Solvation of Chromium(III) Ion in Water–Alcohol Solution[1]

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Abstract: The solvation of chromium(III) ion in acidic water–methanol mixed solvents has been studied over the range of solvent composition Z (mole fraction of alcohol) = 0.20–0.997. Species containing 0–6, inclusive, bound methanol molecules have been separated from one another by column cation-exchange procedures; this allows unambiguous analysis of equilibrated solutions and the evaluation of equilibrium quotients for stepwise replacement of each water molecule in hexaaquochromium(III) ion by methanol. For 60°, these equilibrium quotients are $Q_1 = 0.65$, $Q_2 = 0.21$, $Q_3 = 0.072$, $Q_4 = 0.028$, $Q_5 = 0.012$, and $Q_6 = 0.0022$. (The standard state for each solvent component is the pure liquid.) A slight extension of earlier work on solvation of chromium(III) ion in water–ethanol solution has allowed evaluation of Q_3 and Q_4 for that system at 75°.

Jayne and King[3] have studied the solvation of chromium(III) ion in acidic water–methanol mixed solvents; their data ($\bar{n}$, the average number of methanol molecules bound per chromium(III) ion as a function of solvent composition) allowed evaluation of equilibrium quotients for reactions forming species containing one, two, and three bound methanol molecules. A puzzling feature of their results was the apparently greater stability (after appropriate allowance for the statistical factor) of the species containing two bound methanol molecules. More recent studies on similar systems[4–6] have shown that differently solvated species can be separated from one another by appropriate ion-exchange elution procedures. Such separation procedures have been applied successfully to chromium(III) species in water–methanol solutions in the present study. (In the earlier study,[3] it was found that hexaaquochromium(III) ion was the most easily eluted of the differently solvated species, but essentially quantitative separation was not accomplished.) The earlier study has been extended, and equilibria involving species containing four, five, and six bound methanol molecules have been characterized.

In addition to extending the solvent composition range of the earlier study, the present work allows investigation of possible medium effects upon the equilibrium quotients. (If medium effects are appreciable, $\bar{n}$ data cannot lead to correct values for the equilibrium quotients.[4])

Experiments also have been performed which extend the earlier study[4] of solvation of chromium(III) in water–ethanol mixed solvents.

Experimental Methods and Results

Reagents. Chromium(III) perchlorate was prepared by the reaction of chromium(VI) oxide with hydrogen peroxide in perchloric acid solution. The crystalline hydrated solid, obtained by partial evaporation of the reaction mixture, was found to contain inappreciable polymeric chromium(III) species; the ratio of absorbance at 230–260 nm was 0.26.[7]

Solutions for equilibration were prepared from doubly distilled water, reagent grade anhydrous methanol or ethanol (used without further purification), perchloric acid, and a stock solution of chromium(III) perchlorate in aqueous perchloric acid. For some of the water–ethanol solutions, the water content was lowered by addition of 2,2-diethoxypropane.[8] (The solvent composition will be expressed in terms of the mole fraction of alcohol Z, in the calculation of which only free water and alcohol are taken into account. As in the earlier study,[3] it is assumed in the calculation of Z that hydrogen ion is solvated preferentially by one water molecule.)

Equilibration of Methanol–Water Solutions and Their Analysis. Solutions with 0.002–0.010 M chromium(III) perchlorate and 0.02–0.10 M perchloric acid were equilibrated at 60.0° for 11–22 hr, a time shown to be long enough for solvation equilibrium to be established. Portions of equilibrated solution containing 2–5 mmol of chromium(III) were quenched by cooling to −14°; in some cases samples were stored at this temperature for up to 7 days before analysis. Chromium(III) species from the quenched sample were absorbed into Dowex 50W-X12 (200–400 mesh) resin in a batch operation. Free methanol was rinsed from this resin with chilled 0.10 M perchloric acid. The resin containing chromium(III) was then added to the top of a previously prepared column containing resin in the hydrogen ion form. Two types of elution procedures were employed. In one procedure, short columns (∼16 in.) were used, the eluting agent employed was 1.8 M sulfuric acid, and the elapsed time during a complete elution was 14–24 hr. In the other procedure, longer columns (∼4 ft) were used, gradient elution with 1.0–2.5 M sulfuric acid was employed, and the elapsed time during elution was ∼5 days. These two different elution procedures were employed to check whether partial aquation of the methanolchromium(III) species occurred during elution. Analyses of eluent portions for chromium and methanol (by described procedures[3]) showed the order of elution of differently solvated species to be the order of increasing numbers of bound methanol

