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Contribution from the Department of Inorganic Chemistry,
University of Melbourne, Parkville, Victoria, 3052, Australia

Stability of Alkaline Earth Monofluoride Complexes in Methanol

J. W. BIXLER[1] and A. M. BOND*

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Fluoride complexes occupy a central role in ligand-acceptor classification schemes. Depending upon the nature of the acceptor, a given aqueous fluoride complex is either much stronger or much weaker than the other corresponding halide complexes. The extension of these classifications to other solvent systems is made difficult by the dearth of data concerning the stability of nonaqueous fluoride complexes. In this paper, the use of fluoride ion-selective-electrode potentiometry to obtain such data is illustrated with results obtained for alkaline earth monofluorides in methanol and methanol–water mixtures. The weak alkaline earth monofluorides show the stability trend $MgF^+ > CaF^+ > SrF^+ > BaF^+$ in water. The same trend is observed in methanol but the complex stabilities are greatly enhanced compared to the aqueous cases. This enhancement decreases as the atomic number of the alkaline earth increases. The effect of the dielectric constant upon complex stability is illustrated and SrF^+ is shown to obey the Born equation for all water and/or methanol solvent systems, while MgF^+ shows a deviation arising from the strong hydration of Mg^{2+}. Enthalpy and entropy information for MgF^+ and SrF^+ was estimated from temperature variation experiments. The results show that both reactions are entropy-controlled in methanol, as is characteristic for aqueous monofluoride complexes. The variation of the electrode system reference potential as a function of solvent composition is illustrated. Experimental procedure is briefly outlined and difficulties encountered in the nonaqueous measurements using a fluoride ion-selective electrode are described.

Introduction

The schemes developed by Ahrland et al.[2] and Pearson[3] (class a and class b, hard/soft) to systematically classify ligand and acceptor behavior in complexation reactions have proved very useful for making predictions about the stability of various species in aqueous media. However, it is interesting to speculate if these schemes are generally valid in all solvents or are limited to aqueous systems. Ahrland et al. have recently reported some studies of chloride, bromide, iodide, and thiocyanate complexes in the aprotic solvent dimethyl sulfoxide (Me_2SO).[4-8] They report that the class "a" acceptor zinc remains class "a" in Me_2SO, while the "border-line" cadmium ion is class "a" in Me_2SO but class "b" in water. Besides the work of Ahrland and co-workers, little data are available in nonaqueous solvents from which any firm conclusions on the generality of the classification schemes can be made.

The behavior of the fluoride ion, the hardest known ligand, is of major significance in any consideration of the general validity of the classifications. Group "a" acceptors show the halide complex stability trend fluoride $\gg$ chloride $>$ bromide $>$ iodide, while "b" acceptors show the stability trend fluoride $\ll$ chloride $<$ bromide $<$ iodide. Stability constant measurements of fluoride complexes relative to those of the other halides therefore provide a very significant criterion for classifying the metals.

Apart from the direct use in classification studies, another unique feature of fluoride complexes has been noted in aqueous media. Unlike most other systems, there is a strong correlation between the stability of aqueous monofluorides and simple electrostatic interactions arising from the strongly ionic properties of the fluoride ion.[9] Again, no data are available to test this concept as a unifying principle in nonaqueous media. Thus, from at least two important points of view related to systematic classification of stability constants, the paucity of fluoride data in media other than water is unfortunate.

The lack of information regarding the stability of fluoride complexes in nonaqueous media can be attributed to the absence of a simple technique suitable for measuring fluoride activity or concentration in solvents other than water. In particular, the generally low solubility of many metal fluorides in organic solvents means that detection limits must be excellent. In this paper, we report the commencement of our investigation of the stability of fluoride complexes in nonaqueous solvents using a fluoride ion-selective electrode (ISE) to monitor the free ligand concentration.

The utility of ISE potentiometry for the study of complexation equilibria in aqueous solutions is well established.[9-15] The same should be true in other media, although only a few investigations of complex stabilities in nonaqueous systems have been reported.[15] For example, Nakamura and co-workers have reported complex studies undertaken in acetonitrile using cation-sensitive glass electrodes.[16-18] Heerman and Rechnitz have used a cuprous sulfide membrane electrode to study copper(I) complexes in acetonitrile,[19] and Burdin et al. have studied cadmium and zinc chloro complexes in mixed solvents[20] using a chloride ISE. While the fluoride electrode has been used as an end-point detector for titrations in mixed solvents,[21,22] it has only been used as a reference electrode in previous nonaqueous equilibrium studies,[23] and the performance in such media is therefore not well documented. In addition to the intrinsic interest in the stability constant data obtained, the evaluation of the fluoride electrode in nonaqueous solvents also forms an important part of the present communication.

