrm{Co(CN)_5Cl}]^{3-}$, where volumes of activation also show approximately maximum extension of the $\mathrm{Co^{3+}\cdots Cl^-}$ bond in the transition state(6), plots of log(rate constant) versus D_s^{-1} are approximately linear with no extrema in ΔH^* and ΔS^* in mixtures of H_2O with hydrophilic cosolvents(7,8) compared with a nonlinear $\log k - D_s^{-1}$ plot and extrema in ΔH^* and ΔS^* in H_2O + *t*-butyl alcohol(9). In this paper the solvolysis of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ has been investigated in H_2O using 2-methoxyethanol and *t*-butyl alcohol as cosolvents.

Experimental

Materials and conditions were as described previously(1,2), but 2-methoxyethanol was of Fluka puriss p.a. grade (g.c. assay >99.5%). The change in $[\mathrm{Co(NH_3)_5Cl^{2+}}]$ with time was followed spectrophotometrically(1,2).

Results and discussion

Variation of rate with solvent composition and temperature

Plots of $\log(A_t - A_\infty)$ versus time t (A = absorbance) were always found to be linear to low values of $(A_t - A_\infty)$. The solvolysis was investigated in 3.94, 7.92, 11.99, 16.02, 20.15, 24.41, 33.19 and 42.28 wt% *t*-butyl alcohol and in 4.83, 9.63, 14.63, 19.21, 28.77, 38.28 and 47.88 wt% 2-methoxyethanol at 55.0, 60.0, 65.0, 70.0 and 75.0° C for all compositions. Triplicate determinations were performed for each composition at each temperature and rate constants were determined from the slopes of the $\log(A_t - A_\infty)$ versus time plots. For H_2O + *t*-butyl alcohol mixtures, it was found that the deviation of individual values for k never exceeded 3.0% for 80% of the results, with 89% of the results lying within ±4.0% of the mean and 100% lying within 4.6% of the mean. For H_2O + 2-methoxyethanol, 83% of the individual values for k lay within ±3.2% of the mean, with 94% having a deviation of less than 3.5% and 100% less than 5.4% of the mean. The mean values for k are collected in Table 1.

Variation of transition state parameters with solvent composition

Values for the Gibbs energy of activation, ΔG^*, and of ΔH^* and ΔS^* were calculated by least squares procedures

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Table 1. First order rate constant ($/10^{-5}\,s^{-1}$) for the solvolysis in mixtures of H_2O with 2-methoxyethanol (A) or *t*-butyl alcohol (B) of $[Co(NH_3)_5Cl](ClO_4)_2$.

Cosolvent			Temperature (°C)				
	wt%	mole fraction	55.0	60.0	65.0	70.0	75.0
A	4.83	0.0119	5.9	9.5	16.1	24.3	39.7
A	9.63	0.0246	5.5	9.2	14.7	23.2	38.3
A	14.63	0.0384	4.59	7.7	11.4	18.6	31.3
A	19.21	0.053	4.00	6.1	9.4	14.2	26.6
A	28.77	0.087	3.27	4.87	8.5	12.1	22.6
A	38.28	0.128	2.61	3.85	6.7	10.4	19.6
A	47.88	0.179	1.78	2.99	4.78	7.9	13.8
B	3.94	0.0099	5.4	9.2	15.2	23.1	39.1
B	7.92	0.0205	5.0	8.3	13.9	22.0	37.7
B	11.99	0.0320	4.68	7.4	12.3	20.6	35.3
B	16.02	0.0443	5.9	9.6	16.1	23.7	40.1
B	20.15	0.0578	5.3	9.3	14.9	22.5	39.5
B	24.41	0.0728	4.09	6.6	10.8	19.1	32.3
B	28.75	0.0893	3.43	5.5	9.3	16.5	27.5
B	33.19	0.108	3.08	4.88	7.8	14.7	24.8
B	42.28	0.151	2.72	4.36	6.8	12.1	20.9

using the individual values for k at each solvent composition quoted above (Table 2).

