racemization of the active form in D_2O. This difference in inversion rates explains the failure to detect the *meso* form in the racemic product and implies that the energy difference between the isomers is ~1.3 kcal/mole.

In the racemization step not only does the arrangement about the N invert but the Co–N-Meen ring must also interchange its conformation so that in the *meso* intermediate both methyl groups are in equatorial positions.[2] It could not be decided, however, if the conformational interchange precedes or antecedes the inversion act, but regardless of which of these possibilities pertains, $\Delta H_R^{\ddagger}$ should exceed that found for the tetraammine sarcosinato ion, where little or no conformational effect exists. This aspect of the problem has been discussed previously[2] for the $[Co(NH_3)_4N\text{-Meen}]^{3+}$ ion where $\Delta H_R^{\ddagger}$ exceeded that for the sarcosinato ion by ~ 5 kcal/mole. In the present instance $\Delta H_R^{\ddagger}$ exceeds that for the sarcosinato ion by ~10 kcal/mole which agrees with the rationalization in terms of the conformational effect. However, the relative magnitude of these values is uncertain in relation to the enthalpy of deprotonation of the complex ion since a rationalization of $\Delta H_R^{\ddagger}$ in terms of the conformational effects alone assumes that the enthalpy of deprotonation is reasonably constant for the complexes considered.

Acknowledgment. We wish to thank the Microanalytical Unit of the John Curtin School of Medical Research for C, N, and H analyses and Mr. S. Brown for technical assistance with the pmr measurements.

Solvation of Chromium(III) Ion in Acidic Water–Ethanol Mixed Solvents[1,2]

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Abstract: The solvation of chromium(III) ion in acidic water–ethanol mixed solvents has been studied at 50.0 and 75.0°. Separation by ion-exchange methods of individual, differently solvated species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ ($n = 0$, 1, 2, and 3), present in equilibrated solutions with mole fraction of ethanol up to ~0.95 allows calculation of equilibrium quotients for stepwise replacement by ethanol of water in the first coordination shell of chromium: $Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+} + C_2H_5OH = Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+} + H_2O$. Values of the equilibrium quotients, Q_j (involving the ratio of activities of the solvent components), show a medium dependence, increasing with increasing ethanol content of the solvent. The ratio of activity coefficients of differently solvated chromium(III) ions is not, therefore, constant as the solvent composition varies. Values extrapolated to pure ethanol as solvent (for 75°) are $Q_1{}^0 = 0.42 \pm 0.01$, $Q_2{}^0 = 0.128 \pm 0.005$, and $Q_3{}^0 \cong 0.04_2$. Values of $\bar{n}$, the average number of ethanol molecules bound per chromium(III), are the same within experimental error, at 50 and 75°, indicating that the enthalpy change associated with the solvent replacement reaction is small (0 ± 0.5 kcal mole^{-1}). The rate of aquation of $Cr(OH_2)_5(OHC_2H_5)^{3+}$ has been studied in aqueous 4.4 *M* perchloric acid at 39.6°, under which conditions the first-order rate constant is 2.16×10^{-5} sec^{-1}. Problems associated with correlation of $\bar{n}$ data and solvent composition to obtain equilibrium quotient values are discussed.

Direct evaluation of primary solvation of chromium(III) ion in mixed solvents is possible because of the slowness of exchange with the environment of ligands bonded to this metal ion. In earlier studies, the solvation of chromium(III) ion in acidic water–methanol solutions has been established.[3] The present study of chromium(III) in acidic water–ethanol solutions[4] resembles these published studies on the water–methanol system in its general plan: values of $\bar{n}$, the average number of ethanol molecules bound per chromium(III) ion, have been determined as a function of solvent composition. In addition, quantitative separation by an ion-exchange procedure of individual differently solvated chromium(III) species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ ($n = 0$, 1, 2, and 3), has been accomplished in the present study; this allows evaluation of equilibrium quotients for the solvent displacement reactions

$$Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+} + C_2H_5OH = Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+} + H_2O$$

with $j = 1$, 2, and 3 as a function of solvent. The solvent dependence of the equilibrium quotients is appreciable, with the stability of ethanol-containing species being enhanced in solutions of increasing ethanol content. Separation of individual, differently solvated species has allowed also measurement of the spectrum of the individual species ($n = 0$, 1, and 2) and the direct evaluation of the rate of aquation of monoethanolchromium(III) ion.

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(1) Based upon the Ph.D. thesis of D. W. Kemp, University of Colorado, Aug 1966. Presented in part before the Analytical Division, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 13, 1966.

(2) This work was supported by the National Science Foundation (Grant GP-680).

(3) (a) J. C. Jayne and E. L. King, *J. Am. Chem. Soc.*, **86**, 3989 (1964); (b) R. J. Baltisberger and E. L. King, *ibid.*, **86** 795 (1964).