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[2] National Science Foundation Predoctoral Trainee, 1968–1969.

[3] J. C. Jayne and E. L. King, *J. Amer. Chem. Soc.*, **86**, 3989 (1964); see also R. J. Baltisberger and E. L. King, *ibid.*, **86**, 795 (1964).

[4] D. W. Kemp and E. L. King, *ibid.*, **89**, 3433 (1967), on chromium(III) in water–ethanol solutions.

[5] T. J. Weeks, Jr., and E. L. King, *ibid.*, **90**, 2545 (1968), on chromium(III) in water–pyridine N-oxide solutions.

[6] L. P. Scott, T. J. Weeks, Jr., D. J. Bracken, and E. L. King, *ibid.*, **91**, 5219 (1969), on chromium(III) in water–dimethyl sulfoxide solution.

[7] C. Altman and E. L. King, *ibid.*, **83**, 2825 (1961).

[8] Analogous to the use of 2,2-dimethoxypropane to remove water: K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1956).

Table I. Composition of Equilibrated Solutions of Chromium(III) in Acidic Water–Methanol Solution (60°, C_{Cr} = 0.010 *M*, C_H = 0.10 *M*)

100*Z*	20.3	26.1[d]	37.2	47.4[e]	62.0	64.2	68.1	75.1[f]	78.4	80.4	84.6[g]	90.8	92.2
P_0	77.2	73.6	67.1	57.1	45.5	39.1	38.6	25.6	23.2	20.2	16.5	7.0	5.4
P_1	18.3	20.9	26.8	34.1	37.3	41.5	42.1	44.5	41.9	42.6	37.8	29.0	26.1
P_2			2.7	6.8	11.7	13.8	15.2	22.4	24.6	26.2	30.2	39.0	39.7
P_3									5.3	7.9	9.3	16.2	20.8
% recovery of Cr	95.5	94.5	96.6	98.0	94.5	94.4	95.9	92.5	95.0	96.9	93.8	91.2	92.0
$\bar{n}$ (exptl)[a]	0.19	0.22	0.33	0.49	0.64	0.73	0.76	0.94	1.13	1.23	1.37	1.71	1.82
$\bar{n}$ (calcd)[b]	0.23	0.29	0.37	0.51	0.76	0.81	0.90	1.11	1.25	1.31	1.52	1.92	2.05
$\bar{n}$ (calcd)[c]	0.23	0.29	0.35	0.48	0.68	0.75	0.81	0.98	1.12	1.17	1.40	1.86	2.04

[a] Calculated from the experimentally observed relative concentrations of various species. [b] Calculated from the equilibrium quotients based upon $\bar{n}$ data presented in ref 3. [c] Calculated from the equilibrium quotients presented in this study. [d] Data averaged from two experiments (both at *Z* = 0.261). [e] Data averaged from two experiments (at *Z* = 0.469 and 0.479). [f] Data averaged from two experiments (at *Z* = 0.748 and 0.754). [g] Data averaged from three experiments (at *Z* = 0.841, 0.847, and 0.850).

