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The Reaction of Aquapentaamminecobalt(III) Ion with Dimethyl Sulfoxide in Acidic Aqueous Mixed Solvents[1]

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The reaction $Co(NH_3)_5OH_2^{3+} + (CH_3)_2SO = Co(NH_3)_5(OS(CH_3)_2)^{3+} + H_2O$ has been studied in acidic aqueous dimethyl sulfoxide solution, with emphasis placed upon observation of the dependence of rate coefficients and equilibrium quotients upon the solvent composition. This system behaves similarly to aquachromium(III) ion in this binary solvent. In particular, for the reaction given above an equilibrium quotient involving the activities of the solvent components decreases with increasing amount of dimethyl sulfoxide in the binary solvent. This is interpreted as indicating that the dominant outer-sphere interaction involves solvent dimethyl sulfoxide and the coordinated water molecule in $Co(NH_3)_5OH_2^{3+}$. Outer-sphere interactions also are manifested in the dependence of light absorption by each cobalt species upon solvent composition; uncertainties in interpretation of small spectral changes with major changes in solvent composition may be caused, however, by physical effects due to changes of the refractive index of the solvent.

Introduction

Dimethyl sulfoxide has a greater affinity than water for most metal ions. The enthalpies of solvation of alkali metal ions in dimethyl sulfoxide are more negative than the corresponding quantities for solvation in water,[2] and, based upon the cesium-133 NMR chemical shift, cesium ion is judged to be preferentially solvated by dimethyl sulfoxide in water–dimethyl sulfoxide mixed solvents.[3]

The problem of distinguishing primary solvation (coordination in the first shell) and secondary solvation (outer-sphere coordination) generally is not solved in studies of the type just cited. Appropriate study of a system in which the rate of exchange of ligands in the first coordination shell with the bulk solvent is low on the time scale of the analytical probe allows unambiguous characterization of the primary solvation. For aluminum(III) ion, the exchange rate is low enough that the proton magnetic resonance of the methyl protons in dimethyl sulfoxide gives distinct peaks for coordinated and free dimethyl sulfoxide.[4,5] For chromium(III) ion, the exchange rate is low enough that column ion-exchange procedures can be used to separate individual differently solvated species. All ten inert species of the composition $Cr(OH_2)_{6-d}(OS(CH_3)_2)_d^{3+}$, with $d = 0$–6, inclusive (with two geometrical isomers for $d = 2$, 3, and 4), have been shown to be present in acidic aqueous solutions of dimethyl sulfoxide.[6] Equilibrium quotients for reactions for the formation of these species are not constant as the solvent composition changes. The equilibrium quotient for the reaction in which $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ is formed from $Cr(OH_2)_6^{3+}$ increases slightly with an increase of the mole fraction of dimethyl sulfoxide if the equilibrium quotient involves the ratio of mole fractions of the solvent components, but the equilibrium quotient decreases dramatically with this solvent composition change if it involves the ratio of activities of the solvent components. The formulation of the equilibrium quotient involving activities of the solvent components seems preferable, despite the greater variation with solvent composition, because this variation, which measures the solvent dependence of a ratio of activity coefficients of chromium(III) species, provides information regarding outer-sphere interaction of the chromium(III) species with the solvent components.

The present work deals with the competition of dimethyl sulfoxide and water for the sixth coordination site in the pentaamminecobalt(III) entity. The reaction

$$Co(NH_3)_5OH_2^{3+} + (CH_3)_2SO = Co(NH_3)_5(OS(CH_3)_2)^{3+} + H_2O$$

like analogous reactions of aquachromium(III) species,[6] occurs very slowly at ordinary temperatures. This allows characterization of the position of equilibrium by the ion-exchange separation procedures used for various inert chromium(III) systems.[6,7] The proton magnetic resonance method also has been used in equilibrium and kinetic studies of this reaction.[8] Of particular interest in the present study are the dependences upon solvent composition of the equilibrium quotients

$$Q(X) = \frac{[Co(NH_3)_5(OS(CH_3)_2)^{3+}]X_W}{[Co(NH_3)_5OH_2^{3+}]X_D}$$

and

$$Q(a) = \frac{[Co(NH_3)_5(OS(CH_3)_2)^{3+}]a_W}{[Co(NH_3)_5OH_2^{3+}]a_D}$$

in which X_W and X_D are the mole fractions of water and dimethyl sulfoxide in the solvent, and a_W and a_D are the corresponding activities. Differences of outer-sphere interactions of reactant and product cobalt(III) species with the two solvent components determine the dependence of $Q(a)$ upon X_D. Study of the rate of establishment of equilibrium in this reaction allows evaluation of the dependence of the rate constants for the forward and reverse reactions upon solvent composition.