(4) C. K. Jørgensen, *Acta Chem. Scand.*, **8** 175 (1954). This study of slow spectral changes in water–ethanol solutions of chromium(III) nitrate is not amenable to a quantitative interpretation.

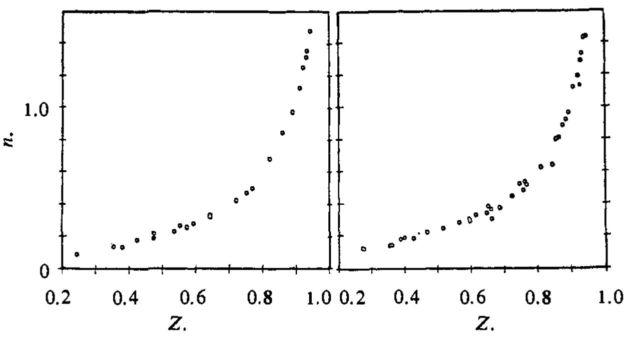

Figure 1. $\bar{n}$ *vs.* Z: (left) 50°, (right) 75°. Solutions shown had composition 0.011 ± 0.001 M $Cr(ClO_4)_3$, 0.12 ± 0.02 M $HClO_4$. (Solutions were studied at 75° with wider range of solute concentrations, but these points are not shown.)

Experimental Methods

Reagents and Equipment. Solutions were prepared with water which was distilled, then passed through an ion-exchange demineralizer (Barnstead Bantum), and finally redistilled from an all-glass (Pyrex) still. Reagent grade ethanol was redistilled. Its water content was determined by pycnometric determination of density. Chromium(III) perchlorate was prepared by the reaction of reagent grade chromium(VI) oxide with hydrogen peroxide in perchloric acid solution. After partial evaporation of water at 80°, crystalline material was obtained upon cooling, and the salt was recrystallized from approximately 1 M perchloric acid. A stock solution (0.508 M chromium(III) perchlorate, 5.12 M perchloric acid) prepared from the recrystallized salt was used in preparation of solutions for equilibration. Measurement of light absorption at 230 and 260 mμ showed the stock solution of chromium(III) to be relatively free of polymeric chromium(III) species.[5] Reagent grade Dowex 50-W resins were used in the ion-exchange procedures. In experiments designed to evaluate $\bar{n}$, X-8 (50–100 mesh) resin was used after first being heated with successive portions of 6 M hydrochloric acid until no color was extracted from the resin by the acid treatment. In experiments designed to separate individual, differently solvated chromium(III) species, X-12 (200–400 mesh) resin was used after a purification procedure which included the acid treatment already mentioned plus treatment with dilute alkaline hydrogen peroxide. The ion-exchange resin was used in the hydrogen form.

Spectral measurements were made at room temperature using a Cary Model 15 spectrophotometer.

Analytical Methods. The chromium content of solutions was determined from the light absorption at 372 mμ due to chromate ion[6] (a = 4820 l. mole^{-1} cm^{-1}) formed in alkaline solution by peroxide oxidation. Unbound ethanol was determined by its reaction with chromium(VI) in ~3.5 M sulfuric acid at room temperature to produce acetic acid, followed by dilution, addition of phosphoric acid, and then back-titration of excess chromium(VI) with standardized iron(II) solution. Ethanol bound to chromium(III) is not oxidized in this procedure carried out at room temperature. To determine bound ethanol, the acidic eluent containing solvated chromium(III) ion was treated with chromium(VI) and heated at 85° for 30 min. (One can estimate the half-time for aquation of monoethanolchromium(III) ion at 85° to be *ca.* 4 min.[7] The success of this procedure for determination of bound ethanol does not prove, therefore, that direct oxidation of bound ethanol occurs under conditions of these experiments.)