Table II. Composition of Equilibrated Water–Methanol Solutions (*Z* > 0.96, 60°)

% Cr recovered	P_n, per cent of chromium(III) present as $Cr(OH_2)_{6-n}(OHCH_3)_n^{3+}$ P_1	P_2	P_3	P_4	P_5	P_6	r_a[a]
87.4	7.2	26.0	35.9	18.3			19[b]
93.0	7.3	28.0	38.0	19.7			19[b]
74.0	5.7	20.3	31.2	16.8			20[b]
88.0		9.6	26.1	36.6	(16)[c]		38[d]
91.5		7.8	23.9	34.3	25.5		51[e]
90.7		8.4	23.2	37.8	21.3		56[e]
73.8		3.7	9.3	18.6	35.4	6.8	135[f]
83.6			6.9	19.5	41.2	16.0	160[f]
64.3			5.1	13.7	32.2	13.3	180[f]

[a] The ratio of activities of methanol to water, r_a, calculated as described in text, and given in footnotes *b*, *d*, *e*, and *f*. [b] Calculated using Q_2 = 0.21 and Q_3 = 0.072, appropriately weighted.[9] [c] Recovery of this band was incomplete. [d] Calculated using Q_3 = 0.072. [e] Calculated using Q_3 = 0.072 and Q_4 = 0.028, appropriately weighted.[9] [f] Calculated using Q_4 = 0.028 and Q_5 = 0.012, appropriately weighted.[9]

molecules. Table I presents P_n, the percentage of chromium present as a species with *n* bound methanol molecules, as a function of solvent composition. There was no evidence for separation of isomeric species for the compositions *n* = 2 and 3 in the ion-exchange elutions reported in Table I. The $\bar{n}$ values calculated using the complete set of equilibrium quotients are generally somewhat higher than the values obtained from the concentrations of the individual species determined in the elution procedure. This is expected since small amounts of species with higher *n* are undoubtedly lost in the elution procedure. For example, in a solution with *Z* = 0.62, species containing three and four methanol molecules are not recovered in the elution. Yet these species account for ~1.2% of the chromium and 0.036 unit of $\bar{n}$; if their contribution is omitted, the calculated $\bar{n}$ has a value of 0.65.

Because of the unknown solvation of perchlorate ion in the mixed solvent, it is not possible from the stoichiometric composition to estimate the relative amounts of free water and methanol in solutions containing little water. For this reason experiments in the earlier study[3] were not attempted at *Z* > 0.98. Although this limitation has not been overcome, ion-exchange separations have been applied to solutions containing an appreciable amount of species containing four, five, and six bound methanol molecules. The results are summarized in Table II. There was no evidence for separation of isomeric species with *n* = 2, 3, and 4 in the elutions reported in Table II. It is seen that the recovery of chromium was poor (<80%) in two of these samples. The concentration of polymeric chromium(III) species increases slowly during equilibration of solutions of high *Z*, and the low recovery is attributed to this. These difficultly eluted polymeric species do not contaminate appreciably the other elution bands, and there is no evidence that the relative concentrations of the monomeric species are influenced to an appreciable extent by this slow side reaction.

Equilibration of Ethanol–Water Solutions and Their Analysis. Solutions were equilibrated at 75° for 0.5–5 hr. (In one experiment at *Z* > 0.95, the half-time for establishment of equilibrium was found to be ~7 min at 75°. Solutions were equilibrated at this temperature for ≥3 hr in the earlier study of this system.[4]) In order to reduce the complicating effects due to production of polymeric chromium(III) species during long equilibration, some solutions were equilibrated for a shorter time. The equilibrated solutions, which had stoichiometric composition 0.0013–0.010 *M* chromium(III) perchlorate, and 0.013–0.13 *M* perchloric acid, were processed and analyzed as already described.[4] The results are summarized in Table III. Separation of the individual differently solvated monomeric chromium(III) species by column cation-exchange procedures is accomplished more readily for the water–ethanol system than for the water–methanol system, and effective

Table III. Composition of Equilibrated Water–Ethanol Solutions (75°)

