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Stability of Monofluoride Complexes of the Irving–Williams Series Acceptors in Methanol

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The thermodynamics (K_{stab}, ΔG_1, ΔH_1, ΔS_1) for the formation of monofluoride complexes, MF^+ ($M^{2+} = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), have been studied in methanol and water at an ionic strength of 0.05 M with use of fluoride ion selective electrode potentiometry. These complexes are weak and have very similar stabilities in aqueous medium. However, they are substantially more stable in methanol and definite conclusions may be made concerning trends in stability. Unlike most complexes having nitrogen or oxygen atoms, these fluoride complexes clearly disobey the Irving–Williams stability trend. These complex formation reactions are all distinctly entropy controlled. Although electrostatic considerations play a crucial role, the stability order does not follow the trend predicted by ionic radii.

Introduction

Three decades ago Irving and Williams[2] first described their observation that, for a given ligand and coordination number, the stability trend for aqueous complexes of certain first-row divalent transition-metal ion acceptors generally is

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This stability sequence has become known as the "Irving-Williams Series" and has been the subject of numerous phenomenological and conceptual studies over the ensuing years.[3] The trend is obeyed by a large number of complexes in aqueous solution, especially in cases where the donor atom is oxygen or nitrogen.

The monohalide complexes appear to pose a special set of problems with regard to the Irving-Williams sequence. These acceptors are weakly "a" type with respect to halide complexation,[4] but even the monofluoride complexes are extremely weak, and all have very similar stabilities. Fluoride ion selective electrode potentiometry has proved to be a convenient technique for determining the stability of these complexes in aqueous solution.[5,6] Although the copper(II) monofluoride complex is clearly the most stable, the monotonic increase in stability from manganese(II) to copper(II), as predicted by Irving–Williams behavior, appears to be violated. Large relative experimental uncertainties are unavoidably present in the values of the very small and similar stability constants, raising questions regarding whether the stability differences are real or merely experimental artifacts.

In an attempt to gain further insight into this problem, we have studied the stabilities of these monofluoride species in methanol using potentiometric techniques recently developed in our laboratories.[7] Although methanol is water-like in many respects, it has a smaller dielectric constant and weaker ionic solutions capability as well as weaker hydrogen-bonding solvation of anions. These solvent differences should result in enhanced complex stability and, hopefully, enhanced differentiation in complex strengths. This could provide helpful supporting evidence concerning the validity of the anomalous aqueous stability sequence and also contribute information toward the broader question concerning the general validity of the Irving–Williams series in nonaqueous systems.

Experimental Section

Chemicals and Solutions. Eastman tetraethylammonium perchlorate (TEAP) was recrystallized several times from deionized distilled water and finally from methanol to remove included water. Deionized distilled water was used for all aqueous and mixed-solvent solutions. Analytical reagent grade methanol (0.01–0.03% nominal water content) was used as received. Our rationale for not attempting to rigorously exclude water has been described previously,[7] and all measurements were made in the open laboratory. TEAP (0.05 M) was present in all solutions to control ionic strength. The pH of all aqueous TEAP solutions was 5–6 except solutions containing iron(II) were below pH 5.

Tetraethylammonium fluoride (TEAF) obtained from ICN K & K Laboratories was used as received for preparing stock fluoride solutions in both methanol and water. These solutions were standardized against a standard sodium fluoride solution by Gran's standard addition technique. Stock aqueous solutions of the transition-metal ions were prepared from their hydrated perchlorate salts. The same salts were dried in a vacuum desiccator over phosphorus pentoxide for several hours before being used to prepare stock solutions in methanol. The various stock solutions of transition-metal ions were each standardized with use of conventional complexometric or redox titration procedures. All solutions were stored in polyethylene bottles.