Results

Evaluation of $\bar{n}$. Solutions containing water, ethanol, perchloric acid, and chromium(III) perchlorate were sealed in Pyrex tubes and maintained in thermostats at 75.0 or 50.0°. After an appropriate time (0.5 to 7.5 days at 50°, 3 hr to 7.5 days at 75°), samples were quenched by placing the tubes in an ice–water mixture. (If analysis was delayed, the samples were stored at ~−15°). Samples were analyzed by dilution with dilute aqueous perchloric acid and adsorption of chromium species on a cation-exchange column (~10 cm × 1 cm), followed by rinsing of the column with 350–400 ml of cold (2°) ~0.015 M sulfuric acid to remove free solvent ethanol. After rinsing of all solvent ethanol from the column, elution with 3 M sulfuric acid resulted in 97–99% recovery of chromium. Generally 5–6 hr was required for the entire ion-exchange procedure. Eluted samples were analyzed for chromium and ethanol (all of which was bound to chromium(III)) by the methods already described. Generally an amount of sample was taken which contained 0.5 to 1.0 mmole of chromium(III), and this was finally collected for analysis in 50 ml. The estimated uncertainty in the ethanol analysis was ±3% and in the chromium analysis was ±1%. The experimental values of $\bar{n}$ for 50° ranged from 0.094 at a solvent composition[8] Z = 0.24 to 1.48 at Z = 0.94. Those for 75° ranged from 0.089 at Z = 0.18 to 1.45 at Z = 0.95. The dependence of $\bar{n}$ upon Z is shown in Figure 1.[9] In solutions of high ethanol content, the gross $\bar{n}$ value for species elutible with 3 M sulfuric acid decreases with increasing time of equilibration if these times are excessively long. Such changes of $\bar{n}$ were accompanied by a decrease in recovery of chromium in the elution procedure. In an experiment at 75° with Z = 0.88 (0.0102 M $Cr(ClO_4)_3$, 0.102 M $HClO_4$), values of $\bar{n}$ of species eluted by 3 M sulfuric acid and the percentage of chromium recovered by this elution procedure as a function of equilibration time are (given as t (hr), $\bar{n}$, % recovery): 3.2, 0.893, 97.5; 5.2, 0.895, 97.5; 8.2, 0.894, 98.5; 14.2, 0.844, 96.5; 21.2, 0.845, 96.1; 30.0, 0.761, 96.3; 49.0, 0.746, 95.9; 85, 0.707, 95.6; and ~1400, 0.645, 88.5. In experiments involving very long equilibration periods (2 months) at 75°, the values of $\bar{n}$ for species eluted by 3 M sulfuric acid were smaller the lower the concentration of perchloric acid and the higher the concentration of chromium(III). Data from experiments which show these trends are given in Table I. It is assumed that values obtained in short equilibration periods at 75° with $Z > 0.88$ represent equilibrium with respect to monomeric species. In solutions of lower ethanol content, no decrease in $\bar{n}$ was observed at long times at 75°; no decrease in $\bar{n}$ of species elutible with 3 M sulfuric acid was observed at 50°.

Evaluation of Equilibrium Concentrations of Individual Species. In the $\bar{n}$ experiments just described no attempt was made to separate individual species, and it was intended initially to base conclusions upon such $\bar{n}$ data. After completion of the $\bar{n}$ experiments it was discovered, however, that use of a longer column (100 cm) and more highly cross-linked resin (Dowex 50-W, 12X (200–400 mesh) allowed separation of indi-

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(5) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83** 2825 (1961).

(6) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48** 414 (1952).

(7) This estimate is based on rate data presented later in this paper and on an assumed activation energy of 24 kcal mole^{-1} for the aquation reaction.

(8) The solvent composition is expressed in terms of Z, the mole fraction of ethanol with only the solvent components water and ethanol being taken into account.

(9) Data on $\bar{n}$ as a function of solvent composition at 50 and 75° as well as a tabulation of spectral data for $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5(OHC_2H_5)^{3+}$, and $Cr(OH_2)_4(OHC_2H_5)_2^{3+}$ have been deposited as Document No. 9461 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $3.75 for photoprints, or $2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table I. Values of $\bar{n}$ for Species Elutible with 3 M H_2SO_4 (Equilibration for 2 Months at 75°, Z = 0.88)

C_{H}[a]	C_{Cr}[b]	$\bar{n}$	% Cr recovered
0.52	0.010	0.86	98.2
0.41	0.010	0.88	98.2
0.30	0.010	0.88	98.8
0.20	0.010	0.87	98.2
0.15	0.010	0.83	89.3
0.10	0.010	0.65	88.5
0.052	0.010	0.28	86.5
0.10	0.0082	0.67	. . .[c]
0.10	0.0164	0.56	. . .[c]
0.10	0.0247	0.50	. . .[c]
0.10	0.0329	0.49	. . .[c]

[a] Stoichiometric molarity of perchloric acid. [b] Stoichiometric molarity of chromium(III) perchlorate. [c] Not determined.

vidual differently solvated chromium(III) species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ (n = 0, 1, 2, and 3). Individual species from ten different equilibrated solutions were separated. These separations (on samples containing 4.0 mmoles of chromium) involved a procedure which lasted much longer than those associated with the $\bar{n}$ experiments. The column was maintained at low temperatures (0–5°) throughout the adsorption, rinsing, and elution phases of the procedure. An elution curve from one of the experiments is shown in Figure 2. These data demonstrate that essentially quantitative separation of differently solvated species is possible and that hexaaquochromium(III) ion is the most easily eluted species (as in the water–methanol system[3a]) followed by the species in order of increasing number of bound ethanol molecules. Three of the experiments were of the type illustrated by Figure 2; in the remaining seven experiments, larger fractions each containing all of a particular species were collected. The separate colored bands could be seen easily on the light colored resin, and this method of collection of the individual portions was satisfactory. Results of these experiments are presented in Table II, which includes values of r, the ratio of activities of ethanol and water in electrolyte-free solvents of the compositions studied. Species containing two or three bound ethanol molecules may exist as *cis* or *trans* isomers. Separation of isomeric species was not achieved in the present study.