Using ΔH^* and ΔS^* in Table 2, values for k at 25° C can be calculated. Figure 1 shows the variation of $\log k$ with the reciprocal of the dielectric constant D_s at 25° C for both sets of solvent mixtures: D_s at 25° C for H_2O + 2-methoxyethanol was interpolated from the data of Sadek *et al.*(10) and that for H_2O + *t*-butyl alcohol from the combined data of Broadwater and Kay(11) and of Brown and Ives(12). Log k varies linearly with D_s^{-1} for mixtures of H_2O with the more hydrophilic 2-methoxy-EtOH; $(\bar{V}_2 - V_2^0)$ for this mixture shows only a shallow minimum at $x_2 \simeq 0.06$(8). However, the variation of $\log k$ with D_s^{-1} in H_2O + *t*-butyl alcohol is not linear, as shown by the plot of $\log k$ versus D_s^{-1} in Figure 1, which was constructed using the experimental values of k at 60° C in Table 1 and D_s at 60° C interpolated from the data of Åkerlöf(13). *t*-Butyl alcohol has a hydrophobic influence when added to H_2O, as shown by the deep minimum in $(\bar{V}_2 - V_2^0)$ at $x_2 \simeq 0.015$ at 50° C(14), the positive structural contribution, ΔT^E_{max}, to the change in the maximum density of H_2O when *t*-butyl alcohol is added(15), the extent of the deviation of the minimum in the excess enthalpy of mixing, ΔH^E_{mix}, of H_2O and *t*-butyl alcohol(14) from $x_2 = 0.5$ at 26–70° C and the very sharp, high maximum in the ultrasonic absorption of the mixtures at $x_2 \simeq 0.1$(5,16). The minimum in $(\bar{V}_2 - V_2^0)$ for H_2O + *t*-butyl alcohol is very much deeper(14) than that found for H_2O + 2-methoxyethanol(8). However, for both mixtures, $(\bar{V}_1 - V_1^0)$ for H_2O remains near zero in the same composition range as the minimum in $(\bar{V}_2 - V_2^0)$, showing that the overall structure of the Frank-type clusters of H_2O molecules(17) remains unchanged when the hydrophobic hydrocarbon tail of *t*-butyl alcohol is excluded from these structures into the interstices, although some alteration to the bonding within the Frank-type H_2O clusters may occur. The minimum in $(\bar{V}_2 - V_2^0)$ occurs when the accumulation of hydrocarbon tails in the interstices is sufficient to assume some of the properties of pure *t*-butyl alcohol; at higher x_2, $(\bar{V}_2 - V_2^0)$ then rises gradually towards the value for the pure alcohol. At the minimum, these hydrocarbon micro-micelles will exert considerable pressure on the Frank-type H_2O clusters, leading to their breakdown; the real onset of this breakdown may be registered by the maximum in the ultrasonic absorption.

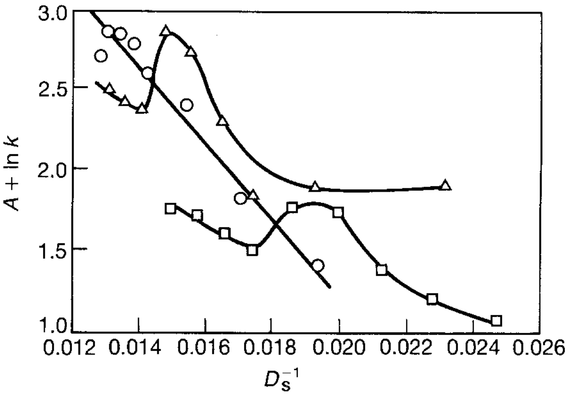

Figure 1. Variation of the logarithm of the rate constant with the reciprocal of the dielectric constant for the solvolysis of $[Co(NH_3)_5Cl]^{2+}$ in mixtures of H_2O with 2-methoxyethanol at 25° C (○, A = 16) and with *t*-butyl alcohol at 25° C (Δ, A = 16) and at 60° C (□, A = 11).