Apparatus. The measurement cells were polyethylene beakers equipped with thermostated water jackets, which maintained the cell temperature to within ±0.1 °C of the desired value. The sensors were Orion 94-09A fluoride electrodes. Orion 90-02 double-junction reference electrodes with 1.0 M $NaNO_3$ outer filling solution were used for all aqueous measurements. Two equally reliable and stable reference electrodes were used in methanol and mixed-solvent systems; one was the above-mentioned double-junction electrode fitted with a fritted glass bridge containing 0.05 M TEAP in the solvent being used in the cell. The alternate reference was a nonaqueous silver–silver chloride reference electrode filled with 1.0 M lithium chloride in methanol and also equipped with a fritted glass bridge containing TEAP solution. Voltage and pH measurements were made with Corning Model 130 digital pH meters. Controlled-potential electrolysis experiments were undertaken with a Princeton Applied Research Model 173/179 potentiostat. The electrolysis vessel was a PAR 9600 coulometry system equipped with a platinum-gauze working electrode.

Procedure. The simple general procedure and computations used when the acceptor is Mn(II), Co(II), Ni(II), Cu(II), or Zn(II) will be described first. This will be followed by a description of modifications arising from the air oxidizability of Fe(II) and the potential formation of hydroxide species.

General Procedures. Fifty milliliters of 0.05 M TEAP in the desired solvent was pipetted into the polyethylene cell, a measured portion of stock TEAF solution was added with a 2.0 mL capacity micrometer buret, the electrode pair was introduced into the cell, the cell was capped to minimize evaporation, and the emf was recorded at steady state (less than 0.1-mV drift in 90 s). Several more successive portions of TEAF were added, with the steady-state emf recorded for each addition. This provided data for an electrode response calibration plot of emf vs. pF. After the last TEAF addition, several successive additions of a standard transition-metal ion solution were made, with the emf recorded at steady state after each addition. The final TEAF concentration prior to metal ion addition ranged from about 2×10^{-5} to 4×10^{-4} M, while the total metal ion concentration range was typically 2×10^{-4} to 8×10^{-3} M. A more extensive discussion of

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(1) (a) State University College at Brockport. (b) Deakin University.

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experimental considerations, including electrode response, is found elsewhere.[7] For each addition of metal ion solution, a quantity, $f(C)$, can be calculated from the change in potential.[7,8]

$$f(C) = \frac{C'_F - [F^-]}{(C_M - C'_F + [F^-])[F^-]} = \frac{\beta_1 + 2\beta_2[F^-] + \ldots + n\beta_n[F^-]^{n-1}}{1 - \beta_2[F^-]^2 - \ldots - (n-1)\beta_n[F^-]^n} \qquad (1)$$

A knowledge of $f(C)$ enables the stability constant to be calculated. C'_F represents the total concentration of fluoride, excluding HF, $[F^-]$ is the free or uncomplexed fluoride concentration, and C_M is the total acceptor concentration. The concentration of HF in aqueous solution is negligible above pH 5. The value of $f(C)$ is independent of metal ion concentration for mononuclear complexation and is also independent of free fluoride concentration if only 1:1 complexation occurs, in which case $f(C) = \beta_1$. Since we are interested in the monofluoride complexes, this situation can be favored experimentally by high metal-to-ligand ratios.

In order to verify that the experimental values of $f(C)$ do, in fact, correspond to β_1, we have varied C'_F, C_M, and the metal-to-ligand ratios as widely as are experimentally feasible. The limitations include inherent electrode response factors,[7] the minimum metal ion addition required to produce an emf change, and the 0.05 M total ionic strength restriction due to the limited solubility of TEAP in methanol. Within these restrictions, we were generally able to vary the total acceptor and fluoride concentrations by at least an order of magnitude for each metal investigated. The range of free fluoride concentrations in experiments with varying metal ion concentration always exceeded an order of magnitude, obviously increasing in proportion to complex stability.

Special Procedures for Fe(II) Studies. The presence of even trace amounts of Fe(III) in fluoride complexation experiments introduces an intolerably large error due to the strong complexation of Fe(III) by fluoride.[9] Moreover, air oxidation of Fe(II) solutions is a well-known problem, and we have observed that it occurs much more rapidly in methanol than in water. While the work could be carried out in an oxygen-free environment, small amounts of Fe(III) arising from the reagents remain a problem. Bond and Hefter solved this problem by in situ formation of ferrous perchlorate by chemical means,[5] but this approach proved to be unsatisfactory under our conditions of much lower ionic strength. We chose, instead, to electrochemically reduce all Fe(III) to Fe(II) under oxygen-free conditions, which also has the advantage of not requiring the addition of reagents not present in the experiments with the other metal ion acceptors.