In experiments designed to provide individual differently solvated species for kinetic runs, 4.5 M perchloric acid was used as eluting agent. This solution, with a concentration of hydrogen ion comparable to that in 3 M sulfuric acid, was less effective as an eluting agent than 3 M sulfuric acid.

Study of the Aquation of Monoethanolchromium(III) Ion. For use in kinetic experiments, a solution containing monoethanolchromium(III) ion as the only Cr species was prepared by an ion-exchange procedure using ~4.5 M perchloric acid as eluting agent. The production of free ethanol in solution was followed by oxidation with chromium(VI) at room temperature, under which conditions bound ethanol does not react. For two experiments at 39.6° in aqueous 4.42 M perchloric acid, the data are (given as t (hr), fraction aquated): (experiment with chromium(III) concentration of 6.7×10^{-3} M) 4.0, 0.266; 7.0, 0.423; 11.0, 0.563; 14.8, 0.662; 20.0, 0.793; and 24.0, 0.830; (experiment with chromium(III) concentration of 5.3×10^{-3} M): 2.0, 0.13; 4.0, 0.288; 7.5, 0.443; 10.0, 0.538; 14.0, 0.660; 18.5, 0.767; and 24.0, 0.832. These data, which conform nicely to first-order kinetics, lead to a rate constant of 2.16×10^{-5} sec^{-1}.

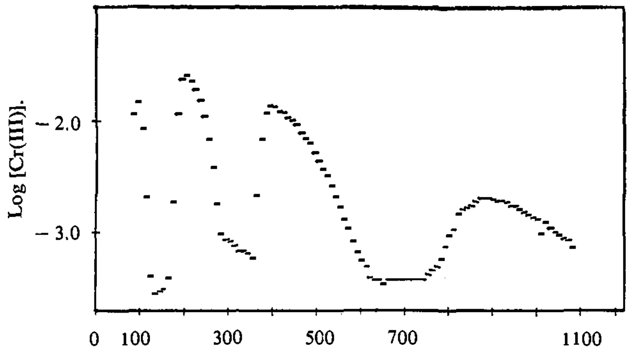

Figure 2. Elution curve for equilibrated solution with the composition Z = 0.949, 0.0102 M $Cr(ClO_4)_3$, 0.102 M $HClO_4$, 75°. Approximate values of $\bar{n}$ for species under peaks are (from left to right): 0.0, 1.0, 2.0, and 3.0.

Table II. Equilibrium Distribution of Chromium among the Species $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ (0.010 M $Cr(ClO_4)_3$, 0.10 M $HClO_4$, 75°)

Z	r = a_E/a_W	Amount of chromium, mmoles[a] n = 0	n = 1	n = 2	n = 3	% recovery
0.237	0.525	3.56	0.40_4			$98._0$
0.359	0.645	3.41	0.51			$97._0$
0.468	0.778	3.24	0.73			$98._3$
0.609[b]	1.053	2.61	0.94	0.0974		102.
0.703	1.351	2.46	1.17	0.174		$94._0$
0.861	2.99	1.48	1.68	0.59_3		$93._5$
0.884[c]	4.44	1.00	1.76	0.94_4	. . .[d]	. . .[d]
0.910	4.74	0.95	1.78	1.03	0.181	$97._5$
0.946[e]	8.45	0.37_3	1.32	. . .[e]	. . .[e]	. . .[e]
0.949	8.74	0.40_3	1.43	1.52	0.52_3	$95._8$

[a] 4.03 ± 0.01 mmoles of chromium present in each case except where noted. [b] 3.57 mmoles of chromium present. [c] 0.50 M $HClO_4$ in equilibrated solution; Z (cor) = 0.911. (The value of Z was corrected for assumed preferential binding of one water molecule by hydrogen ion.[3a]) [d] Band with n = 3 not collected. [e] Elution with 4.5 M $HClO_4$; bands with $n \geqslant 2$ not collected.

Spectra of $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ (n = 0, 1, 2). The visible spectrum of each of the separated species was measured in 3 M sulfuric acid promptly after the ion-exchange separation procedure.[9] It is assumed that inner-sphere sulfatochromium(III) ion did not form to an appreciable extent in these solutions at the time of the spectral measurement. The replacement of water by ethanol in the first coordination shell does not have much effect upon the visible spectrum, as is shown by the summary of Table III.