Methanol was chosen as the solvent for this initial investigation for several reasons: Its moderate dielectric constant ($\epsilon = 33$) means that it is a reasonably good ionic medium, while still being significantly different from water in solvent

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properties. Furthermore, fluoride reactions should not be complicated by acid–base side reactions in methanol. The logarithm of the autoprotolysis constant is −16.7 for methanol,[24] so it will have little tendency to protonate the very weakly basic fluoride ions in the absence of a much stronger acid.

The alkaline earth ions chosen as the complexes to be studied in this investigation represent an interesting group of class "a" acceptors. The stability constants of their monofluoro complexes show the trend $Be^{2+} \gg Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ in aqueous solution and conform closely to the predictions of an electrostatic model.[9] Thus, it can be seen by comparison with available data whether the group 2 metal ions remain class "a" in methanol and whether the electrostatic model also explains the stability trend observed in changing the solvent from water to methanol.

Experimental Section

Chemicals and Solutions. The sodium perchlorate and tetraethylammonium perchlorate (TEAP) salts used to maintain constant ionic strength were recrystallized from methanol. Triply distilled water was used for all aqueous and mixed-solvent solutions. Analytical reagent grade methanol was used as received. The water content of 0.05 M TEAP solutions in methanol was found to be 0.06 ± 0.01% (w/w) water by the Karl Fischer method. By comparison, a portion of distilled AR methanol contained 0.04% (w/w) water after storage under the same conditions used for the 0.05 M TEAP solution. Attempts to dry and store the methanol solution over molecular sieves failed because dissolved materials from the molecular sieve were sufficient to completely complex the low concentrations of fluoride used in these studies and were also deleterious to the response of the fluoride electrode. No further attempts were made to purify the methanol or rigorously exclude water, as vacuum-line techniques seemed likely to be necessary to achieve these goals. Rather, we determined the water levels present in the methanol and worked in the open laboratory. The presence of the analytically determined water concentration was then allowed for as far as possible in considering the interpretation of data.

The stock 0.1000 M solution of sodium fluoride in aqueous 0.05 M sodium perchlorate was prepared by weighing the dried reagent grade salt. The 9.8×10^{-5} M sodium fluoride solution in methanolic 0.05 M sodium perchlorate was made by slightly diluting a filtered saturated solution. Aliquots were evaporated, taken up in aqueous medium, and standardized using the fluoride electrode by Gran's standard addition technique. All stock solutions of tetraethylammonium fluoride (TEAF) were prepared from the salt as received (ICN K & K Laboratories) and were also standardized with the fluoride electrode. Stock magnesium solutions were prepared from anhydrous magnesium perchlorate and filtered. The stock aqueous solutions of calcium, strontium, and barium were prepared from hydrated perchlorate salts. These salts were dehydrated on a vacuum line and stored in a vacuum desiccator over phosphorus pentoxide until they were used to prepare stock solutions in methanol. The stock metal ion solutions were standardized by titration with EDTA. All solutions were stored in polyethylene bottles.

Apparatus. The cell was a polyethylene beaker equipped with a thermostated water jacket which maintained the temperature of the cell contents to within ±0.2 °C of the desired value. The sensor was an Orion 94-09A fluoride electrode used in conjunction with a silver–silver chloride reference electrode in aqueous 1 M sodium chloride. A fritted-glass double-electrolyte bridge was used with the reference electrode for nonaqueous and mixed-solvent measurements; the outer bridge solution matched the cell's electrolyte and solvent composition, while the inner bridge contained an aqueous solution of the same electrolyte at the same ionic strength. In the case of aqueous measurements, only a single aqueous bridge was used. The voltage measurements were taken with a digital multimeter, the input of which was equipped with a high input impedence buffer amplifier based on conventional FET operational amplifier circuitry.

Procedure. Unless otherwise stated, 50 mL of solvent at the required ionic strength was pipetted into the thermostated cell. The electrolyte used was chosen to result in the presence of a single diverse cation in each experiment; sodium perchlorate and TEAP were used when the fluoride sources were sodium fluoride and TEAF, respectively. The ionic strength of 0.050 M was chosen for the nonaqueous work because of the limited solubility of TEAP in methanol.

Electrode calibration solutions were prepared from five or more successive additions of 0.1 or 0.01 M standard fluoride solution to the cell with a micropipet. The concentration range of the calibration solutions was chosen to encompass some of the free fluoride concentrations expected in the presence of metal ions. After the last fluoride addition, several additions of standard 0.01 to 1.0 M metal ion solution were made to the cell with a micropipet. The free fluoride concentration was measured after each metal ion addition. In both calibration and complexing solutions, equilibrium was presumed to have been reached when the drift rate of the cell was less than 0.1 mV in 90 s.