The modified form(18) of the Laidler-Landskroener equation(3) can be applied to the solvolysis process (Equation 1) with $C = [Co(NH_3)_5Cl]^{2+}$ and $M = [Co(NH_3)_5^{3+}]$, as in Equation 2;

$$RT\ln\frac{k_w}{k_s} = \frac{Ne^2}{2}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \times \left[\frac{z_M^2}{r_M} + \frac{z_X^2}{r_X} - \frac{z_C^2}{r_C} + \frac{3}{2}\left(\frac{G_M}{r_M^3} + \frac{G_X}{r_X^3} - \frac{G_C}{r_C^3}\right)\right] + \Delta G_t^0(M)_n + \Delta G_t^0(X^-)_n - \Delta G_t^0(C)_n \qquad (2)$$

where N is Avogadro's number, z_i is the charge on species i of radius r_i, G_i is related to the dipole moment and $\Delta G_t^0(i)_n$ is the Gibbs energy of transfer of species i from H_2O w into the mixture s minus the electrostatic contribution from the first term on the right hand side of Equation 2. For H_2O + 2-methoxyethanol mixtures with

Table 2. Transition state parameters for the solvolysis in mixtures of H_2O with 2-methoxyethanol (A) or *t*-butyl alcohol (B) of $[Co(NH_3)_5Cl](ClO_4)_2$.

Cosolvent			ΔH^{*a}	ΔS^* at 25° C^b	ΔG^* at 25° C^a
	wt%	mole fraction			
A	4.83	0.0119	88 ± 1	−59 ± 3	105 ± 2
A	9.63	0.0246	89 ± 1	−56 ± 3	106 ± 2
A	14.63	0.0386	87 ± 2	−63 ± 5	106 ± 3
A	19.21	0.053	86 ± 2	−68 ± 6	106 ± 3
A	28.77	0.087	88 ± 2	−63 ± 8	106 ± 3
A	38.28	0.128	93 ± 2	−51 ± 8	106 ± 3
A	47.88	0.179	94 ± 1	−51 ± 4	107 ± 2
B	3.94	0.0099	91 ± 1	−52 ± 4	106 ± 2
B	7.92	0.0205	93 ± 1	−46 ± 3	106 ± 2
B	11.99	0.0320	94 ± 2	−43 ± 5	107 ± 3
B	16.02	0.0443	88 ± 1	−59 ± 4	106 ± 2
B	20.15	0.0578	91 ± 2	−50 ± 4	106 ± 3
B	24.41	0.0728	96 ± 2	−37 ± 5	107 ± 3
B	28.75	0.0893	98 ± 2	−34 ± 4	107 ± 3
B	33.19	0.108	97 ± 2	−37 ± 7	107 ± 3
B	42.28	0.151	94 ± 2	−47 ± 6	107 ± 3

^{a}kJ mol^{-1}; ^{b}J K^{-1} mol^{-1}.

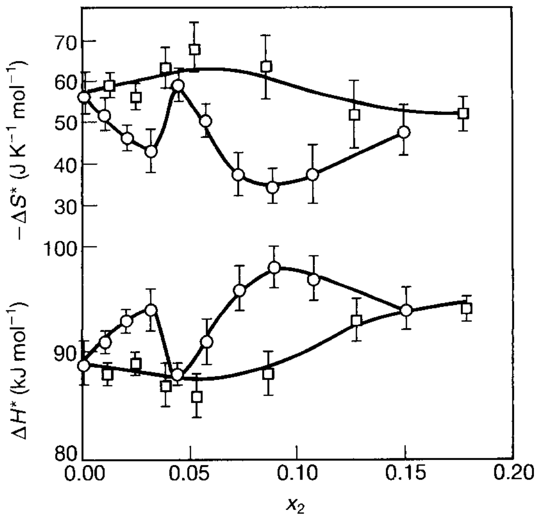

Figure 2. Variation with the mole fraction of cosolvent of the enthalpy and entropy of activation for the solvolysis of $[Co(NH_3)_5Cl]^{2+}$ in mixtures of H_2O with 2-methoxyethanol (□) and with *t*-butyl alcohol (○).