Table III. Spectral Peaks in the Visible Region for Differently Solvated Chromium(III) Ions[a]

	λ, mμ (a, l. mole^{-1} cm^{-1})	
$Cr(OH_2)_6{}^{3+}$	573 (14.2)	407 (16.1)
$Cr(OH_2)_5(OHC_2H_5)^{3+}$	577 (14.6)	410 (16.8)
$Cr(OH_2)_4(OHC_2H_5)_2{}^{3+}$	582 (15.2)[b]	414 (17.7)[b]

[a] Solvent 3 M H_2SO_4, room temperature. [b] Values for $Cr(OH_2)_4(OHC_2H_5)_2{}^{3+}$ are for an equilibrium mixture of two isomers.

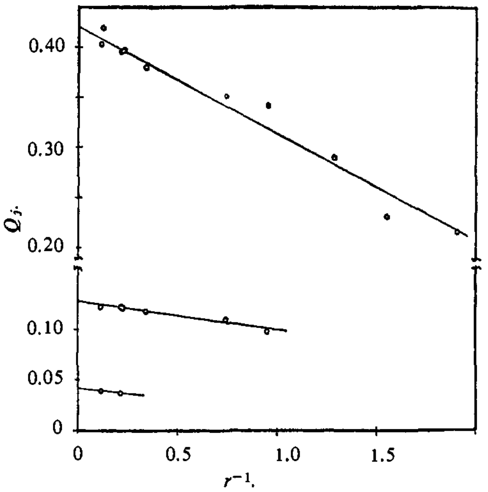

Figure 3. Q_j vs. r^{-1} (75°): upper line Q_1, middle line Q_2, and lower line Q_3. The lines correspond to equations given in the text.

Interpretation

Evaluation of Equilibrium Quotients. A measured concentration ratio $[Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+}]/[Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+}]$ (j = 1, 2, or 3) is but one factor in the equilibrium constant for a reaction in which a bound water molecule is displaced by an ethanol molecule. The other factors, the ratio of activity coefficients f_j/f_{j-1} (where f_j is the activity coefficient of the chromium(III) species with j bound ethanol molecules) and the ratio of activities of solvent components r_a (where r_a is the ratio of the activity of ethanol to the activity of water, a_E/a_W), are not known directly. With correct values of these two ratios, calculated values of the equilibrium constants

$$K_j = \frac{[Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+}]f_j}{[Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+}]f_{j-1}r_a}$$

would be independent of solvent. For purposes of discussion, we will consider equilibrium quotients defined as

$$Q_j = \frac{[Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+}]}{[Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+}]r}$$

where r is the ratio a_E/a_W calculated for a binary solvent mixture containing no electrolyte,[10] but corrected for the measured binding of solvent by chromium(III) and the assumed preferential binding of one water molecule by hydrogen ion.[3a] The data in Table II allow calculation of the solvent-dependent values of Q_j (j = 1, 2, and 3). The values, which are given in Figure 3, can be represented adequately by the equations

$$Q_j = Q_j{}^0(1 - \alpha_j r^{-1})$$

$$Q_1 = 0.420(1 - 0.25r^{-1})$$

$$Q_2 = 0.128(1 - 0.22r^{-1})$$

$$Q_3 = 0.042(1 - 0.5r^{-1})$$

Since Q_j depends upon solvent composition (as defined by r), (f_j/f_{j-1}) is not independent of solvent composition and/or $r \neq r_a$. If the assumption $r = r_a$ were grossly in error, it would be expected that values of Q_j would depend upon the concentration of electrolyte.[11] This is not observed in the data presented in Figure 3, and also the $\bar{n}$ data do not disclose appreciable dependence upon electrolyte concentration. It is concluded, therefore, that the dependence of Q_j upon solvent composition is due to variation of the activity coefficient ratios (f_j/f_{j-1}) with solvent composition. The fractional change in Q_j shown in Figure 3 is interpreted to indicate a corresponding fractional change in (f_j/f_{j-1}).