Experimental Section

Reagents. Pentaammineaquacobalt(III) perchlorate was prepared from pentaamminecarbonatocobalt(III) nitrate using published procedures.[9,10] It was recrystallized from perchloric acid (2 mol L^{-1}) and from water. Pentaammine(dimethyl sulfoxide)cobalt(III) perchlorate was prepared from pentaammineaquacobalt(III) perchlorate by reaction with excess dimethyl sulfoxide.[11] Hexaaquachromium(III) perchlorate was prepared and purified as described earlier.[6,7] Reagent grade solvents and acids were used without additional purification. (Dimethyl sulfoxide for some experiments was distilled under vacuum before use; there was no observable difference in these experiments.) Water which was distilled twice and was passed through an ion-exchange demineralizer between distillations was used in preparing all solutions. Cation-exchange resin (Dowex 50W-X4 (100–200 mesh)) was purified as described earlier.[6,7]

Analytical Procedures. Dimethyl sulfoxide was analyzed by oxidation to dimethyl sulfone with excess permanganate ion in acidic solution. The excess permanganate was analyzed using standardized iron(II) solution, with the end point determined potentiometrically. Cobalt(III)–dimethyl sulfoxide species were allowed to aquate in aqueous acid prior to analysis for dimethyl sulfoxide. The presence of cobalt and ammonium ion was shown to have no effect on the analysis. The cobalt content of various species was determined spectrophotometrically after conversion to tetrathiocyanatocobalt(II) ion.[12] Pentaamminecobalt(III) species were decomposed by heating in alkaline solution prior to this analysis. The ammonia content of complexes was determined after decomposition of the species by excess sodium hydroxide in an all-glass distillation apparatus. The liberated ammonia was distilled into aqueous boric acid solution, where its amount was determined by titration with hydrochloric acid to the bromcresol green end point. The free acid content of solutions containing cobalt(III) complexes was determined using an ion-exchange procedure for evaluation of the total normality.[13]

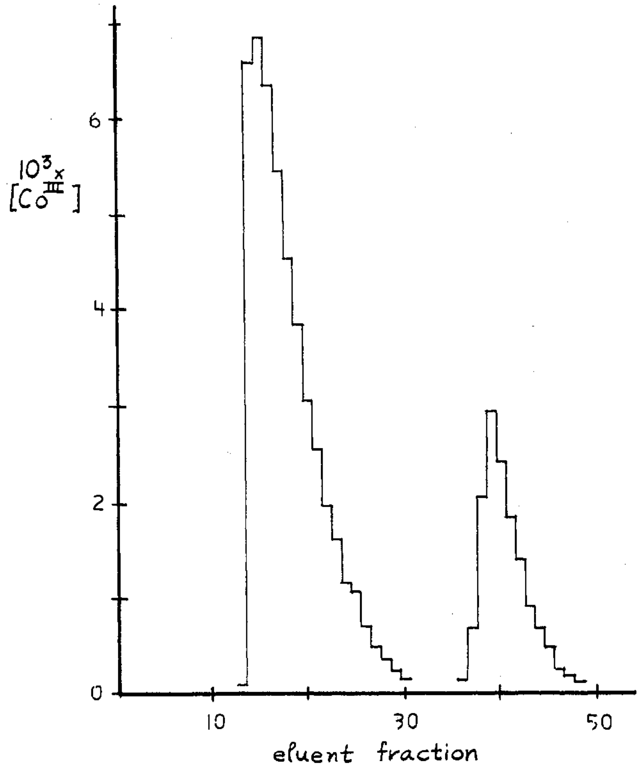

Figure 1. The separation of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5OS(CH_3)_2^{3+}$ by an ion-exchange column procedure. (Composition of equilibrated solution: 7.0×10^{-3} M Co^{III}, 0.034 M $HClO_4$, $X_D = 0.49$; temperature of equilibration, 35 °C.) Eluting agent: fractions 1–32, 2.5 M H_2SO_4; fractions 33–62, 4.0 M H_2SO_4. The first elution peak contains $Co(NH_3)_5OH_2^{3+}$ and the second elution peak contains $Co(NH_3)_5(OS(CH_3)_2)^{3+}$.

Equipment. Spectrophotometric studies were made using Cary recording spectrophotometers (Models 15 or 17). A thermostated cell holder was used in all measurements designed to study outer-sphere interactions at a particular temperature. Refractive index measurements were made using an Abbé refractometer (Bausch and Lomb Optical Co.), with calibration using water, ethanol, and carbon disulfide.