The above procedure had to be modified somewhat when sodium fluoride was used as the fluoride source in methanol as a consequence of its very limited solubility in this solvent. The modified procedure commenced with 25.00 mL of 9.8×10^{-5} M sodium fluoride in methanolic 0.05 M sodium perchlorate in the cell. In this case, the calibration solutions were generated by successive dilution with portions of electrolyte solution, followed by metal ion additions in the usual manner. There are two disadvantages to this approach: the range of fluoride calibration solutions which can be prepared is very limited and the concentrations of all of the calibration solutions are higher than the free fluoride concentrations of the complexing solutions.

The pH of all aqueous solutions were in the range 5–6 where fluoride is not significantly associated with hydrogen ions.

All calculations were performed in the off-line mode on a PDP-11 minicomputer using programs written in Basic language.

Theory

The fluoride ISE responds to free fluoride in solution according to eq 1, where E is the potential difference between

$$E = E_c - S \log [F^-] \tag{1}$$

the fluoride and reference electrodes. E_c is a constant reference potential which incorporates such factors as fluoride ion activity coefficients, solvent activity coefficients, ion-pairing factors, liquid junction potential, ISE membrane asymmetry potential, and reference electrode potential. $[F^-]$ is the concentration of free fluoride ions and S is the temperature-dependent ISE span, which has an ideal (Nernstian) value of 59.2 mV/decade concentration change at 25 °C.

In the absence of complexing species, the dynamic range of the fluoride ISE extends down nearly to the micromolar region in both water and methanol. In the absence of acid–base or ion-pairing side reactions by the metal or fluoride, the stability constants can be extracted as follows:[14]

$$\frac{C_F - [F^-]}{(C_M - C_F + [F^-])[F^-]} = f(C) \tag{2}$$

where

$$f(C) = \frac{\beta_1 + 2\beta_2[F^-] + \ldots + n\beta_n[F^-]^{n-1}}{1 - \beta_2[F^-]^2 - \ldots - (n-1)\beta_n[F^-]^n} \tag{3}$$

C_F and C_M represent total concentration of fluoride and metal ions, respectively. The value of $f(C)$ is independent of the metal ion concentration if only mononuclear complexes are present in significant concentrations. Complexes with low coordination numbers are favored by high metal-to-ligand concentration ratios. Under such conditions, it is often easy to obtain β_1. The situation where only the 1:1 complex is present in significant concentration is readily recognized by the independence of $f(C)$ upon the free fluoride concentration. Under these conditions, eq 3 simplifies to eq 4. As a con-

$$f(C) = \beta_1 \tag{4}$$

sequence of the low solubilities of the alkaline earth fluorides in methanol, data had to be obtained near the lower limit of linear electrode response. The onset of precipitation was easily detected by the electrode behavior; the emf drifted positive at a rate of about 0.4 mV/min and failed to reach a steady state, even after 20–30 min. The solubility problem was most severe with the calcium fluoride system where precipitation occurred if the total fluoride concentration in methanol exceeded 1.0×10^{-5} M, while magnesium represented the best system, with total fluoride concentrations up to 10^{-4} M being tolerable under some conditions.

Results and Discussion

Electrode Response. The low solubility of sodium fluoride in methanol made work in the sodium fluoride–sodium perchlorate system experimentally difficult. Consequently, except for a few comparison trials to examine possible medium effects, all other experiments were made with 0.05 M TEAP as the ionic strength controlling electrolyte and TEAF as the fluoride source. Unless otherwise stated, results therefore refer to this system.

The lower part of the dynamic response range for the fluoride ISE in methanol is similar to that seen in water. A plot of mV vs. pF in methanol becomes nonlinear with decreasing span in the region above about pF 4.8–5.2. Calibration curves made near this lower limit were less reproducible in span and linearity with methanol than with water solutions. The electrode span in the 10^{-5} M concentration region ranged from 47.8 to 62.6 mV/decade concentration change at 25.0 °C. Results of the complexing experiments were anomalous when the span was outside the range of 51–59.2 mV/decade. Very low or super-Nernstian spans were observed with about one-third of the trials, and data from these experiments were rejected. We also rejected all trials for which calibrations were nonlinear.