Although there is no assurance that linear extrapolation in Figure 3 to the ethanol axis ($r^{-1} = 0$) is justified, values of $Q_j{}^0$ obtained in such extrapolations are assumed to be equilibrium constants based on a standard state of solute species in ethanol solvent. Since the number of solute species on each side of the balanced chemical equation is the same, their concentration scale need not be specified. (It is assumed that the experimental values of Q_j and $\bar{n}$ would not change with dilution of chromium(III) and acid to infinitely low concentrations.) These extrapolated values are $Q_1{}^0$ = 0.42 ± 0.01, $Q_2{}^0$ = 0.128 ± 0.005, and $Q_3{}^0$ = 0.042. Extrapolation of Q_j values to pure water as the solvent is not possible in Figure 3. Although alternate figures might be drawn[12] and linear extrapolations attempted to obtain values of Q_j appropriate for pure water, the significance of such values would be highly uncertain, particularly in view of the unusual properties of the water-rich mixtures in this solvent system.[13]

Before the concentrations of individual differently solvated species had been determined, an attempt was made to evaluate the equilibrium quotients from the $\bar{n}$ data. To do this it was necessary to assume that these derived quantities Q_j would be medium independent. For reasons to be discussed, such attempts were only partially successful. With medium-dependent values of the equilibrium quotients established, values of $\bar{n}$ can be calculated as a function of solvent composition. The temperature dependence of $\bar{n}$ is negligible, and the same set of equilibrium quotients was used to calculate $\bar{n}$ for each temperature. The agreement between the calculated and observed values is good, the average difference between observed and calculated values of $\bar{n}$ being 0.017 unit at 50° and 0.023 unit at 75°.

Discussion

The present study shows that chromium(III) ion discriminates in favor of water over ethanol in its first coordination shell. The quantity $(6 - n)Z(\text{cor})/$

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[10] Activities of the components of the binary solvent mixtures were taken from C. A. Jones, E. M. Schoenborn, and A. P. Colburn, *Ind. Eng. Chem.*, **35**, 666 (1943). The temperature dependence of the activity coefficients in this solvent system over the composition range of interest (Z = 0.24–0.95) is small. (This point is confirmed by G. L. Bertrand, F. J. Millero, C. Wu, and L. G. Hepler, *J. Phys. Chem.*, **70**, 699 (1966), who find small values, <250 cal mole^{-1} for $|\bar{L}_W|$ and <50 cal mole^{-1} for $|\bar{L}_E|$, where the subscripts W and E refer to water and ethanol. The ratio of activities of the solvent components for solutions on which fractionation was performed are given in Table II.

[11] If the dependence of Q_j upon solvent composition were due solely to the fact that $r \neq r_a$, the values of α_j would be independent of j, which for the equilibrium quotients that are accurately determined (Q_1 and Q_2) is the case. This does not, however, prove that $r \neq r_a$.

[12] A plot of Q_j vs. Z is also essentially linear over the solvent composition range studied.

[13] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965); F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966); see also Bertrand, *et al.*, ref 10.

$\bar{n}(1 - Z(\mathrm{cor}))$, which is the ratio of water to ethanol in the first coordination shell divided by the corresponding ratio for the free solvent, is one possible measure of this discrimination. The value of this quantity is 28 at $\bar{n} \cong 0.5$ and 40 at $\bar{n} \cong 1.0$. For comparison, values of this quantity for chromium(III) in water–methanol solutions[3a] (at 60°) are 8.5 at $\bar{n} \cong 0.5$ and 12.8 at $\bar{n} \cong 1.0$.

Steric factors may be partially responsible for greater discrimination in favor of water over ethanol (compared to that observed in the water–methanol system). If so one should see evidence for this in the values of equilibrium quotients for the successive stepwise reactions. Sound comparisons of this type depend, however, upon statistical corrections which are uncertain for Q_2^0 and Q_3^0. These equilibrium quotients correspond to composite reactions involving unknown relative amounts of isomeric species containing two and three bound ethanol molecules. If one assumes the isomers are present in the statistically expected relative amounts, the statistical correction is that which corresponds to all of the coordination sites being equivalent,[14] and the expected relative values of Q_1^0, Q_2^0, and Q_3^0 are 1, 0.42, and 0.22. The observed relative values are 1, 0.31, and 0.1. Although the stability of species containing two and three ethanol molecules is slightly lower than expected statistically, the effect is not large, and steric effects seem unimportant.

Species other than monomeric solvated chromium(III) species are formed slowly in the ethanol-rich mixed solvents. The data given in Table I are consistent with formation of elutible dimeric species in which the amount of bound ethanol per chromium is lower than is bound in monomeric species in the same solvent. Species which are not elutible are probably trimeric (or with higher degree of aggregation), and it seems reasonable that formation of such species would be favored under the same concentration conditions as those which favor formation of dimeric species. In spite of the lower ethanol content of dimeric species, their formation occurs to a greater extent and/or more rapidly in solutions with greater ethanol content. It cannot be certain, of course, that the inferred lower binding of ethanol by dimer corresponds to equilibrium. The formation of the dimeric species might occur predominantly through loss of ethanol by monomeric species containing at least one ethanol. Experiments in which the more highly cross-linked resin was used to separate species formed in solutions of high ethanol content which had been heated for long periods of time would probably allow isolation of dimeric species. Such experiments have not been attempted.