% Cr re-covered	Equilibration time, hr	P_n, % of chromium present as $Cr(OH_2)_{6-n}(OCH_2H_5)_n^{3+}$ P_0	P_1	P_2	P_3	P_4	r_a
96.0	5	11.7	40.5	34.9	8.9		7.1[a]
90.0	5	6.9	30.5	39.2	13.4		10.2[a]
89.9	5	5.8	27.1	38.1	18.9		11.0[a]
88.9	1	1.1	12.1	34.9	32.0	8.8	23.2[b]
95.8	0.5	1.1	12.2	36.1	36.5	10.0	24.3[b]
75.0	0.5		3.4	19.9	31.8	19.9	41[b]

[a] Calculated using Q_1 = 0.42 and Q_2 = 0.128, appropriately weighted.[9] [b] Calculated using Q_2 = 0.128 and Q_3 = 0.039, appropriately weighted.[9]

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(9) In obtaining the average, each value of Q_n was weighted by a factor ($f_n \times f_{n-1}$), where f_n is the fraction of chromium(III) present as the species with *n* bound alcohol molecules. This same weighting procedure was employed in calculation of r_a values (see text and Tables II and III).

separation of species containing 0–4 bound ethanol molecules was achieved. No separation of isomeric species was achieved. It was found that separations on solutions with high ethanol content were complicated by the presence of chromium species, presumably polymeric, which were eluted partially with bands due to the monomeric species. The consistency of the data reported in Table III suggests that complications due to these polymeric species were not appreciable in these particular experiments.

Spectra of $Cr(OH_2)_{6-n}(OHCH_3)_n^{3+}$ (n = 0–3, Inclusive). The substitution of methanol for water in the first coordination shell around chromium(III) causes little variation in the visible spectrum of the species. Spectral measurements were made upon 1.8–2.3 *M* sulfuric acid solutions of species containing 0–3 bound methanol molecules. The positions of maxima and the molar absorbancy indices for these species [given as n, λ_{max} (nm) (a (l. mol^{-1} cm^{-1}))] are: 0, 409 (15.6), 574 (13.4); 1, 410 (16.2), 575 (13.8); 2, 410 (16.8), 578 (14.2); and 3, 414 (17.2), 580 (14.5).

Derived Results

Calculation of the equilibrium quotients Q_n

$$Q_n = \frac{[Cr(OH_2)_{6-n}(OHR)_n{}^{3+}]}{[Cr(OH_2)_{7-n}(OHR)_{n-1}{}^{3+}]r_a}$$

in which $r_a = a_{ROH}/a_{H_2O}$, is possible from the measured relative concentrations of species with (n − 1) and n bound alcohol molecules if the ratio of activities of the solvent component is known. (The solvent component activity coefficient data were the same as employed earlier.[3,4] The gross solvent composition was corrected for the known binding of solvent components by chromium(III) and for the assumed preferential solvation of hydrogen ion by one water molecule.[3]) This is the situation for the data on the methanol–water system summarized in Table I. Values of Q_1 and Q_2 obtained from these data are plotted as a function of solvent composition in Figure 1. This plot shows no marked dependence of the equilibrium quotients upon solvent composition (such as observed in the water–ethanol system[4]), nor is there any evidence that results from the separations conducted with different column lengths differed appreciably. Considering the scatter of the data, it seems appropriate to obtain the best values of these equilibrium quotients (and Q_3) as the weighted average of the individual values.[9] The values of Q_1, Q_2, and Q_3 so obtained are $Q_1 = 0.65 \pm 0.04$, $Q_2 = 0.21 \pm 0.02$, $Q_3 = 0.072 \pm 0.011$ (in which the uncertainty is the weighted-average[9] difference between these average values and individual experimental values).