$X^- = Cl^-$, Equation 3 holds;

$$\Delta G_t^0(M)_n + \Delta G_t^0(Cl^-)_n = \Delta G_t^0(C)_n \qquad (3)$$

Whereas, for mixtures of H_2O with the hydrophobic, structure forming *t*-butyl alcohol, Equation 3 does not hold.

Table 2 shows that, whereas ΔG^* varies little with solvent composition in these H_2O-rich conditions, this conceals compensating variations of ΔH^* and ΔS^* with x_2. This can be compared with the solvolyses of other complexes(7–9) in H_2O + cosolvent mixtures and the solvolysis of $[Co(NH_3)_5Cl]^{2+}$ in mixtures of H_2O with other cosolvents(1,2). Figure 2 shows that, although no extremum is distinguishable in the variation of ΔH^* with x_2 in H_2O + 2-methoxyethanol, ΔH^* in H_2O + *t*-butyl alcohol mixtures shows two maxima outside the error margins, a sharp one at $x_2 \simeq 0.25$ and a smoother one at $x_2 \simeq 0.10$. Similarly, in the variation of ΔS^* with x_2 in Figure 2, the curve for H_2O + 2-methoxyethanol has no distinguishable extremum, whilst maxima significant, appear at $x_2 \simeq 0.025$ and $\simeq 0.10$ in H_2O + *t*-butyl alcohol; the compositions for these maxima correspond with those where the minimum(14) in $(\bar{V}_2 - V_2^0)$ and the maximum(5,16) in the ultrasonic absorption occur. This suggests that the maxima in ΔH^* and ΔS^* arise from the differential effects of changes in the solvent structure on the initial and transition states caused by the extreme situations involved in the filling of the interstices between the Frank-type clusters(17) with the hydrocarbon groups, as discussed above.

Application of a Gibbs energy cycle

To a process such as Equation 1, with $X^- = Cl^-$ in H_2O (w) and in H_2O + cosolvent mixtures (s) a Gibbs energy cycle can be applied(18):

$$\begin{tikzcd}
{[Co(NH_3)_5Cl^{2+}]_w} \arrow[r, "\Delta G_w^*"] & {[Co(NH_3)_5^{3+}*]} \arrow[r, phantom, "\cdots\cdot"] \arrow[d, "-\Delta G_t^0[Co(NH_3)_5^{3+}*]"'] & Cl_w^- \arrow[d, "\Delta G_t(Cl^-)"'] \\
{[Co(NH_3)_5Cl^{2+}]_s} \arrow[u, "-\Delta G_t^0[Co(NH_3)_5Cl^{2+}]"] \arrow[r, "\Delta G_s^*"] & {[Co(NH_3)_5^{3+}*]_s} \arrow[r, phantom, "\cdot\cdots"] & Cl_s^- \\
\text{Initial state} & \text{Transition state} &
\end{tikzcd}$$

where $*$ indicates a species in the transition state and now $\Delta G_t^0(i)$ is the total Gibbs energy of transfer of species i from H_2O into the mixture, Equation 4 results.

$$\Delta G_s^{\ne} = \Delta G_w^{\ne} - \Delta G_t^0[Co(NH_3)_5Cl^{2+}] + \Delta G_t^0[Co(NH_3)_5^{3+}*] + \Delta G_t^0(Cl^-)* \qquad (4)$$

Rearranging Equation 4 and replacing ΔG^* by Equation 5,

$$\Delta G^* = RT\ln(kT/kh) \qquad (5)$$

where k is Boltzmann's constant, results in Equation 6

$$RT\ln(k_w/k_s) - \Delta G_t^0(Cl^- *) = \Delta G_t^0[Co(NH_3)_5^{3+}*] - \Delta G_t^0[Co(NH_3)_5Cl^{2+}] \qquad (6)$$

As discussed above, it has been shown for the hydrolysis of $[Co(NH_3)_5X]^{(3-x)+}$ in H_2O that X^{x-} in the transition state corresponds very closely with X^{x-} in the bulk solvent, so that $\Delta G_t^0(Cl^- *)$ in Equation 6 can be replaced by $\Delta G_t^0(Cl^-)$. The latter has been evaluated for the two mixtures using two different methods for separating $\Delta G_t^0(M^+ \cdot Cl^-)$ into Gibbs energies of transfer for individual ions.

