Preferential Solvation and the Composition of the Solvation Shell of (Dimethyl Sulphoxide)penta-amminechromium(III) Ion in Dimethyl Sulphoxide–Water Mixtures

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The number of solvent molecules in the solvation shell of the title complex ion has been found to be 10, the stepwise equilibrium constants for the replacement of the 10 water molecules by 10 dimethyl sulphoxide molecules have been obtained, and the free energy increment per replacement step has been found to be $\sim +1.42$ kJ mol^{-1}.

The composition of the second co-ordination shell (solvation shell, solvent cage) surrounding the first co-ordination shell of a transition metal ion is of much importance in the study of mechanisms and kinetics of enzymic, homogeneous catalytic, and substitution reactions involving transition metal complexes, in the interpretation of solvent effects on i.r., Raman,

visible, and u.v. spectra of transition metal complexes, in the study of electrochemical transport phenomena, and in theoretical studies of electrolyte solutions. We have obtained data from ^1H n.m.r. line broadening studies of solvent molecules which, in conjunction with the theory of Covington[1] and co-workers, have allowed us to calculate the number, n_o,

Table 1. Excess Gibbs free energies of mixing (1 cal = 4.184 J), activities of water and DMSO, and calculated and experimental values of (n_w/n_o) and (n_D/n_o), the fractions of water and DMSO in the second co-ordination shell of $[Cr(NH_3)_5(OSMe_2)]^{3+}$ at 40 °C.

X_D	$\Delta G^E/\text{cal mol}^{-1}$	a_w	a_D	$\left(\dfrac{n_w}{n_o}\right)$ [a] calc.	$\left(\dfrac{n_w}{n_o}\right)$ [b] exp.	$\left(\dfrac{n_D}{n_o}\right)$ [a] calc.	$\left(\dfrac{n_D}{n_o}\right)$ [b] exp.
0	0	1.00		1.0	1.0	0	0
0.1	−146.4	0.841	0.015	0.66	0.57	0.34	0.27
0.2	−226.0	0.668	0.058	0.50	0.40	0.50	0.43
0.3	−277.7	0.503	0.137	0.38	0.32	0.62	0.52
0.4	−294.9	0.368	0.247	0.29	0.25	0.71	0.60
0.5	−284.5	0.263	0.373	0.22	0.19	0.78	0.67
0.6	−252.4	0.183	0.502	0.16	0.14	0.84	0.74
0.7	−205.3	0.120	0.630	0.11	0.11	0.89	0.81
0.8	−145.6	0.070	0.755	0.070	0.066	0.93	0.88
0.9	− 82.7	0.030	0.874	0.032	0.030	0.97	0.91
1.0	0		1.00	0	0		

[a] Calculated values using the ten stepwise equilibrium constants given in the text. [b] After correction for effects of viscosity changes in the mixtures on the line widths.

of solvent molecules in the second co-ordination shell of $[Cr(NH_3)_5(OSMe_2)]^{3+}$ in dimethyl sulphoxide (DMSO)–water binary mixtures, the stepwise equilibrium constants, K_{iD}, for the stepwise replacement of H_2O molecules by DMSO molecules in the second co-ordination shell, and the difference in free energy, exclusive of statistical factors, between successive replacement steps. The K_{iD} values were then used to calculate $(n_w/n_o)_c$ and $(n_D/n_o)_c$, the fractions of the solvent molecules in the solvation shell which are water and DMSO, respectively. These fractions agree satisfactorily, as shown in Table 1, with the values obtained experimentally from line broadening of bulk water and DMSO proton peaks in $[Cr(NH_3)_5(OSMe_2)]^{3+}$ solutions after correction for the viscosity changes which occur with changing binary solvent composition. The viscosity-corrected line broadening Δv_c for a solvent component was calculated from the experimental line broadening Δv_e and η_o and η, the viscosities of the pure solvent component and the binary mixture, respectively, using $\Delta v_c = \Delta v_e(\eta_o/\eta)$. We believe that this is the first time such results have been obtained for the second co-ordination shell of a metal ion.

The stepwise replacement of second shell water by DMSO may be written as in reaction (1) where M represents

$$MW_{n_o - i + 1}D_{i - 1} + D \underset{}{\overset{K_{iD}}{\rightleftharpoons}} MW_{n_o - i}D_i + W \qquad (1)$$
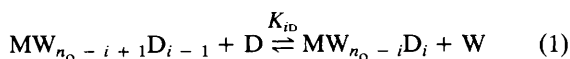
$[Cr(NH_3)_5(OSMe_2)]^{3+}$ and W and D represent water and DMSO molecules, respectively. The stepwise equilibrium constant for the i th replacement is given by equation (2) where a_w and a_D are the activities of water and DMSO, respectively, in a binary solvent mixture. The activities in equation (2) were obtained from the excess Gibbs free

$$K_{iD} = \frac{[MW_{n_o - i}D_i]a_w}{[MW_{n_o - i + 1}D_{i - 1}]a_D} \qquad (2)$$