For the alcohol-rich solutions summarized in Table II (methanol–water system) and Table III (ethanol–water system), the situation is different; the values of r_a are not known from the composition of the solvent. The values of Q_n can be obtained nonetheless from the relative concentrations of species with n, (n − 1), and (n − 2) bound alcohol molecules if the value of Q_{n-1} is known. The value of r_a in a solution can be calculated from the relative concentrations of species with (n − 1) and (n − 2) bound alcohol molecules

$$r_a = \frac{[Cr(OH_2)_{7-n}(OHR)_{n-1}{}^{3+}]}{[Cr(OH_2)_{8-n}(OHR)_{n-2}{}^{3+}]Q_{n-1}}$$

if the value of Q_{n-1} is known for the solvent in question. If the relative concentrations of species with (n − 2) and (n − 3) bound alcohol molecules and the value of Q_{n-2} are known, these data provide another source of a value for r_a.

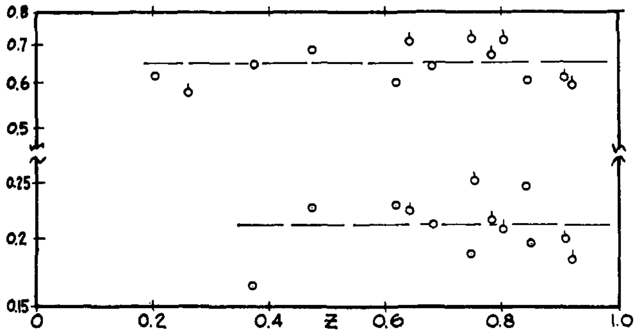

Figure 1. Q_1 (upper points) and Q_2 (lower points) as a function of solvent composition (Z = mole fraction of methanol). ȯ designates short column separation of species (see text). Horizontal lines show weighted-average values of Q_1 (0.65) and Q_2 (0.21). (The ordinate is a logarithmic scale.)

The data in Table II allowed the following calculations. Data from the first three solutions were used to evaluate Q_4, the value of r_a being a weighted-average[9] value obtained from the values of Q_2 and Q_3. The value of r_a for the fourth solution is based upon the value of Q_3; it allows calculation of Q_4. The weighted-average value of Q_4 obtained from these four solutions is 0.028 ± 0.003. Data from the next two solutions were used to evaluate Q_5, the values of Q_3 and Q_4 being used to evaluate r_a. The value of Q_5 so obtained is 0.012 ± 0.002. Data from the next three solutions allowed the calculation of Q_6, the values of Q_4 and Q_5 being used to evaluate r_a. The value of Q_6 so obtained is 0.0022 ± 0.0002. Values of each equilibrium quotient are summarized in Table IV. (Since the data are

Table IV. Equilibrium Quotients[a] for the Reactions $Cr(OH_2)_{7-n}(OHR)_{n-1}{}^{3+} + ROH = Cr(OH_2)_{6-n}(OHR)_n{}^{3+} + H_2O$

n	Q_n(exptl)	Q_n(cor)[b]	Q_n(calcd)	Q_n(calcd)
		R = CH_3 (t = 60°)		
1	0.65	0.11	0.70[d]	(0.70)[f]
2	0.21	0.084	0.20[d]	0.20[f]
3	0.072	0.054	0.072[d]	0.072[f]
4	0.028	0.038	0.027[d]	0.027[f]
5	0.012	0.030	0.0099[d]	0.0097[f]
6	0.0022	0.0132	0.0028[d]	(0.0028)[f]
		R = C_2H_5 (75°)		
1	0.42[c]	0.070	0.46[e]	(0.46)[g]
2	0.128[c]	0.051	0.118[e]	0.122[g]
3	0.039	0.029	0.039[e]	0.039[g]
4	0.0134	0.018	0.0134[e]	0.0133[g]