Firstly, using the solvent sorting method(19–21), $\Delta G_t^0(H^+)$ is determined in two steps. The Gibbs energy of transfer for the spherical H_{aq}^+ from H_2O into the mixture is calculated using the Born equation, ΔG(Born). Then the Gibbs energy of the rearrangement of solvent molecules, $\Delta G(H^+)_{re}$, around the proton in the mixture containing the cosolvent, S, as in Equation 7,

$$H^+(H_2O)_m + S \overset{K_{re}}{\rightleftharpoons} H^+(H_2O)_{m-1}S + H_2O \qquad (7)$$

is determined by investigating the competitive equilibria of $H^+(H_2O)_m$ and $H^+(H_2O)_{m-1}S$ for a trace concentration of 4-nitroaniline. It is always found that the experimental $\Delta G(H^+)_{re} \gg \Delta G$(Born), with

$$\Delta G_t^0(H^+) = \Delta G(\text{Born}) + \Delta G(H^+)_{re} + A \qquad (8)$$

where A is a constant changing the scale from molar to mole fraction. $\Delta G_t^0(Cl^-)$ is then calculated from $\Delta G_t^0(HCl)$, obtained from E^0 data for a suitable cell, using Equation 9:

$$\Delta G_t^0(Cl^-) = \Delta G_t^0(HCl) - \Delta G_t^0(H^+) \qquad (9)$$

where k_s is calculated from the data in Table 2 and k_w from similar data for ΔH^* and ΔS^* obtained in H_2O(1). Figure 3 shows that $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)]$ at first becomes increasingly negative as x_2 increases, reaching a minimum at $x_2 \simeq 0.06$ for *t*-butyl alcohol and levelling off for 2-methoxyethanol in the region $x_2 \simeq 0.13$–0.18; $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)]$ for *t*-butyl alcohol is always more negative than the same function for 2-methoxyethanol.

Alternatively, $\Delta G_t^0(Cl^-)$ can be assigned values using the TATB method(9,24). With $\Delta G_t^0(Ph_4As^+ \cdot BPh_4^-)$ determined from solubility measurements, values for the separate ions are assigned using the assumption

$$\Delta G_t^0(Ph_4As^+) = \Delta G_t^0(BPh_4^-) = \tfrac{1}{2}\Delta G_t^0(Ph_4As^+ \cdot BPh_4^-) \qquad (10)$$

which also involves the assumptions

$$\Delta G_t^0(BPh_4^-)_e \ll \Delta G_t^0(BPh_4^-)_n \qquad (11)$$

$$\Delta G_t^0(Ph_4As^+)_e \ll \Delta G_t^0(Ph_4As^+)_n \qquad (12)$$

where e indicates contributions from the transfer of the charge alone on species i and n indicates the transfer of the electrically neutral species i. $\Delta G_t^0(M^+)$ can then be calculated using $\Delta G_t^0(MBPh_4)$ from solubility measure-