The equilibration time of an ISE is a function of both the concentration being sensed and the size of the concentration change experienced. Equilibration of the fluoride ISE required about twice as long in methanol as in water (e.g., about 3–4 min vs. 2 min for a small concentration change in the 1×10^{-5} to 5×10^{-5} M fluoride concentration region). Rational values of $f(C)$ were obtained for the group 2 complexes in methanol even though the free fluoride concentrations measured in complexing systems were often well below the linear dynamic response region observed for the complex-free calibration data. This extension of the linear dynamic response range in the presence of stable complexes has been noted and explained for aqueous media by Baumann.[25]

Solvent Effects upon E_c. The strong dependence of the reference potential, E_c, upon solvent composition is shown in Figure 1. This suggests that E_c is a linear function of the mole fraction of either solvent in methanol–water mixtures, except possibly at very low concentrations of either methanol or water. The values of E_c obtained for TEAF with 0.05 M TEAP in methanol (−305 ± 7 mV vs. Ag/AgCl) and water (−172 ± 5 mV vs. Ag/AgCl) agree well with the corresponding values (−317 ± 5 and −186 ± 1 mV vs. Ag/AgCl) using NaF with 0.05 M $NaClO_4$. This indicates the absence of significant ion pairing between fluoride and the diverse cation in both electrolyte systems, since E_c is in good agreement using diverse cations of very different size.

A similar negative shift in E_c was observed with fluoride ISE studies in ethanol–water mixtures[21,22] and acetonitrile–water mixtures.[23] When comparing the thallium response of a cation-sensitive glass electrode in various solvents vs. an acetonitrile silver reference electrode, Nakamura noted a difference of about −100 mV between emf values in aqueous and methanol solutions.[18] Parker et al. observed a −81 mV drop across a methanol–water interface using a cell configuration without appreciable liquid junction potential.[26] This would suggest that a large portion of the difference in E_c we observed is due to solvent activity coefficients arising from the solvent interface at the reference electrode bridge.

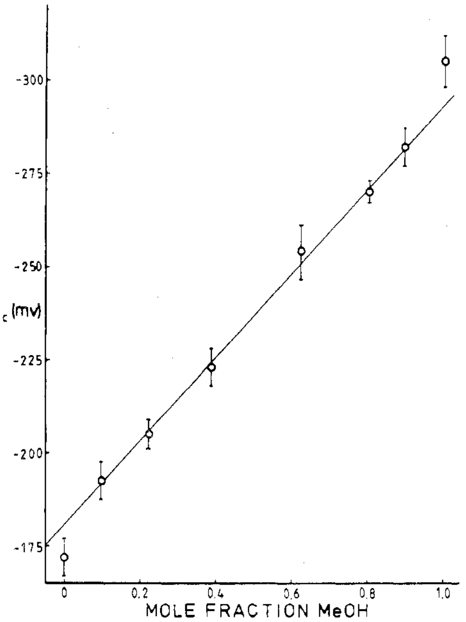

Figure 1. Reference potential dependence upon solvent composition for TEAF in 0.05 M TEAP at 25 °C. Error bars indicate ±1 average deviation.

Table I. Summary of β_1 Values for MF^+ Complexes in Methanol and Water at 25 °C

metal ion	solvent	electrolyte	β_1 ($\pm 1\sigma$)[a]
Mg^{2+}	methanol	0.05 M $NaClO_4$	2.5 (±0.1) × 10^4
	methanol	0.05 M TEAP	3.6 (±0.2) × 10^4
	water	0.05 M TEAP	72 (±4)
	water	0.05 M $NaClO_4$	63 (±3)
	water	1.0 M $NaClO_4$	22 (±1)
	water	1.0 M $NaClO_4$	24 (±1)[b]
Ca^{2+}	methanol	0.05 M TEAP	4.4 (±0.3) × 10^3
	water	0.05 M TEAP	37 (±3)
	water	0.05 M $NaClO_4$	33 (±3)
	water	1.0 M $NaClO_4$	6.3 (±0.2)
	water	1.0 M $NaClO_4$	3.4 (±0.9)[b]
Sr^{2+}	methanol	0.05 M TEAP	409 (±36)
	water	0.05 M TEAP	24 (±1)
Ba^{2+}	methanol	0.05 M TEAP	151 (±14)
	water	0.05 M TEAP	21 (±1)

[a] Average of 16 or more determinations. [b] Value from ref 13.

The addition of up to 1% (v/v) of water to a cell containing TEAF in a methanol solution of 0.05 M TEAP results in no significant shift in E_c. This indicates that no solvation effects occur with fluoride which affect the cell potential.