[a] These equilibrium quotients are based upon the pure liquids as standard states for each of the solvent components. [b] Corrected under the assumption that the isomeric species for n = 2, 3, and 4 are present in the statistically expected relative amounts; under these circumstances $Q_n(cor) = Q_n[n/(7 - n)]$. [c] Values from ref 4 extrapolated to pure ethanol as solvent. [d] Calculated using $\log\{Q_n[n/(7 - n)]\} = -0.763 - 0.169n$. [e] Calculated using $\log\{Q_n \cdot [n/(7 - n)]\} = -0.910 - 0.209n$. [f] Calculated using $\alpha = 0.117$ and $\beta = 0.615$, parameters obtained by making calculated values the same as the values of Q_1 and Q_6 calculated using the other model. [g] Calculated using $\alpha = 0.077$ and $\beta = 0.545$, parameters obtained by making calculated values the same as the values of Q_1 and Q_6 calculated using the other model.

not highly accurate, slightly different sets of numerical values for the equilibrium quotients are obtained if a different weighting procedure is used[1b] in averaging the individually determined equilibrium quotients and the values of r_a. The procedure used here[9] seems rational.)

Values of the equilibrium quotients have been determined for the stepwise solvation reactions in water–ethanol solutions in the same manner as that used for the reactions with larger n in the water–methanol system. The earlier reported values of Q_1 and Q_2[4] extrapolated to pure ethanol serve as a starting point. The values of r_a for the first three solutions of Table III were calculated using Q_1 and Q_2 and the observed concentrations of species containing zero, one, and two bound ethanol molecules. With r_a values established, a value of Q_3 was calculated: $Q_3 = 0.039 \pm 0.005$. With this value of Q_3 (and the value of Q_2), the values of r_a were calculated for the last three solutions, and then the values of Q_4 were calculated; the average value is $Q_4 = 0.013 \pm 0.002$.

The value of Q_3 obtained in this study is within experimental error of the value obtained in the earlier study[4] ($Q_3 = 0.042$) in which the value of r_a was calculated from the solvent composition. Although medium effects are pronounced in this system,[4] all of the solutions in the present study were very concentrated in ethanol ($Z > 0.94$), and it is assumed that medium effects are not appreciable in the range $0.94 < Z < 1.00$.

Discussion

A rational comparison of equilibrium quotients for the stepwise reactions in which alcohol replaces water in the first coordination shell around chromium(III) cannot be made without first correcting the empirical values for the statistical contribution. If one assumes that the isomeric species with $n = 2$, 3, and 4 are present in the statistically expected relative amounts, the correction can be made by considering simply the total number of sites available for alcohol to replace water in the reactant ($7 - n$) and for water to replace alcohol in the product (n).[10] These corrected values given in

$$Q_n(\text{cor}) = Q_n[n/(7-n)]$$

Table IV are not constant for either system; this indicates that the relative tendency for binding of water and alcohol to chromium(III) depends upon the composition of the coordination shell.

Since alcohol molecules are larger than water molecules, the trend in stability may be due to steric repulsion. A model based upon the assumption that steric interactions are localized along the 12 edges of the octahedron defined by the six ligands gives rise to two adjustable parameters;[11] one is $q(ab)^4$, and the other is $(bb)/(ab)^2$. The quantity q is the statistically corrected equilibrium quotient in the absence of steric effects, (ab) is a factor in an equilibrium quotient due to one AB interaction (a water–alcohol interaction) replacing one AA interaction (a water–water interaction), and (bb) is a factor due to one BB interaction (alcohol–alcohol interaction) replacing one AA interaction. Each of the experimental equilibrium quotients is related to these two adjustable parameters (which for conciseness will be represented $q(ab)^4 = \alpha$ and $(bb)/(ab)^2 = \beta$).[12]

$$Q_1 = 6\alpha \qquad Q_4 = \frac{\alpha\beta^3 + {}^1/_4\alpha\beta^2}{1 + {}^2/_3\beta}$$

$$Q_2 = 2\alpha\beta + {}^1/_2\alpha \qquad Q_5 = \frac{{}^1/_2\alpha\beta^3}{1 + 1/(4\beta)}$$

$$Q_3 = \frac{\alpha\beta + {}^2/_3\alpha\beta^2}{1 + 1/(4\beta)} \qquad Q_6 = {}^1/_6\alpha\beta^4$$