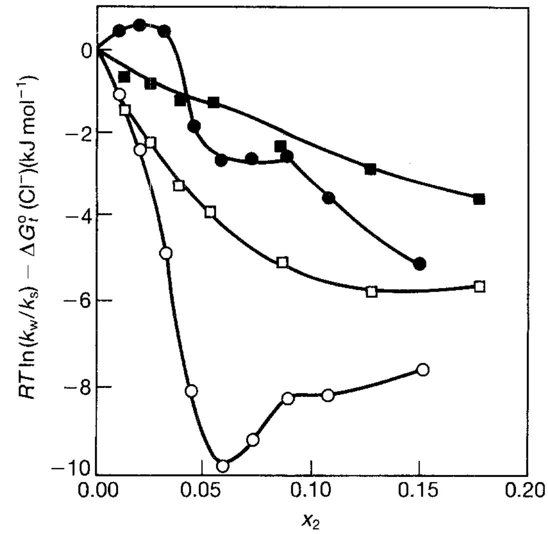

Figure 3. Variations with the mole fraction of cosolvent of $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(solvent sorting)$]$ for cosolvents 2-methoxyethanol (□) and *t*-butyl alcohol (○) and of $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(TATB)$]$ for cosolvents 2-methoxyethanol (■) and *t*-butyl alcohol (●) for the solvolysis of $[Co(NH_3)_5Cl]^{2+}$ in H_2O + cosolvent mixtures at 25° C.

ments which, in turn, allows the calculation of $\Delta G_t^0(Cl^-)$ from $\Delta G_t^0(MCl)$ obtained from E^0 measurements on a suitable cell. Figure 4 shows that $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(TATB)$]$ becomes increasingly negative as x_2 increases with 2-methoxyethanol as cosolvent. For H_2O + *t*-butyl alcohol mixtures, $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(TATB)$]$ is positive for $x_2 < 0.035$ (Figure 3), thereafter becoming increasingly negative as x_2 rises.

Comparing plots of $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)]$ for the same cosolvent with the two sets of $\Delta G_t^0(Cl^-)$, Figure 3 shows that $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(solvent sorting)$]$ is always more negative than $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$-(TATB)$]$; this may arise from a breakdown in assumptions 11 and 12(9). This criticism has been amplified by the inability of $\Delta G_t^0(H^+)$(TATB) in mixtures of H_2O with MeOH, EtOH or *t*-butyl alcohol at low x_2 to explain the rapid rise in the Hammett Acidity Function H_0, in H_2O rich mixtures(25). This particularly applies to H_2O + *t*-butyl alcohol with $x_2 < 0.05$; therefore, the positive values for $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)$(TATB)$]$ in Figure 3 using *t*-butyl alcohol with $x_2 < 0.035$ for this solvolysis and others(26) may be spurious. With $\Delta G_t^0(H^+)$(TATB) known to be in error for H_2O + MeOH with $x_2 < 0.2$, for H_2O + EtOH with $x_2 < 0.1$ and for H_2O + *t*-butyl alcohol with $x_2 < 0.05$ and, therefore, also possibly ΔG_t^0(i) (TATB) for other ions at low x_2, perhaps greater reliance should be placed on ΔG_t^0(i) (solvent sorting) in such H_2O rich media. The ΔG_t^0(i) (solvent sorting) values for simple cations are all negative in H_2O rich H_2O + 2-methoxyethanol(23) and H_2O rich H_2O + *t*-butyl alcohol mixtures(19,22), as found also for i = Ph_4As^+ and i = BPh_4^-, and this is usually negative for i = complex cobalt cations in H_2O + alcohol mixtures.

However, $\Delta G_t^0[Co(NH_3)_5Cl^{2+}]$ (solvent sorting) is only available for H_2O + MeOH, where it is negative for $x_2 < 0.2$(27). Nevertheless, it is safe to conclude that this is negative also in H_2O + 2-methoxyethanol and in H_2O + *t*-butyl alcohol, as ΔG_t^0(i) (solvent sorting) for simple cations is more negative in the former mixture with $x_2 < 0.2$(23) and much more negative in the latter mixture with $x_2 < 0.1$(19,22) than in H_2O + MeOH(19). Therefore, using Equation 6, we can also conclude from the negative values for $[RT\ln(k_w/k_s) - \Delta G_t^0(Cl^-)]$ in Figure 3 that $\Delta G_t[Co(NH_3)_5^{3+}*]$ for $Co(NH_3)_5^{3+}*$ in the transition state is also negative in both mixtures, with $-\Delta G_t^0[Co(NH_3)_5^{3+}*] > -\Delta G_t^0[Co(NH_3)_5Cl^{2+}]$.