Solvents Effects upon β_1. The results of β_1 measurements in both methanol and aqueous solutions are summarized in Table I. The data show a striking increase in the stabilities of the complexes in methanol compared to those in aqueous solution. This enhancement of stability decreases down the group 2 metals, and results mirror the marked increase in the stabilities of cadmium and zinc halide complexes in Me_2SO, compared to those in water, seen by Ahrland et al.[5,7] They noted that the stability increase for the class "a" acceptor zinc was greater the harder the ligand. By analogy, for the very hard fluoride one might anticipate the considerable change in moving to methanol.

It should be noted that a direct comparison of the data in water and methanol is not strictly valid, since the "A" term in the Debye–Hückel limiting expression is 4 times larger for methanol than for water.[27] That is, activity coefficients are much smaller in methanol than in water for a given ion and ionic strength and this contributes to the differences in the concentration stability constants quoted. The difference

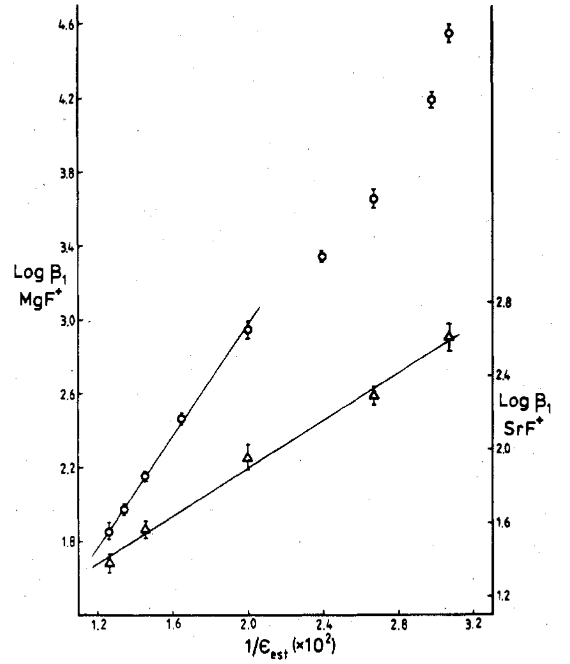

Figure 2. Plot of Born equation variables for methanol–water mixtures containing 0.05 M TEAP at 25 °C: (△) SrF^+, (○) MgF^+. Error bars indicate ±2 standard deviations.

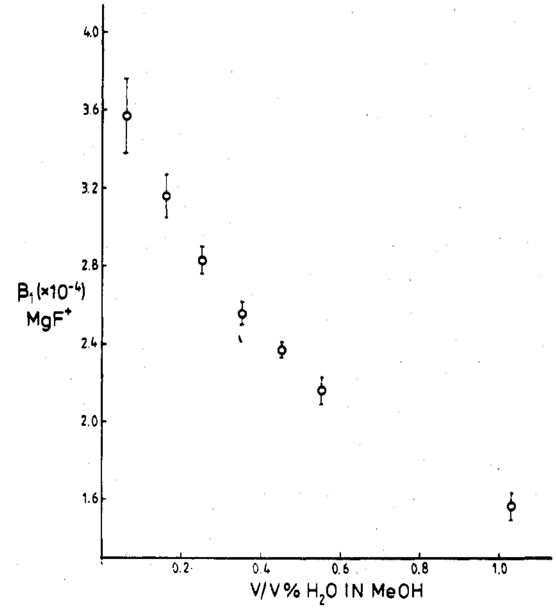

Figure 3. Effect of low water content upon the stability of MgF^+ in methanol containing 0.05 M TEAP at 25 °C. Error bars indicate ±1 standard deviation.

between the stability constants for magnesium obtained in methanolic TEAP and in sodium perchlorate solutions appears to be outside the limit of experimental error, although the agreement in water is within 2 standard deviations. This difference in the two solvents can be attributed to significant ion pairing by TEAP in methanol ($K_{ip} = 41$),[28] which is insignificant in water ($K_{ip} \approx 2$).[29]

The Born equation predicts a linear relationship between the logarithm of the stability constant and the reciprocal of the dielectric constant for an electrostatic interaction.[30] This prediction assumes that changing solvents does not alter the solvation or standard state activities of the participating species. Plots of the Born equation variables for magnesium and strontium monofluorides in methanol, water, and methanol–water mixtures are shown in Figure 2. Approximate values of the dielectric constants for the methanol–water mixtures were estimated from the mole fractions. The plot for strontium monofluoride is linear within an uncertainty margin of 2 standard deviations. This indicates that the stability differences for the strontium complex over the entire range of solvent composition are essentially governed by electrostatic effects and that solvation changes for the participating ions either are small or are essentially nulled. This type of linearity has been reported by Turyan et al. in polarographic studies of chloride, iodide, and thiocyanate complexes of cadmium and lead in alcohol–water mixtures up to 80% (v/v) alcohol.[31-33] These workers observed that the Born equation plot for a given complex was the same when methanol or ethanol was used, indicating that solvation changes are insignificant below 80% alcohol. Turyan also used estimated values of dielectric constants, evidently obtained by interpolation of the w/w percent data of Harned and Owen,[34] ignoring the effect of the very high ionic strength of 2.0 M. This uncertainty should be somewhat less in our estimates, since the ionic strength is only 0.05 M.