The equations for Q_2, Q_3, Q_4, and Q_5 involve a sum in the numerator and/or denominator because the reactant and/or product species occur in isomeric forms; the reactions associated with these equilibrium quotients are composite reactions.[10] As shown in Table IV, this two-parameter model correlates the data within experimental error. The parameter β ($(bb)/(ab)^2$), a measure of the destabilization of a *cis* isomer relative to the corresponding *trans* isomer, is smaller than unity; this is consistent with the expected greater steric repulsion between two alcohol molecules in *cis* configuration than between a water molecule and an adjacent alcohol molecule. Within the framework of this simplified model, the steric repulsion of ethanol molecules is greater than that between methanol molecules ($\beta = 0.545$ for water–ethanol system; $\beta = 0.615$ for water–methanol system).

The data are correlated equally well with a two-parameter equation which is based upon a less specific model. If the chromium–water and chromium–alcohol bond strengths depend upon the composition of the first coordination shell around chromium(III) (*i.e.*, upon the value of n), and if all other factors (*e.g.*, solvation energies) except the statistical factor are constant, a linear dependence of log ($Q_n[n/(7 - n)]$) upon n is expected. The data are consistent within experimental error with such a relationship. The equation

$$2.3RT \log\left(Q_n \frac{n}{7-n}\right) = a - bn$$

with $a = -1165$ cal mol^{-1} and $b = 258$ cal mol^{-1} for the water–methanol system (at 60°), and $a = -1452$ cal mol^{-1} and $b = 334$ cal mol^{-1} for the water–ethanol system (at 75°), correlates the data. In this model, the parameter b is the difference between the changes in chromium–water and chromium–alcohol bond strengths per unit increase of n. It is worth noting that the same change of chromium–water and chromium–alcohol bond strengths with change of n results in no dependence of Q_n upon n from this source. The values of Q_n calculated with this equation are presented in Table IV. The two two-parameter equations fit the data equally well. With only a range of a factor of ~8 in Q_n.

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[10] E. L. King, *J. Chem. Educ.*, 43, 478 (1966).

[11] This approach resembles that used by D. E. Koshland, Jr., G. Nemethy, and D. Filmer (*Biochemistry*, 5, 365 (1966)) in interpreting hemoglobin-oxygen combination in terms of models which allow subunit interactions.

[12] In forming MA_5B from MA_6, four A–A edge interactions are transformed into four A–B edge interactions. The statistical factor for this reaction is 6. The equation relating Q_1 and the parameters of this model is, therefore, $Q_1 = 6\alpha$. In forming *cis*-MA_4B_2 from MA_5B one B–B edge interaction and two A–B edge interactions are gained at the loss of three A–A edge interactions. The statistical factor for the reaction is 4/2. The equation relating this part of the composite Q_2 is, therefore, $Q_2(cis) = 2q(ab)^2(bb) = 2q(ab)^4(bb)/(ab)^2 = 2\alpha\beta$. To this must be added $Q_2(trans)$ to obtain Q_2: $Q_2 = Q_2(cis) + Q_2(trans)$.

$[n/(7-n)]$ for the water–methanol system, and a factor of ~ 4 for the water–ethanol system, the data do not demand much of the theory.

The trend in values of Q_n with increase in n for the alcohol–water systems is the opposite of that observed in the dimethyl sulfoxide-water system,[6] for which Q_n(cor) increases slightly as n increases. This does not necessarily weaken the argument that the trend in Q_n with n for the alcohol–water systems is caused by steric interactions of alcohol molecules. The coordination of dimethyl sulfoxide with chromium(III) is through the oxygen atom[13] and the methyl group is, therefore, not bonded to the atom to which the chromium is bonded.