Experimental Results

Determination of $\bar{d}$. Solutions containing pentaammineaquacobalt(III) perchlorate or pentaammine(dimethyl sulfoxide)cobalt(III) perchlorate in acidic mixed solvents of various compositions were kept at 35, 50, and 60 °C for approximately 10 half-times for the establishment of equilibrium. (It was shown by pH measurements on several solutions that loss of coordinated ammonia does not occur.) The equilibrated solution was quenched with cold (~0 °C), dilute (~0.1 mol L^{-1}), aqueous perchloric acid to make the mole fraction of dimethyl sulfoxide less than 0.1. The cobalt(III) species in the quenched solutions were taken into a cation-exchange resin phase (Dowex 50W-X4, 100–200 mesh, hydrogen ion form). The dimethyl sulfoxide containing solvent was rinsed away with dilute perchloric acid (~0.1 mol L^{-1}), which does not elute the cobalt(III) species. Removal of all cobalt(III) species ($Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5(OS(CH_3)_2)^{3+}$) was accomplished by elution with sulfuric acid (4 mol L^{-1}). In some experiments, the cobalt(III) species were separated from one another by eluting first with 2.5 M H_2SO_4 (which elutes $Co(NH_3)_5OH_2^{3+}$) and then with 4.0 M H_2SO_4 (which elutes $Co(NH_3)_5(OS(CH_3)_2)^{3+}$). In the former procedure, lasting 4–5 h, a column of resin 1 cm in diameter × ~3 cm in length was used, and in the latter procedure, lasting 30–40 h, a 1-cm diameter × ~34-cm length column was used. The columns were maintained at 0–2 °C in both types of separations. An elution profile showing the separation of the two cobalt(III) species is shown in Figure 1. The ratio of amounts of bound dimethyl sulfoxide to cobalt, n_D/n_{Co}, in a portion of eluent was determined by the analyses for dimethyl sulfoxide and cobalt, already described. Applied to the separated species (see Figure 1), these analyses identify the more easily eluted species as $Co(NH_3)_5OH_2^{3+}$ ($n_D/n_{Co} = 0.00 \pm 0.03$) and the less easily eluted species as $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ ($n_D/n_{Co} = 1.00 \pm 0.03$). Applied to the entire eluent in the short column experiments, in which the recovery of cobalt was 99 ± 1%, the values of n_D/n_{Co} are the values of $\bar{d}$, the average number of dimethyl sulfoxide molecules bound per cobalt(III) ion.

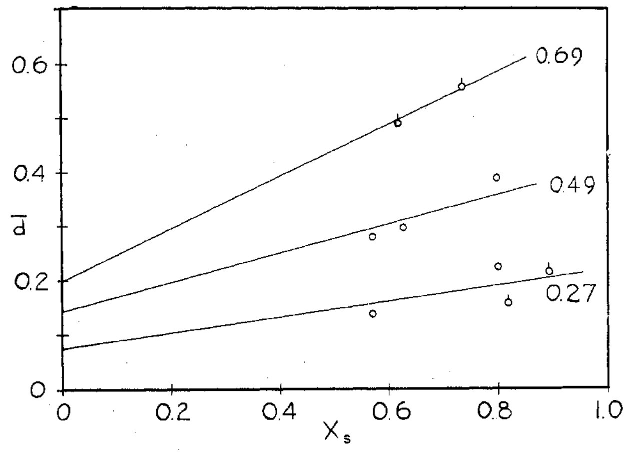

Figure 2. The influence of a third solvent component upon the value of $\bar{d}$. t = 35 °C: (○) p-dioxane, (ȯ) tetrahydrofuran. Each line is labeled with the value of X_D/X_W; the intercept of each line at $X_S = 0$ is the value of $\bar{d}$ for the binary solvent with this value of X_D/X_W.