energies, ΔG^E, of mixing at 40 °C and application of the Duhem–Margules equation. The ΔG^E values were, in turn, obtained from the enthalpies of mixing and the excess entropies of mixing reported by Kenttamaa and Lindberg.[2] The ΔG^E values and activities so obtained are given in Table 1 along with X_D, the bulk mol fraction of DMSO. In the application of the Duhem–Margules equation the repeated approximations were carried out until the activity coefficients of both solvent components became constant to ten significant

figures to prevent error accumulation in going across the entire range of solvent composition. The mol fraction increments were 0.01 for the ranges $0 \leqslant X_D \leqslant 0.10$ and $0.90 \leqslant X_D \leqslant 1.0$ and 0.02 for the range $0.1 < X_D < 0.9$. Two sets of activity coefficients were calculated for each solvent, one set for beginning the calculations at the pure water end of the solvent composition range and one set for beginning at the pure DMSO end. The two sets of activity coefficients for water agreed to within 1% or better over the range $0.5 < X_D \leqslant 1.0$; the disagreement increased to ~4% as $X_D \to 0$. The discrepancy in the two sets for DMSO was about 4% for $0.5 < X_D \leqslant 1.0$ and increased to about 9% as $X_D \to 0$.

The parameters of the Covington equation† are n_o, $K(\prod_{i=1}^{n_o} K_{iD})$, and k which allows for a change in the free energy of successive solvent replacement steps exclusive of the change due to statistical factors. The Covington equation is of the type shown in equation (3) where A_1 and B_1', the numerator and

$$n_1/n_o = A_1/B_1' \qquad (3)$$

denominator of the equation, respectively, are rather complicated expressions and need not be reproduced here and n_1 and n_o are the number of molecules of solvent component 1 in the solvation shell of the complex ion in a binary solvent mixture and in the neat solvent 1, respectively. This equation is readily arranged to $B_1 = n_1 B_1'/n_o$, and $A_1/B_1 = 1.0$. There is a similar equation for solvent component 2, namely, $A_2/B_2 = 1.0$, where $B_2 = n_2 B'_2/n_o$. Experimental values of the ratios (n_1/n_o) and (n_2/n_o) are obtained from experimental line broadenings[3] after the latter have been corrected for viscosity effects as explained above. Because $(A_1/B_1) = (A_2/B_2) = 1.0$ one obtains equation (4) which can be solved by trial and error for

$$A_1B_2 = A_2B_1 \qquad (4)$$

different n_o values to get the best data fit. The best fit was obtained for $n_o = 10$, $k = 0.565$, and $K = 5.67 \times 10^{10}$ with a standard deviation for a single determination of K of ± 12% over a 1600-fold change in the ratio, a_D/a_w, of the activities of DMSO to water.

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† Equation 6 (ref. 1) was corrected before use.

The value of $K = 0.565$ means that each replacement of a water molecule by a DMSO molecule is $+1.42 \text{ kJ mol}^{-1}$ more difficult than the preceding replacement from the first to the last replacement.

The ten stepwise formation constants for the solvation shell are: $K_{1D} = 1.55 \times 10^3$, $K_{2D} = 395$, $K_{3D} = 132$, $K_{4D} = 49.0$, $K_{5D} = 19.0$, $K_{6D} = 7.45$, $K_{7D} = 2.88$, $K_{8D} = 1.07$, $K_{9D} = 0.358$, $K_{10D} = 9.11 \times 10^{-2}$ as defined by equation (1).

The values of 6, 8, 10, and 12 were used for n_o in the best-fit calculations. The values of 8 and 12 gave significantly larger errors in K for the full concentration range and were rejected as giving poorer fit for the experimental data. The value of 6 gave a fit equal to that for 10 but was rejected on chemical grounds. If a DMSO molecule is pictured as being at the centre of a triangular octahedron face with the oxygen atom directed inward and methyl groups outward so that the Cr–O–S nuclei lie along a straight line then the angle subtended by the DMSO molecule at the Cr nucleus is less than the angle subtended by the width of a triangular face at its centre. Therefore it seems unlikely that six DMSO molecules occuping six of the eight faces of an octahedral complex ion could successfully prevent the seventh and eighth DMSO molecules from taking positions near the two vacant faces. Of course, we do not picture the solvent cage molecules as being rigidly attached to any one position in the second co-ordination shell and instantaneous positions and orientations will be affected by bulk solvent structural fluctuations.

It is seen from Table 1 that DMSO strongly preferentially solvates the complex ion at the smaller X_D values; this is reflected in the K_{iD} values.

The sum $(n_w/n_o)_{exp.} + (n_D/n_o)_{exp.}$ is approximately constant over the X_D range as it should be if n_o does not change with composition of the solvation shell. However, its value is ~ 0.84—0.86 rather than unity; the reason for this is not known at present but is suspected to lie in over-correction for the viscosity effect.

References

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3 S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Am. Chem. Soc.*, 1969, **91**, 2236.