In the absence of additional information, the interpretations of $\bar{n}$ data in terms of equilibrium quotient values for the stepwise replacement reactions must be based upon the unproved assumption that ratios of activity coefficients (f_j/f_{j-1}) are independent of solvent composition. Since the differently solvated species in question have the same net charge, this seemed to be a reasonable assumption when it was used in interpretation of $\bar{n}$ data on the aquomethanolchromium(III) system.[3a] The present study proves the assumption to be incorrect for the aquoethanolchromium(III) system, but it seems appropriate to consider the consequences of a treatment of the present $\bar{n}$ data based upon the assumption of medium independent values of (f_j/f_{j-1}). One point is immediately obvious. With a maximum value of $\bar{n}$ of *ca.* 1.4, a meaningful value of Q_3 could not possibly be obtained, and one would make the reasonable (but incorrect) assumption that an inappreciable amount of triaquotriethanolchromium(III) was present in the solutions of highest ethanol content ($Z = 0.95$). Correlation of the $\bar{n}$ data in terms of the equation

$$\bar{n} = \frac{Q_1 r + 2Q_1Q_2r^2}{1 + Q_1 r + Q_1Q_2r^2}$$

gives $Q_1 \cong 0.2$, $Q_2 \cong 0.4$, but the fit of the equation to the data is not adequate, and it is not improved appreciably with the incorporation of terms in Q_3. In this system, therefore, the $\bar{n}$ data suggest that the assumption regarding (f_j/f_{j-1}) may be incorrect. Failure of an equation of the form

$$\bar{n} = \frac{\Sigma jQ_1Q_2\cdots Q_jr^j}{1 + \Sigma Q_1Q_2\cdots Q_jr^j}$$

is expected if values of Q_j are medium dependent since this equation imposes a strict relationship upon the coefficients of each power of r in the numerator and denominator. For instance, the coefficient of r^2 in the numerator must be two times the coefficient of r^2 in the denominator. If $Q_j = K_j(1 + \beta_j r)$ expresses the medium dependence of the equilibrium quotient, the coefficient of r^2 in the numerator $(2K_1K_2 + K_1\beta_1)$ is not two times the coefficient of r^2 in the denominator $(K_1K_2 + K_1\beta_1)$. If $Q_j = K_j(1 - \alpha_j r^{-1})$, as is approximately true for the present system, here also the coefficients of particular powers of r do not have the required relationships.[15]

It is interesting to note that correlation of the solvent dependence of $\bar{n}$ to obtain medium-independent equilibrium quotients leads to $Q_2 > Q_1$. Any reasonable statistical correction would make the comparison even more unexpected.

Despite the theoretical inadequacy of the equation $\bar{n} = \mathrm{F}(Q_j,r)$ for data from systems with a medium dependence of the equilibrium quotients, the equation may correlate data of moderate quality without disclosing whether (f_j/f_{j-1}) is medium dependent. This may be the situation with the aquomethanolchromium(III) system for which the assumption that $(f_j/f_{j-1}) \neq \mathrm{F}(r)$ was used in interpretation of $\bar{n}$ data.[3a] The consistency of limited data on the fraction of chromium(III) present as hexaaquochromium(III) as a function of solvent composition with the equilibrium quotients derived from the $\bar{n}$ data supported this assumption.[3a] Findings in the present study show, however, that the assumption is incorrect for the ethanol–water system, and the question must be raised whether the assumption is valid in the methanol–water system.

The first-order rate constant for aquation of pentaaquoethanolchromium(III) ion can be compared with the corresponding quantities for pentaaquomethanol-

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(14) E. L. King, *J. Chem. Educ.*, 43, 478 (1966).

(15) It is worth noting that the equation $\bar{n} = \mathrm{F}(Q_j,r)$ is more sensitive to detection of unexpected medium effects than the equation for $\Sigma[\mathrm{Cr^{III}}]/[\mathrm{Cr(OH_2)_6}^{3+}] = \mathrm{F}(Q_j,r)$ (*i.e.*, $\alpha_0^{-1} = \mathrm{F}(Q_j,r)$) since the equation $\alpha_0^{-1} = 1 + \Sigma Q_1Q_2\ldots Q_jr^j$ maintains the same form of a power series if $Q_j = K_j(1 + \beta r)$. (It would not maintain this form, however, if $Q_j = K_j(1 - \beta r^{-1})$.)