Values of $\bar{d}$ for solutions of pentaamminecobalt(III) equilibrated at 35 °C (given as X_D, $\bar{d}$) are: 0.059, 0.015; 0.142 ± 0.002, 0.044 ± 0.004 (five samples); 0.167, 0.048; 0.196, 0.064; 0.264 ± 0.002, 0.105 ± 0.01 (five samples); 0.271, 0.109; 0.364, 0.166; 0.476 ± 0.003, 0.260 ± 0.006 (two samples); 0.481, 0.261 ± 0.01 (two samples); 0.491 ± 0.001, 0.274 ± 0.007 (four samples); 0.663 ± 0.001, 0.480 ± 0.02 (two samples); 0.680, 0.481; 0.728, 0.525; 0.779, 0.62; 0.807, 0.671; and 0.837, 0.688. One or more of the solutions studied at each of the solvent compositions X_D = 0.264, 0.481, 0.491, 0.680, 0.728, and 0.779 were analyzed by the long column procedure which allowed separation of aquapentaamminecobalt(III) ion and (dimethyl sulfoxide)pentaamminecobalt(III) ion. The concentrations of cobalt(III) and hydrogen ion in most of the equilibrated solutions were 0.007 and 0.032 mol L^{-1}, respectively. Variations of the concentration of cobalt(III) between 0.0038 and 0.014 mol L^{-1} and the concentration of hydrogen ion between 0.001 and 0.032 mol L^{-1} did not change the value of $\bar{d}$ appreciably. Values of $\bar{d}$ were obtained also at 50 and 60 °C for solutions of composition X_D = 0.142, 0.268, and 0.490. The values of $\bar{d}$ at these temperatures (given as X_D, $\bar{d}_{50}$, $\bar{d}_{60}$) are: 0.142, 0.043, 0.043; 0.268, 0.10, 0.10; and 0.490, 0.26, 0.30.

The value of $\bar{d}$ also was determined for pentaamminecobalt(III) in ternary solvents containing a noncoordinating ether, p-dioxane, or tetrahydrofuran, in addition to water and dimethyl sulfoxide. The solvents studied had ratios of the mole fraction of dimethyl sulfoxide to the mole fraction of water (X_D/X_W) equal to 0.27, 0.49, and 0.69. These data are plotted in Figure 2 as a function of X_S, the mole fraction of the third solvent component.

The Rate of Establishment of Equilibrium. The rate of establishment of equilibrium in mixed solvents of various composition was determined by measurement of light absorption as a function of time. The absorption at peaks in the

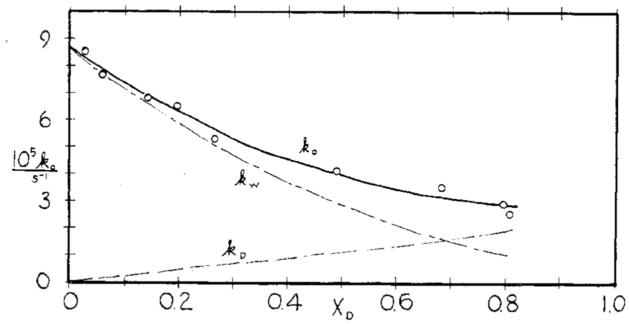

Figure 3. The rate constant for approach to equilibrium, $k_0 = \mathrm{d}\ln(|A_t - A_{t+\tau}|)/\mathrm{d}t$, or $k_0 = \mathrm{d}\ln(|A_t - A_\infty|)/\mathrm{d}t$, as a function of solvent composition. For $X_D < 0.3$, $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ was the starting material; for $X_D > 0.3$, $Co(NH_3)_5(OH_2)^{3+}$ was the starting material. Smooth curve was calculated using equation $10^5 k_0/s^{-1} = 8.64 - 13.3X_D + 7.75X_D^2$. The dashed lines give $k_D = k_0\bar{d}$ and $k_W = k_0(1 - \bar{d})$.

Table I. The Rate Constant k_0 for the Establishment of Equilibrium in the Reaction[a]
$Co(NH_3)_5OH_2^{3+} + (CH_3)_2SO = Co(NH_3)_5(OS(CH_3)_2)^{3+} + H_2O$

	$10^5 k_0$, s^{-1}		
X_D	35 °C	50 °C	60 °C
0.059	7.8[b]	48	150
0.141	6.8	46	160
0.266	5.3	43	130
0.486	4.1[c]	28	90

[a] 0.032 M $HClO_4$, 0.007 M Co^{III}; uncertainty in k_0 is ~3%. [b] $X_D = 0.058$. [c] Average of five experiments at $X_D = 0.481$ to 0.500.

near-ultraviolet and visible regions of the spectrum (λ 345 nm and λ 490 nm for $Co(NH_3)_5OH_2^{3+}$ in acidic aqueous solution) becomes more intense as dimethyl sulfoxide replaces coordinated water. In addition, the peak in the visible region of the spectrum shifts to longer wavelengths. To make the observed changes as large as possible, the starting material at $X_D < 0.3$ was $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ and at $X_D > 0.3$ it was $Co(NH_3)_5OH_2^{3+}$. Both the Guggenheim method[14] and use of the infinity time light absorption were used to evaluate k_0:

$$k_0 = \mathrm{d}\ln(|A_t - A_{t+\tau}|)/\mathrm{d}t \quad \text{or} \quad \mathrm{d}\ln(|A_t - A_\infty|)/\mathrm{d}t$$

in which A_t is the value of $\log(I_0/I)$ at time t, and τ is the constant time interval of the Guggenheim method. A first-order approach to equilibrium was observed in each case. Values of k_0 so determined are uncertain to ±3%; the values for 35 °C as a function of solvent composition are presented in Figure 3. Certain solvent compositions also were studied at 50 and 60 °C.[15] These data are summarized in Table I.