The stock iron solution was not protected from air oxidation, since the iron was quantitatively converted to Fe(II) immediately prior to use. The electrolysis vessel and the potentiometric cell were mounted inside a transparent gas bag. Both cells and the bag were thoroughly purged with prepurified nitrogen saturated with the solvent being used in the experiment. A portion of stock iron solution was reduced to Fe(II) at a controlled potential (0.0 V vs. aqueous SCE for aqueous experiments, −0.5 V vs. aqueous SCE for methanol experiments) until the current decayed to the background value. Meanwhile, the fluoride electrode was calibrated in the usual manner. A micrometer buret was loaded with Fe(II) from the electrolysis cell, working inside the gas bag. A small amount of solution was delivered from the buret into a vial of potassium thiocyanate solution to visually confirm the absence of Fe(III). Buret additions were then made to the potentiometric cell in the usual manner.

A second complication arose in the aqueous iron experiments due to the necessity of maintaining acidic (about pH 3) conditions in the stock iron solution to avoid hydroxide formation in the electrolysis cell. Consequently, the pH in the potentiometric cell fell below 5 as a result of the iron additions, necessitating corrections for the formation of molecular HF in aqueous experiments. This was accomplished by measuring the pH in the potentiometric cell after each addition of iron solution and correcting for HF formation as follows:

$$C'_F = C_F - \frac{a_{H^+}[F^-]}{K'_a} \qquad (2)$$

where C_F is the total concentration of fluoride in the cell. The mixed acid dissociation constant for HF, K'_a, was determined potentiometrically in aqueous 0.05 M TEAP:

$$K'_a = \frac{a_{H^+}[F^-]}{[HF]} = 9.4\ (\pm 0.5) \times 10^{-4}$$

The remaining calculations were made as described previously. There was no evidence of hydroxide or HF formation during the corresponding experiments in methanol.

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

complex	solvent	ionic strength, M	β_1 $(\pm\sigma)^a$	ref^b
MnF$^+$	H_2O	3.0 ($NaClO_4$)	10.0 ± 0.3	6
	H_2O	1.0 ($NaClO_4$)	4.2 ± 0.2	5
	H_2O	0.05 (TEAP)	24 ± 2	PW
	MeOH	0.05 (TEAP)	3.0 (±0.4) × 10^3	PW
FeF$^+$	H_2O	1.0 ($NaClO_4$)	6.7 ± 0.3	5
	H_2O	0.05 (TEAP)	28 ± 4	PW
	MeOH	0.05 (TEAP)	6.1 (±1.0) × 10^3	PW
CoF$^+$	H_2O	3.0 ($NaClO_4$)	4.4 ± 0.2	6
	H_2O	1.0 ($NaClO_4$)	2.5 ± 0.3	5
	H_2O	0.05 (TEAP)	19 ± 1	PW
	MeOH	0.05 (TEAP)	1.1 (±0.1) × 10^3	PW
NiF$^+$	H_2O	3.0 ($NaClO_4$)	5.8 ± 0.2	6
	H_2O	1.0 ($NaClO_4$)	2.2 ± 0.2	5
	H_2O	0.05 (TEAP)	21 ± 2	PW
	MeOH	0.05 (TEAP)	8.1 (±1.1) × 10^2	PW
CuF$^+$	H_2O	3.0 ($NaClO_4$)	11.4 ± 0.4	6
	H_2O	1.0 ($NaClO_4$)	6.9 ± 0.5	5
	H_2O	0.05 (TEAP)	29 ± 2	PW
	MeOH	0.05 (TEAP)	3.3 (±0.2) × 10^4	PW
ZnF$^+$	H_2O	3.0 ($NaClO_4$)	7.5 ± 0.1	6
	H_2O	1.0 ($NaClO_4$)	3.2 ± 0.2	5
	H_2O	0.05 (TEAP)	20 ± 1	PW
	MEOH	0.05 (TEAP)	2.3 (±0.2) × 10^3	PW

[a] All determined by fluoride ion selective electrode potentiometry. [b] PW = present work. β_1 values are mean of 15 or more measurements.