Table IV. Rate Constants for Aquation of Species $Cr(OH_2)_5S^{3-s}$ in Aqueous Solution

Species	Medium	Temp, °C	10^6k, sec^{-1}	10^6k, sec^{-1} at 298.2°
$Cr(OH_2)_6^{3+}$	$I = 0.7\ M$; ClO_4^-	27	3.3	2.4[a]
$Cr(OH_2)_5(OHCH_3)^{3+}$	$\left\{\begin{array}{l}0.10\ M\ HClO_4\\0.13\ M\ NaClO_4\end{array}\right\}$	30.0	11.0	5.2–5.6[b,c]
$Cr(OH_2)_5(OHC_2H_5)^{3+}$	$4.42\ M\ HClO_4$	39.6	21.6	2.6–3.3[b]
$Cr(OH_2)_5Cl^{2+}$	$1.0\ M\ HClO_4$			0.277[d]
$Cr(OH_2)_5Br^{2+}$	$1.0\ M\ HClO_4$			4.6[e]
$Cr(OH_2)_5I^{2+}$	$1.0\ M\ HClO_4$			84.1[d]

[a] J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954). This is $k/6$ to correct for the statistical factor. [b] Extrapolated to 25° assuming $\Delta H^{\ddagger} = 24.0$ and 27.0 kcal mole^{-1} to give range of values listed. [c] Extrapolated to aqueous medium from measurements in water–methanol solutions. [d] Extrapolated from values at other temperatures (T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965)). These are values for rate law term which is zero order in hydrogen ion. [e] Extrapolated from values at other temperatures (F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964)). These are values for rate law term which is zero order in hydrogen ion.

chromium(III) ion and hexaaquochromium(III) ion. This comparison, which is only semiquantitative because of differences in reaction media and uncertain extrapolations to a common temperature, is given in Table IV. Also included are values for aquation of the chloro, bromo, and iodo species. The rates of loss of neutral solvent molecules are very similar; in the O^{18} exchange the chromium(III)–oxygen bond is broken, and, in the reactions in which methanol and ethanol are replaced by water, it is assumed that it is the chromium(III)–oxygen bond, and not the carbon–oxygen bond, which is broken. As might be expected, there is much wider variation in the rates of aquation of the three halo complexes.

Nuclear Magnetic Resonance Studies of Exchange in Stannylamines[1]

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Abstract: The three-bond Sn–N–C–H couplings have been used to investigate exchange processes occurring in stannylamines which involve breakage of the Sn–N bond. We report the first temperature-induced change of spectra for these compounds. On the premise that the temperature required to produce a given rate of exchange (in these cases, *ca.* 250 sec^{-1}) is an index of the difficulty of inducing exchange, the data for $R_nSn[NR'R'']_{4-n}$ (where R = CH_3, C_2H_5, n-C_4H_9, and C_6H_5; R′ = R″ = CH_3 or C_2H_5; and R′ = CH_3, R″ = C_2H_5) can be accommodated by a simple model where exchange is favored by either a decrease in number, n, or in size of the attached groups, R, on tin, and by a decrease in size of the groups on nitrogen. The effect of addition of free amine or ammonium sulfate as a catalyst has been investigated, and it is concluded that, if any intermediate of the exchange reaction is also necessary for the related reaction of transamination, then the formation of this intermediate cannot be rate determining. In the isotopomeric N-trimethylstannylaniline-N^{14} and -N^{15} pairs, both the exchange and transamination are slower than *ca.* 120 sec^{-1}.

It has previously been reported that the three-bond Sn–N–C–H couplings, $J(Sn^{117}$–$H)$ and $J(Sn^{119}$–$H)$, which are present[3,4] in the room-temperature proton magnetic resonance spectra of stannyldiethylamines, $R_nSn[N(C_2H_5)_2]_{4-n}$ (where R = CH_3, C_6H_5; $0 \leqslant n \leqslant 3$), are absent in the case of the methylstannyldimethylamines, $(CH_3)_nSn[N(CH_3)_2]_{4-n}$, presumably because of a fast exchange process.[4] Low-temperature (−50°) spectroscopy on trimethylstannyldimethylamine, however, failed to slow down the postulated exchange.[5] Other workers have similarly noted the absence of satellites in the cases $(CH_3)_3SnN(CH_3)_2$, n-$Bu_2Sn[N(CH_3)_2]_2$, and n-$BuSn[N(CH_3)_2]_3$, but once again no corroboratory evidence has been adduced for the exchange hypothesis. We now report nmr work at various temperatures on both methyl- and ethylamine derivatives of tin which was undertaken to test this hypothesis. Furthermore, a

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[1] A preliminary report of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Author to whom inquiries should be addressed.

[3] M. R. Kula, C. G. Kreiter, and J. Lorberth, *Chem. Ber.*, **97**, 1294 (1964).

[4] J. Lorberth and M. R. Kula, *ibid.*, **97**, 3444 (1964).

[5] J. Lorberth and M. R. Kula, *ibid.*, **98**, 520 (1965).

[6] J. Lee and J. Dyer, personal communication, 1965.