Spectral Studies. Spectrophotometric measurements were made for: (a) acidic solutions (~0.032 M $HClO_4$) with a range of values of X_D containing pentaamminecobalt(III) ion which had been equilibrated at 35 °C; (b) aqueous solutions of the equilibrium mixture of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5(OS(CH_3)_2)^{3+}$, these species having been separated from the binary solvent by ion exchange; and (c) solutions of the separate species ($Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5(OS(CH_3)_2)^{3+}$) in acidic mixed solvents, with the spectral measurements being made immediately after preparation of the solution. In measurements of type (c), the molar absorbancy indices of each of the species depend upon solvent composition. At 505 nm, the molar absorbancy index of $Co(NH_3)_5OH_2^{3+}$ increases from 45.3 to 54.2 L mol^{-1} cm^{-1} in going from $X_D = 0$ to $X_D = 1$; at 345 nm, the increase was from 44.3 to 57.4 L mol^{-1} cm^{-1}. For $Co(NH_3)_5(OS(CH_3)_2)^{3+}$, the changes of absorbancy index for this same solvent change were 57.4 to 62.7 L mol^{-1} cm^{-1} at 505 nm and 58.7 to 69.1 L mol^{-1} cm^{-1} at 345 nm. The same trend in molar absorbancy index with solvent composition was observed for hexaaquachromium(III) ion in acidic solution (0.134 M $HClO_4$). At 590 nm, the value increases from 12.6 to 15.4 L mol^{-1} cm^{-1}, and at 410 nm the value increases from 15.5 to 18.8 L mol^{-1} cm^{-1} with a change of X_D from 0 to 0.896.

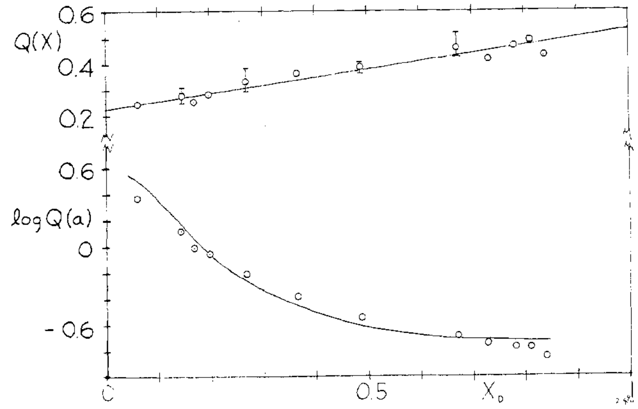

Figure 4. $Q(X)$ and $Q(a)$ as function of solvent composition. Upper figure: $Q(X)$ vs. X_D. Range of values of $Q(X)$ is indicated at X_D values where 2 or more samples were run. The line is $Q(X) = 0.23 + 0.30X_D$. Lower figure: $\log Q(a)$ vs. X_D. The line is calculated using $Q^0(a) = 4.3$, $q_P = 2.6$, $q_R = 60$.

The spectra of equilibrium mixtures of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ in aqueous solution (after separation of the cobalt(III) species from the binary solvent by ion exchange) and in the binary solvent of equilibration differed in an important respect. In the former measurements, those in which the spectra were measured in aqueous solution, isosbestic points were observed at ~420 and ~480 nm. In the latter measurements, those in which the spectra were measured in the mixed solvent, there were not well-defined isosbestic points. For these equilibrated solutions, the peak position in the ultraviolet region (345 nm) does not shift appreciably with solvent composition. At this wavelength, values of the light absorption as a function of solvent composition (given as X_D, $\bar{a} = ((\log I_0/I)/[Co^{III}] \times \text{cell length})/\mathrm{L\ mol^{-1}\ cm^{-1}}$) are: 0.059, 46.0; 0.142, 47.5; 0.263, 50.2; 0.271, 50.5; 0.364, 52.8; 0.476, 55.0; 0.492, 55.8; 0.664, 60.0; and 0.837, 64.5.