The magnesium data in Figure 2 appear linear from 100% water to 80% methanol, in agreement with Turyan's results. However, unlike the strontium case, distinctly nonlinear regions are found in moving toward pure methanol. In particular, a sharply rising region at very low percentage water is found which is certainly due to changes in the solvent coordination sphere of the central atom and/or ligand. This dependency is shown clearly in Figure 3. Considering the sharp decrease in the stability of magnesium monofluoride caused by small amounts of water and the known presence of 0.06 ± 0.01% water, our value of β_1 reported in methanol should be considered as the minimum value for pure methanol. By contrast, small additions of water have essentially no effect upon the strontium and barium systems, so our data for these species should be essentially that for pure methanol. The addition of small amounts of water to methanol solutions containing calcium monofluoride always caused precipitation to occur. This evidently hydrates the calcium, releasing sufficient fluoride from the complex to exceed the solubility product of CaF_2 in methanol.

The effect of adding chloride, bromide, and iodide to the complexing systems was of interest from the point of view of considering whether the classification systems are applicable to the alkaline earths in methanol. When methanol solutions, which were approximately millimolar in magnesium or strontium and 10^{-5} M in fluoride, were made millimolar in chloride, bromide, or iodide, the fluoride ISE potential remained unchanged. Therefore, the other halides do not displace fluoride from the complexes, and the stability constant sequence $F^- \gg Cl^-, Br^-, I^-$ is clearly revealed, as is predicted for class "a" acceptors.

No evidence of complexes with coordination numbers greater than 1 was observed in measurements involving magnesium or calcium; i.e., $f(C)$ was constant and independent of free fluoride concentration. Table II shows some representative data for the magnesium system. In the strontium and barium studies in methanol, evidence for higher complexes was found unless the total metal concentration was considerably greater than the fluoride. However, data were insufficiently accurate to undertake any quantitative calculations to determine the nature or stability of these species.

The aqueous data in Table I for calcium and magnesium clearly illustrate the marked variation of stability with ionic strength in water for these weak complexes. While our result for magnesium in 1.0 M aqueous sodium perchlorate agrees with previous results from this laboratory,[13] the corresponding result for calcium is higher. We believe the discrepancy for the calcium system arises from the extreme difficulty of precisely determining the constants of very weak complexes. The present results may be more reliable, since the electrode

Table II. Summary of Representative Data Obtained for the Magnesium Fluoride System in Methanol (0.05 M TEAP) at 25 °C

titration no.[a]	C_F, M	C_{Mg}(max), M	$10^4 f(C)$ (range)[b]
1	1.1×10^{-5}	9.1×10^{-4}	3.3–3.5
2	2.1×10^{-5}	2.0×10^{-3}	3.2–3.5
3	2.1×10^{-5}	2.0×10^{-4}	3.5–3.7
4	2.1×10^{-5}	2.2×10^{-3}	3.4–3.6
5	8.6×10^{-6}	1.7×10^{-4}	3.3–3.9
6	1.6×10^{-5}	5.5×10^{-4}	3.7–3.9
7	7.5×10^{-6}	1.3×10^{-4}	3.5–3.9
8	3.2×10^{-5}	3.6×10^{-5}	3.3–3.7
9	1.9×10^{-5}	1.8×10^{-4}	3.4–3.6
10	4.2×10^{-5}	3.6×10^{-4}	3.5–3.7

[a] Each titration consists of a minimum of six magnesium additions. [b] Maximum and minimum values obtained from random data points in titration. No systematic trend observed for $f(C)$ values during titration.