However, it is not necessary, as has been suggested(32), for $\Delta G_t(C^{z_c})$ in the general case

$$C^{z_c} \longrightarrow M^{z_m}\cdots X^- \qquad (13)$$

initial state transition state

to be negative. Experimental negative values for $[RT\ln(k_w/k_s) - \Delta G_t^0(X^-)]$ in Equation 14

$$RT\ln(k_w/k_s) - \Delta G_t^0(X^-) = \Delta G_t^0(M^{z_m}) - \Delta G_t^0(C^{z_c}) \qquad (14)$$

with a positive $\Delta G_t^0(C^{z_c})$ would require $\Delta G_t^0(M^{z_m})$ either to be negative or to be positive with $\Delta G_t^0(M^{z_m}) < \Delta G_t^0(C^{z_c})$.

Examples of the latter case have been found for the solvolysis of $[Co(CN)_5Cl]^{3-}$ in H_2O + cosolvent mixtures with a variety of cosolvents(7–9); for this solvolysis, volumes of activation also show that the $Co^{3+}\cdots Cl^-$ bond is sufficiently extended in the transition state as to correspond closely to complete separation(6).

Conclusion

As the solvolysis of $[Co(NH_3)_5Cl]^{2+}$ in aqueous systems has been shown to involve an extension of the $Co^{3+}\cdots Cl^-$ bond in the transition state sufficient for Cl^- to resemble closely Cl^- ions in the bulk solution(2), the Laidler-Landskroener equation(3) can be applied. For H_2O + 2-methoxyethanol, ln(k) varies linearly with D_s^{-1} as predicted(3), but, in mixtures of H_2O with the structure-forming, hydrophobic *t*-butyl alcohol, this variation is not linear. In the latter case, the Laidler-Landskroener equation can only apply when modified(18) to allow for the influence of structural changes in the solvent, as in Equation 2; this is comparable with the solvolysis of the complex ion in H_2O + propan-2-ol(1) and in H_2O + glucose mixtures(2). For the solvolysis of this complex in H_2O + acetone a linear plot of ln(k) against D_s^{-1} is also found(33) and, therefore, in this latter mixture and in H_2O + 2-methoxyethanol, both Equations 2 and 3 operate.

Maxima appear in the variations of ΔH^* and ΔS^* at solvent compositions corresponding to extreme structural situations in H_2O + *t*-butyl alcohol mixtures. For such a solvolysis where, as discussed above, $[Co(NH_3)_5Cl]^{2+}$ is stabilised in the mixture relative to H_2O, two possibilities exist to explain these maxima. The maxima are in ΔH^* found in mixtures of *t*-butyl alcohol, propan-2-ol(1) or glucose(3) with H_2O when the enthalpy of the initial state is reduced more than that of the transition state or the enthalpy of the initial state is lowered with that of the transition state increased in the mixture relative to the values in H_2O(26). Although no extrema are discernable for the variation of ΔH^* and ΔS^* here in H_2O + 2-methoxyethanol and none is detectable in ΔH^* in H_2O + acetone(33), an extremum does occur in ΔS^* in the latter mixtures(33).

As it has been shown that ΔG_t^0(i) (TATB) for H_2O + *t*-butyl alcohol mixtures (and other H_2O + alcohol mixtures) are in error at $x_2 < 0.05$(25), it is safe only to interpret the application of a Gibbs energy cycle to the solvolysis in H_2O and in the mixtures using ΔG_t^0(i) (solvent sorting). It is found for both mixtures investigated here that the emergent solvated cobalt(III) in the transition state is more stabilised than $[Co(NH_3)_5Cl]^{2+}$ in the initial state relative to their respective stabilities in H_2O; this compares with the same effects found in H_2O + propan-2-ol⁽¹⁾ and in H_2O + glucose⁽²⁾. It is shown that similar conclusions can be made where the Gibbs energy cycle is applied to solvolyses where the ion in the initial state is destabilised in the mixtures relative to H_2O. It should be emphasised that any movement of solvent molecules between the bulk solvent and the various species in Equation 1 will be accommodated in these changes in the free energies of solvation.

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