For correlation with spectral measurements, the refractive index of acidic solutions of aquachromium(III) ion (0.134 M $HClO_4$, 0.0285 M $Cr(ClO_4)_3$) was measured in media of different values of X_D. These values (gives as X_D, n_D) are: 0.0050, 1.3405; 0.016, 1.3464; 0.028, 1.3523; 0.058, 1.3672; 0.098, 1.3822; 0.143, 1.3976; 0.264, 1.4274; 0.473, 1.4564; and 0.896, 1.4765.

Derived Quantities

The values of $\bar{d}$ derived from analysis of the total cobalt(III)-containing eluent for cobalt and dimethyl sulfoxide allow calculation of values of the equilibrium quotients, $Q(X)$ and $Q(a)$:

$$Q(X) = \bar{d}X_W/(1 - \bar{d})X_D$$

$$Q(a) = \bar{d}a_W/(1 - \bar{d})a_D$$

Values of $Q(X)$ as a function of solvent composition, which are presented in Figure 4, vary linearly with X_D. The equation $Q(X) = 0.23 + 0.30\,X_D$, obtained by a method of averages fitting of all data points, gives upon substitution into the equation relating $\bar{d}$ to $Q(X)$:

$$\bar{d} = (0.23 + 0.30X_D)X_D/(1 - 0.77X_D + 0.30X_D^2)$$

The average difference between values of $\bar{d}$ so calculated and the experimental values is 0.007.[16] (This average difference omits one point for which the differences is 0.046 units of $\bar{d}$.) Introduction of activity coefficients for the solvent components, calculated from vapor pressure and heat of mixing data,[17] as described earlier,[6] allows calculation of values of $Q(a)$, which are presented in Figure 4. (In this calculation, the standard state for each solvent is the pure solvent component. At 35 °C the limiting value of γ_D at $X_D = 0$ is 0.057, and that of γ_W at $X_W = 0$ is 0.249.)

The rate constant, k_0, for the first-order approach to equilibrium can be resolved into the first-order rate constants for the forward reaction k_D and the reverse reaction k_W, which are defined by the rate law

$$-\frac{d[Co(NH_3)_5OH_2{}^{3+}]}{dt} = k_D[Co(NH_3)_5OH_2{}^{3+}] - k_W[Co(NH_3)_5(OS(CH_3)_2)^{3+}]$$

The values of k_D and k_W for the reaction in each solvent composition are related to the values of k_0 and $\bar{d}$:

$$k_D = k_0\bar{d} \qquad k_W = k_0(1 - \bar{d})$$

Values of d_D and k_W are presented in Figure 3, which shows the dependence of each upon solvent composition.

Since $\bar{d}$ and, therefore, $Q(X)$ do not vary appreciably with temperature, values of the activation energies associated with rate constants for the forward and reverse reactions, k_D and k_W, can be taken as the same as the value associated with k_0, the rate constant for the approach to equilibrium. This value is

$$E_a = 25.4 \pm 1.3 \text{ kcal mol}^{-1}$$

Although variation in the activation energy with solvent composition is small, the trend (E_a increases with an increase of X_D) may be real. If so, extrapolation to $X_D = 0$ gives $E_a = 24.4$ kcal mol^{-1}, which agrees with the value 23.9 ± 0.7 kcal mol^{-1} reported for the aquation of $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ in aqueous 0.001 M perchloric acid.[18]

Discussion

For the reaction under consideration, the complete equilibrium constant equation is

$$K^0 = \frac{[Co(NH_3)_5(OS(CH_3)_2)^{3+}]\,\gamma_P X_W \gamma_W}{[Co(NH_3)_5(OH_2)^{3+}]\,\gamma_R X_D \gamma_D}$$

in which γ_P, γ_R, γ_W, and γ_D are activity coefficients of the product and reactant cobalt(III) species, water, and dimethyl sulfoxide, respectively. The equilibrium quotients which have been presented are related to this equilibrium constant:

$$Q(X) = K^0(\gamma_R\gamma_D/\gamma_P\gamma_W)$$

$$Q(a) = K^0(\gamma_R/\gamma_P)$$

The variation of $Q(X)$ and $Q(a)$ with changing solvent composition is a consequence of variation of the quotient of activity coefficients appearing in each of these equations. The values of $Q(X)$ vary with changing solvent composition less than do the values of $Q(a)$, but this should not be over-interpreted to the conclusion that the ratio of the mole fractions of the solvent components is the variable which determines the extent of reaction. If the ratio of activity coefficients $\gamma_R\gamma_D/(\gamma_P\gamma_W)$ were independent of solvent composition, the extent of reaction in the ternary solvents would be independent of X_S at a constant value of X_D/X_W. The experimental results displayed in Figure 2 show that this is not the case. The trend shown in this figure, an increasing extent of reaction with increasing concentration of ether, the inert solvent component, is consistent with preferential attractive hydrogen bonding between water and the ether. This would cause the ratio of a_D/a_W to increase with an increase of X_S at constant X_D/X_W. Nonetheless, the linear dependence of $Q(X)$ upon the mole fraction of dimethyl sulfoxide allows a particularly simple empirical correlation of $\bar{d}$ with solvent composition. For the purpose of extrapolating the value of $Q(X)$ to $X_D = 0$, use of this linear plot seems superior to other approaches. This correlation disguises, however, the outer-sphere interactions revealed by the dependence of $Q(a)$ upon solvent composition. The value of $Q(a)/Q^0(a)$ decreases from 0.372 at $X_D = 0.059$ to 0.0317 at $X_D = 0.837$. (The value of $Q(X)$ extrapolated to $X_D = 0$ divided by the value of γ_D at $X_D = 0$ gives the limiting value of $Q(a)$, $Q^0(a)$.) A qualitatively similar trend in the values of $Q_1(a)$ for the reaction

$$Cr(OH_2)_6{}^{3+} + (CH_3)_2SO = Cr(OH_2)_5(OS(CH_3)_2)^{3+} + H_2O$$

(and in values of equilibrium quotients for other analogous reactions in this system) has been interpreted[6] in terms of outer-sphere solvation of the coordination complex by solvent dimethyl sulfoxide. This outer-sphere interaction was assumed to involve hydrogen bonding between coordinated water molecules and solvent dimethyl sulfoxide. In each stepwise reaction, the reactant chromium(III) species has one more coordinated water molecule than the product chromium(III) species. This same relationship exists between the product and reactant cobalt(III) species in the reaction studied in the present paper. If variation of $Q(a)$ is due to differences of outer-sphere interactions of solvent components with reactant and product cobalt(III) species, a quantitative correlation of this variation is possible. If the reactions

$$Co(NH_3)_5So^{3+}\cdot H_2O + (CH_3)_2SO \rightleftarrows Co(NH_3)_5So^{3+}\cdot OS(CH)_2 + H_2O$$

where So = H_2O or $(CH_3)_2SO$, are assumed to be an adequate model for the outer-sphere interactions, the dependence of $Q(a)$ upon r_a ($r_a = a_D/a_W$) is:

$$Q(a) = Q^0(a)\frac{1 + q_P r_a}{1 + q_R r_a}$$

in which q_P and q_R are equilibrium quotients for the outer-sphere reactions involving product ($Co(NH_3)_5(OS(CH_3)_2)^{3+}$) and reactant ($Co(NH_3)_5OH_2{}^{3+}$), respectively. With $Q^0(a) = 4.3$, $q_P = 2.6$, and $q_R = 60$, the calculated values of $Q(a)$ are given as the line in the lower part of Figure 4. The values of $\bar{d}$ calculated using these values of $Q(a)$ differ from the observed values by an average of 0.022 units of $\bar{d}$. The corresponding values for $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ (product) and $Cr(OH_2)_6{}^{3+}$ (reactant) at 60 °C are $q_P = 51$ and $q_R = 125$.[19] (To be compared with conventional outer-sphere association constants based upon molar concentration units and assumed ideality of dilute solutions, these values must be multiplied by $\gamma_D/55.5$. The values for $Co(NH_3)_5(OS(CH_3)_2)^{3+}$ and $Co(NH_3)_5OH_2{}^{3+}$ at 35 °C become $q_P = 0.027$ and $q_R = 0.062$, and those for $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ and $Cr(OH_2)_6{}^{3+}$ at 60 °C become $q_P = 0.093$ and $q_R = 0.23$.) Although rigorous quantitative interpretation of these outer-sphere association constants probably is not justified, the relative values of q_P and q_R for the two systems ($Co(NH_3)_5So^{3+}$ and $Cr(OH_2)_5So^{3+}$) support the notion that the dominant factor governing the outer-sphere interactions is hydrogen bonding between coordinated water and solvent dimethyl sulfoxide. Hydrogen bonding between coordinated ammonia and solvent dimethyl sulfoxide would be expected to be weaker.