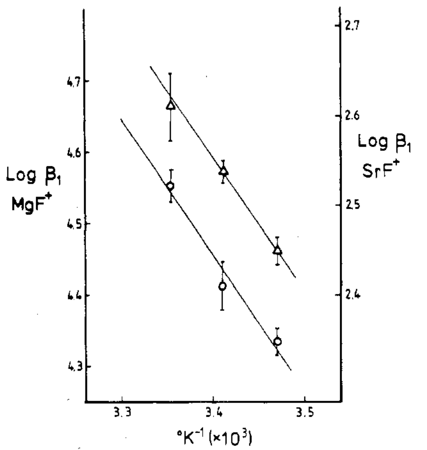

Figure 4. Temperature dependence of β_1 in methanol containing 0.05 M TEAP: (△) SrF^+, (○) MgF^+. Error bars indicate ±1 standard deviation.

was calibrated internally during each experiment compared with independent calibration and complex ion solution measurements in previous work.

Estimates of ΔH_1 and ΔS_1. Some approximate information regarding the magnitude of ΔH_1 and ΔS_1 was obtained by temperature-variation studies of β_1 for magnesium and strontium monofluorides in methanol containing 0.05 M TEAP. A plot of log β_1 vs. the reciprocal of Kelvin temperature is given in Figure 4.

The estimated values of the enthalpy changes for magnesium and strontium monofluorides in methanol are 35 and 28 kJ/mol, respectively, compared to values of 13 and 17 kJ/mol at an ionic strength of unity in aqueous solutions.[9] From this, we calculate entropy changes for magnesium and strontium monofluoride of 200 and 140 J/(K mol), respectively, compared to aqueous values of 71 and 59 J/(K mol) at unit ionic strength.[9] The reactions in methanol are both strongly entropy controlled; the magnesium case is even more so than all comparable aqueous monofluoro complexes except those of the triply charged lanthanide ions.[9] The same marked increase in ΔS_1 was seen by Ahrland in his study in Me_2SO.[6,8] For example, the monochloro zinc complex has an entropy change of 15 J/(K mol) in water but 112 J/(K mol) in Me_2SO.[8] He attributes this difference to the more random nature of the non-hydrogen-bonded dimethyl sulfoxide, resulting in a substantial entropy increase upon desolvation. This argument is also applicable to our case, since liquid methanol is much less ordered than water. However, it is equally important to note that the stability constant of magnesium in methanol is now of the same magnitude as the trivalent metals in water and the very much increased magnitude of the entropy is not surprising, assuming an electrostatic model is valid.

Conclusions

The feasibility of using fluoride ISE potentiometry in nonaqueous solutions is determined by two factors: the limited solubility of many inorganic fluoride salts in solvents of low polarity and the location of the lower end of the linear dynamic response range available for electrode calibration. The "window" between these two limits is barely wide enough to study the thermodynamic properties of alkaline earth monofluorides in methanol. Nonetheless, the utility of this electrode for such studies has been firmly established in methanol for those systems where fluoride concentrations above 10^{-5} M can be obtained. Solvents other than methanol will be examined in later studies.

The enhancement of alkaline earth monofluoride stabilities in methanol is marked and essentially explicable in terms of electrostatic interactions. Further monofluoride stabilization occurs for the more strongly hydrated magnesium and calcium ions, since fluoride competes more favorably for these acceptors in methanol than in water. Three pieces of evidence show that the group 2 metal ions act as class "a" acceptors in methanol, as is the case in water: Their reactions with fluoride are entropy controlled and governed by electrostatic interactions, and their fluoride stability constants are very much larger than for the other halides. Indeed, because of the very much enhanced stability in methanol, the classification is much more readily made than from data obtained in aqueous media. Similar investigations are planned with other metal ion examples regarded, from aqueous data, to be class "b" and border-line acceptors using a range of nonaqueous solvents to see what effect the change of solvent has in those situations.

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Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 39. Catalyzed Reductions of Cobalt(III) by Uranium(III)[1]

MARILYN K. LOAR, Y.-T. FANCHIANG, and EDWIN S. GOULD*

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The reduction of $Co(en)_3^{3+}$ with U^{3+} is strongly catalyzed by uncoördinated pyridine derivatives of the type known to catalyze the outer-sphere reductions of Co(III) complexes by Eu^{2+} and V^{2+}. Catalysis is inhibited by U^{4+}. As with the dipositive reductants, kinetic data are interpreted in terms of a sequence in which the catalyst is first reduced (k_1) to a radical intermediate, which may then undergo reversal of the initial step (k_{-1}) or may react with $Co(en)_3^{3+}$ (k_2). The present results, in conjunction with earlier data,[2] allow us to estimate k_1, k_{-1}, and k_2 for reactions catalyzed by isonicotinamide, nicotinamide, and methylviologen. Values of the composite specific rate k_1k_2/k_{-1} are in agreement with those calculated using the formal potentials of U^{3+} and the catalysts and a linear free energy relationship (eq 3 in the text) which links k_2 to $E°_{Cat}$. The ratio k_{-1}/k_2 lies near 1/3 for nicotinamide and isonicotinamide but is 1/700 for methylviologen, which can participate only in outer-sphere processes. This difference points strongly to an inner-sphere path for the k_{-1} step involving the two amides and, by implication, for the initial reduction (k_1) as well. The high specific rates (10^4–10^6 M^{-1} s^{-1}) for these inner-sphere acts indicate that ligand substitutions about the U(III) and U(IV) centers are rapid. The k_1 value for the reaction catalyzed by methylviologen, in combination with the Marcus treatment,[11] allows us to estimate a self-exchange rate of 5×10^{-2} M^{-1} s^{-1} (25 °C, $\mu = 1.0$) for U^{3+}–U^{4+}.