Results and Discussion

Aqueous Stability Measurements. The complex stabilities were reevaluated in aqueous medium with use of the 0.05 M TEAP conditions to facilitate comparison of measurements in water with those in methanol. The results of these experiments are summarized in Table I, along with previously reported results at high (1 M) and very high (3 M) ionic strength. The variation of the stability with ionic strength is as expected. The anomalous non-Irving–Williams behavior seen for aqueous systems at 0.05 M ionic strength is preserved in methanol. Importantly, the stability differences in methanol are sufficiently large that this conclusion can be reached unambiguously after consideration of experimental uncertainty.

The iron(II) complex deserves special consideration, since its aqueous stability is the most markedly out of line from the Irving–Williams trend. The uncertainty in our iron(II) aqueous stability constant in Table I reflects the more complicated procedure required for studies involving iron(II) but assumes negligible uncertainty in the mixed acidity constant for HF. In fact, the relative standard deviation for this constant, as measured, exceeds 5%. For example, if β_1 for FeF$^+$ is recomputed with $K'_a = 9.9 \times 10^{-4}$ (one standard deviation higher), the value is 32 ± 4 compared to the value of 28 ± 4 seen in Table I. Similarly, using $K'_a = 8.9 \times 10^{-4}$ gives $\beta_1 = 25 \pm 5$. This later value approaches β_1 for MnF$^+$ but is still certainly out of line with the monotonic prediction. Thus, the good qualitative agreement between our aqueous results and those of Bond and Hefter[5] supports the conclusion that the anomalous trend is valid and is not an experimental artifact.

Stability Measurements in Methanol and Methanol–Water Mixtures. The results of β_1 determinations in methanol, as well as in water, are summarized in Table I. Although activity

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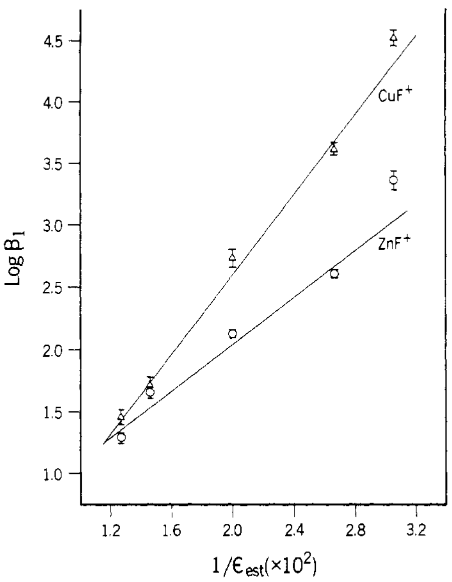

Figure 1. Plot of Born equation variables for methanol–water mixtures containing 0.05 M TEAP at 25 °C: (Δ) CuF^+; (O) ZnF^+. Error bars indicate $\pm 2\sigma$.

coefficients differ as the solvent varies,[10] it is nevertheless useful to compare these concentration stability constants in different solvents. A striking stability increase is seen for all complexes when going from water to methanol solution. The relative magnitudes of the stability increase are comparable to those observed for MgF^+ and CaF^+ in similar studies involving alkaline-earth complexes.[7] A similar marked stability enhancement for zinc halide complexes in dimethyl sulfoxide was reported by Ahrland et al.,[11] who have shown that, the harder the ligand, the greater the stability increase for zinc. Doe and Kitagawa report concentration stability constant values for $CoCl^+$, $NiCl^+$, $CuCl^+$, and $ZnCl^+$ in methanol of 99.2, 64.8, 1.2×10^4, and 757, respectively.[12] Thus, a comparison of these values with the corresponding monofluoride data in Table I indicates that, with the possible exception of copper(II), the Irving–Williams acceptors are hard, or class "a", in methanol. It should be noted that electrode instability permitted only an estimate of the stability of the $CuCl^+$ complex.[12] The likelihood that all of the Irving–Williams acceptors are class "a" is supported by our observation that the addition of amounts of chloride or iodide in excess of the amount of metal present did not displace fluoride from the complexes in methanol.