Outer-shere interaction between the inert coordination complex and the solvent components also is suggested by the spectral measurements. The increase in light absorption with increasing proportion of dimethyl sulfoxide in the solvent is greater for $Co(NH_3)_5OH_2{}^{3+}$ than it is for $Co(NH_3)_5(OS(CH_3)_2)^{3+}$. Because of the similarity of these two systems, it probably is appropriate to interpret this greater spectral change for $Co(NH_3)_5OH_2{}^{3+}$ as indicating a greater interaction of this species with $(CH_3)_2SO$, thereby supporting the relative values of the outer-sphere association constants for $Co(NH_3)_5So^{3+}$ with dimethyl sulfoxide derived from the dependence of $Q(a)$ upon X_D.

The interpretation of mild spectral changes with major changes of solvent composition strictly in terms of a shifting of equilibrium between two differently solvated species is uncertain. A major change of solvent composition may cause an appreciable change of the refractive index of the solvent. The refractive indices of water and dimethyl sulfoxide at 25 °C measured at the sodium D line are 1.333 and 1.476, respectively.[20] If one assumes the simplest theory for this medium dependence of light absorption, the oscillator strength of a transition is related to the function $(n^2 + 2)^2/n$.[21] For water and dimethyl sulfoxide the values of this function are 10.70 and 11.83, respectively. Since the cobalt species in the present study is relatively transparent at the sodium D line, direct calculations pertaining to spectral data obtained for the cobalt species are not possible. Limited measurements on hexaaquachromium(III) ion in aqueous dimethyl sulfoxide suggest that the effect of changing the solvent upon the molar absorbancy index of hexaaquachromium(III) ion at 590 nm is comparable to the expected effect of refractive index upon the oscillator strength of the transition. For a system in which the associative interaction is weak, and for which, therefore, the ligand concentration must be extended to high concentrations, the use of small spectral changes to evaluate the equilibrium quotient for association is fraught with difficulty.

Reynolds, Barber, and Crandall[8] have concluded on the basis of rate comparisons for certain exchange reactions that the reaction under consideration proceeds by a dissociative mechanism. Since we have interpreted the dependence of $Q(a)$ upon solvent composition in terms of outer-sphere association, it is possible to calculate the rate constants and equilibrium constant associated with the dissociative interchange:

$$Co(NH_3)_5OH_2{}^{3+}\cdot OS(CH_3)_2 \underset{k_W'}{\overset{k_D'}{\rightleftharpoons}} Co(NH_3)_5(OS(CH_3)_2)^{3+}\cdot H_2O$$

The relationships are:

$$k_D' = k_D(1 + (q_R r_a)^{-1})$$

$$k_W' = k_W(1 + q_P r_a)$$

The values of k_D' and k_W' calculated in this way increase by a factor of ~4 in going from $X_D = 0.1$ to $X_D = 0.8$. The value of the quotient k_D'/k_W', which is the equilibrium quotient for the interchange reaction, varies between 0.06 and 0.09.

The problems associated with rational quantitative discussion of the stability of species in solution is illustrated amply by this system. If the equilibrium quotient based upon mole fraction units is considered, one would conclude that pentaamminecobalt(III) discriminates in its sixth coordination site in favor of water over dimethyl sulfoxide. The basis for this conclusion is the fact that $Q(X) < 1$ for all values of X_D. If the equilibrium quotient based upon activities of the solvent components is considered, the conclusion that water is favored in the first coordination shell is suggested by the data only for $X_D > 0.16$.

Registry No. $Co(NH_3)_5OH_2{}^{3+}$, 14403-82-8; $Co(NH_3)_5(OS(CH_3)_2)^{3+}$, 44915-85-7.

References and Notes

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(15) Interpolation of values of k at $X_D = 0.059$ and 0.486 to 45 °C gives values within experimental error of values reported by Reynolds, Barber, and Crandall[8] for $X_D = 0.0545$ and 0.480 for this temperature.

(16) Use of this equation $\bar{d} = f(X_D)$ to calculate values of $\bar{d}$ for the compositions of solution studied by Reynolds, Barber, and Crandall[8] at 45 °C gives values which are slightly lower than the observed values. The average difference is 16%.

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(19) In ref 6, the choice of standard state for dimethyl sulfoxide in describing the outer-sphere interaction was the hypothetical pure liquid with properties extrapolated from dilute aqueous solutions. The values of q_P and q_R given above are based upon the same standard states as employed in this study. Since the dependence of Q_1 for aquachromium(III) ion upon solvent composition covered only the range $X_D = 0.00365$ to 0.104 in which range a_W varies only 13%, the activity of water was not incorporated in the equations for q_P and q_R.

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