In previous studies dealing with the outer-sphere reductions of cobalt(III), as catalyzed externally by pyridine derivatives which themselves undergo reversible one-electron reductions, the most straightforward kinetic picture was obtained when europium(II) or vanadium(II) was taken as the reducing center.[2] Although a substantial body of evidence was gathered in support of catalytic sequence 1, it was recognized that

$$\text{Cat} \underset{M^{3+},\ k_{-1}}{\overset{M^{2+},\ k_1}{\rightleftharpoons}} \text{Cat}\cdot \xrightarrow[k_2]{\text{Co(III)}} \text{Cat} + Co^{2+} \qquad (1)$$
$$M = Eu, V, Cr$$

several features could introduce complications in these or in analogous systems. The observed[2a,3] deterioration of catalyst function with use may be attributed to the gradual destruction of the catalyst by a combination of bimolecular termination acts and slow reduction of the radical intermediate, Cat·, to an inactive two-electron product; this attrition would be expected to be most troublesome with the most powerful reducing centers. A second point concerns the degree of reversibility of the initial step, particularly when this is an inner-sphere process. In Cr^{II}–Cr^{III} systems, for example, the slow substitution about the Cr^{III} center curtails reversibility so that inhibition of the catalytic path by M^{3+}, which is quite characteristic of Eu(II) and V(II) reductions, is not observed.[2d]

The present extension of our catalytic studies to the very strongly reducing species U^{3+} ($E° = -0.63$ V)[4] relates to these matters. We were interested particularly in what could be learned about the ease of ligand substitution about the uranium(IV) center, a question on which direct evidence is lacking.

Experimental Section

Materials. Tris(ethylenediamine)cobalt(III) chloride, $Co(en)_3Cl_3$, was prepared as described[5] and converted to the corresponding perchlorate by dissolving in warm water and adding an equal volume of 70% $HClO_4$. The solution and precipitation steps were repeated until the product gave a negative chloride test. Since this complex was used in large excess in most of our kinetics experiments, it was essential that it be free of impurities reducible by U^{3+}. Uranium(III) perchlorate solutions were prepared as described.[6] Uranium(IV) solutions were prepared by bubbling air through acidic U(III) solutions for 15 min. Thorium perchlorate (Alfa) and catalysts (Aldrich) were used as received.

Rate Measurements. Rates were estimated by following absorbance decreases on the Cary 14 recording spectrophotometer as described.[2a,6] All experiments involved $Co(en)_3^{3+}$, which, in the absence of catalysis, is one of the most sluggish Co(III) oxidants known. Measurements were made at 350 nm (where absorption by U^{3+} is dominant).[7] Reactions were carried out under nitrogen. The supporting medium was generally 0.25 M in $HClO_4$ with the ionic strength adjusted to 0.50 M with $LiClO_4$. Reductions were first order in U^{3+} but exhibited a more complex dependence (see below) on $[Co^{III}]$. Experimental runs were generally made under pseudo-first-order conditions with the ratio $[Co^{III}]/[U^{3+}]$ greater than 10. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 5%. No trends indicative of systematic errors within a single run were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 8%, except for those reactions catalyzed by isonicotinic acid, which showed somewhat greater scatter. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Deterioration of catalyst function with use, as described in earlier reports,[2a,3] was more serious for U^{3+} than for Eu^{2+} or V^{2+}, although experimental conditions were chosen to minimize this difficulty. Successive runs with the same sample of catalyst were characterized by apparent rate constants which decreased by 10–15% for each charge of U^{3+}.

Stoichiometry. Stoichiometry experiments, in which solutions of properly purified $Co(en)_3(ClO_4)_3$ and catalyst in 0.25 M $HClO_4$ were treated with a measured, deficient quantity of U^{3+}, were carried out in a manner similar to that described.[8] After these mixtures were allowed to react for 10 min, the quantity of Co^{2+} formed was estimated