Medium effects upon the equilibrium quotients are not appreciable in the water–methanol system, they cause Q_n to increase with Z for the water–ethanol system, and they cause Q_n to decrease with Z for the water–dimethyl sulfoxide system. Where such effects exist, they may be rationalized in terms of preferential outer-sphere interaction between solvated chromium(III) ions and one or the other of the solvent components, as was illustrated in the water–dimethyl sulfoxide system.[6] It is reasonable that preferential outer-sphere interaction would be minimal in the water–methanol system. It seems clear, however, that the magnitude of such medium effects cannot be predicted. Their demonstrated existence in some systems[4,6] does cause concern regarding the conventional treatment of $\bar{n}$ data in which one must assume the absence of such effects.

The value of Q_2 obtained in the present study does not confirm the abnormal value derived in the earlier study based upon $\bar{n}$ data.[3] Values of $\bar{n}$ obtained in the earlier study agree reasonably well with values based upon the equilibrium quotients derived in the present study (see Table I). The disagreement is greatest in the range of $\bar{n} = 0.6$–1.9, with the previously determined values being higher. It is primarily due to this difference that the Q_2 from the earlier study is too high.

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[13] C. V. Berney and J. H. Weber, *Inorg. Chem.*, 7, 283 (1968).

Anomalous Temperature Dependence of Isotropic Proton Nuclear Magnetic Resonance Shifts in Paramagnetic Chromium(II) and Cobalt(II) Complexes

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Abstract: The anomalous temperature dependence of the isotropic shifts of tris Cr(II) and Co(II) complexes with unsymmetrically methyl-substituted *o*-phenanthrolines has been investigated. These complexes exist in solution as statistical mixtures of *cis* and *trans* isomers, which produce four equally intense proton peaks per ligand position. The extent of deviation from Curie behavior is found to depend markedly on ligand position, and also to differ for each of the four peaks from certain ligand protons in the isomer mixture. For the Cr(II) complexes, the anomalous contact shifts appears to result from a temperature-dependent redistribution of unpaired spin between two d orbitals which interact differently with the three nonequivalent ligands in the *trans* isomer. This analysis leads to the assignment of the electronic ground state of the tris chelates as ^3E. The applicability of this nmr technique for determining ground states in tris bidentate complexes is discussed. The analysis of the isotropic shifts for the Co(II) complexes reveals that the extent of deviation from Curie behavior for the observed shifts at any ligand position correlates very well with the magnitude of the dipolar contribution to the observed shift. The significantly greater deviation from Curie behavior of the dipolar contribution relative to the contact contribution to the observed shifts is interpreted as arising from a sizable difference in the magnetic anisotropy between the various populated Kramer doublets.

A characteristic of isotropic nmr shifts for paramagnetic transition metal complexes is their strong temperature dependence, which results from the temperature dependence of the spin magnetization on the metal.[1-3] Although all isotropic shifts must approach zero as $T \rightarrow \infty$, the form of the temperature dependence may differ with the origin of the isotropic shift and the particular complex.

The contact shift for a complex possessing an essentially spin-only magnetic moment has been shown to exhibit Curie behavior according to eq 1 where all

$$\left(\frac{\Delta H}{H}\right) = -A\,\frac{\gamma_e}{\gamma_H}\,\frac{g\beta S(S+1)}{3kT} \qquad (1)$$

notations are standard.[1] For complexes with degenerate ground states which possess sizable orbital contributions to the magnetic moments, the net spin magnetization on the metal, as well as on all ligand nuclei, will deviate[2] from simple Curie behavior, usually in the form of a slight curvature to the $(\Delta H/H)$ *vs.* T^{-1} plot. The deviation from Curie behavior must be the same for all ligand contact shifts.[4]

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