It is of interest to examine the dependency of complex stability upon the solvent composition in methanol–water mixtures, since the Born relationship predicts linearity for a plot of the logarithm of the stability constant vs. the reciprocal of the dielectric constant for electrostatic interactions. This simple dependency assumes no changes occur in solvation and standard state. We have examined this dependency for copper(II) and zinc(II) monofluorides in water, methanol, and the water–methanol mixtures. The results are shown in Figure 1. The dielectric constants of the solvent mixtures were estimated from the mole fractions.[7] The plots both appear linear up to 95% methanol, which suggests that water is not appreciably displaced by methanol solvation if more than 5% water is present. The linearity also suggests that stability change with solvent composition is largely governed by electrostatic effects. This is similar to what was previously observed for the corresponding magnesium and strontium complexes.[7] The marked stability increase seen in reagent-grade methanol suggests that small amounts of water suppress complex stabilities. Since our methanol has not been rigorously dried, the β_1 values cited for methanol should be taken as minimum values. This does not affect the interpretation of the data, since the various complexes show markedly different, but parallel, stabilities under all conditions considered.

Table II. Results of a Representative Study of CuF^+ in Methanol (0.05 M TEAP) at 25 °C

amt of 0.209 M Cu^{2+} added,[a] mL	$10^3 C_{Cu}$, M	pF[b]	$10^{-4} f(C)$[c]
0.20	0.81	4.84	3.17
0.40	1.61	5.22	3.21
0.60	2.40	5.42	3.21
0.80	3.19	5.55	3.23
1.00	3.98	5.65	3.92
1.50	5.91	5.80	3.34
2.00	7.80	5.93	3.19

[a] Added to 51.50 mL of 2.71×10^{-5} M TEAF in methanol (0.05 M TEAP). [b] As determined from the calibration equation E (mV) = −242.0 + 58.0pF. [c] From eq 1.

Table III. Results of a Representative Study of MnF^+ in Methanol (0.05 M TEAP) at 25 °C

amt of 0.208 M Mn^{2+} added,[a] mL	$10^3 C_{Mn}$, M	$E_c = -334.0$, $S = 59.3$		$E_c = -340.9$, $S = 60.9$	
		pF[b]	$10^{-3} f(C)$[c]	pF[b]	$10^{-3} f(C)$[c]
0.05	0.21	4.081	3.26	4.087	3.42
0.10	0.41	4.214	3.11	4.217	3.16
0.20	0.82	4.413	3.09	4.411	3.08
0.40	1.63	4.648	3.01	4.639	2.94
0.60	2.43	4.803	2.99	4.790	2.89
1.20	4.81	5.076	2.93	5.056	2.79
1.60	6.37	5.189	2.88	5.166	2.72
2.00	7.90	5.277	2.83	5.251	2.67

[a] Added to 50.60 mL of 1.27×10^{-4} M TEAF in methanol (0.05 M TEAP). [b] Calculated from pF = (E (mV) − E_c)/S. [c] From eq 1.

No evidence of metal complexes with fluoride coordination numbers greater than 1 were seen in experiments with iron(II), cobalt(II), nickel(II), copper(II), or zinc(II) in methanol. In each of these cases, $f(C)$ was constant within the limits of experimental error, was independent of all concentrations, and therefore was equal to β_1. A representative set of data for a typical experiment in methanol is shown in Table II.

In the case of manganese(II), a slight decreasing trend in $f(C)$ was observed as the free fluoride concentration decreased. This is illustrated by a representative set of data in Table III. This behavior is characteristic of the presence of small amounts of complexes with coordination numbers greater than 1. The metal-to-ligand ratio could not be made sufficiently large to avoid this effect because of electrode response and ionic strength limitations. The formation of two- and three-coordinate manganese(II) fluoride species in acetonitrile has been reported by Coetzee and Martin.[13] Attempts to extract a set of β_n values from our data were unsuccessful for several reasons. The change in $f(C)$ is about 20% over the entire accessible range of experimental conditions, indicating that the higher complexes are minor components. The second set of data in Table III illustrates what happens to the values of $f(C)$ if a single point is dropped from the calibration set, slightly altering the calibration constants. This illustrates that, although the trend is visible, it nearly lies within the experimental uncertainty, considering that run-to-run reproducibility is generally in the 5–10% range. Consequently, the value of β_1,

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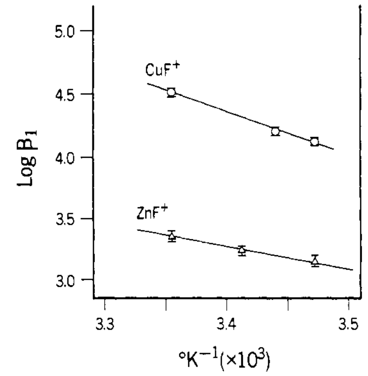

Figure 2. Sample plots showing temperature dependence of β_1 for methanol containing 0.05 M TEAP: (○) CuF$^+$; (△) ZnF$^+$. Error bars indicate ±1σ.

taken as the mean of $f(C)$, is undoubtedly somewhat high, but the standard deviation of the pooled data is no larger than that for NiF$^+$ and smaller than that for FeF$^+$, where a more complicated experimental technique is required.

Doe and Kitagawa have studied M^{2+}–ClO$_4^-$ ion-pairing equilibria in methanol.[12] They report that the thermodynamic ion-pairing constant is about 100 for Co(ClO$_4$)$^+$, Ni(ClO$_4$)$^+$, and Cu(ClO$_4$)$^+$ and about 60 for Zn(ClO$_4$)$^+$. Correction of our concentration-based values in Table I for this ion pairing would increase the reported constants by 8% or less and would not alter the trends seen in Table I.

The results reported in Table I clearly indicate that the Irving–Williams sequence is not obeyed in methanol. Moreover, the anomalous stability sequence closely mimics the pattern seen in aqueous systems, but considerable absolute and relative enhancement of the stability differences is seen for each ligand acceptor. It is also consistent with the CoCl$^+$ > NiCl$^+$ << CuCl$^+$ > ZnCl$^+$ stability sequence obtained in methanol.[12]

Enthalpy and Entropy Considerations. Rationalizations of the Irving–Williams sequence are usually based upon a combination of effects, including electrostatic considerations, ligand field stabilization energy, and Jahn–Teller tetragonal distortion.[14] These concepts all speak to the enthalpy of complex formation; hence it is not surprising that the vast majority of reactions that obey the Irving–Williams sequence are enthalpy controlled; i.e., the enthalpy term in free energy predominates over the entropy term.[15] Ligands with oxygen or nitrogen donor atoms generally produce complexes whose stabilities follow this trend and are nearly always enthalpy controlled. However, the stabilities of most aqueous monofluoride complexes are entropy controlled.[9] Although their enthalpies of formation are endothermic, monofluoride complexes generally have negative free energies of formation.

Table IV. Summary of Thermodynamic Functions for Monofluoride Monofluoride Complexes at 25 °C

complex	solvent	ΔG_1,[a] kJ mol^{-1}	ΔH_1,[b] kJ mol^{-1}	ΔS_1, J K^{-1} mol^{-1}
MnF$^+$	water[c]	−5.7 ± 0.1	15.1 ± 0.8	44 ± 4
	methanol[d]	−19.8 ± 0.3	(0)[e]	(66)[f]
FeF$^+$	methanol	−21.6 ± 0.4	31 ± 2	175 ± 6
CoF$^+$	water	−3.7 ± 0.1	13.8 ± 0.8	59 ± 4
	methanol	−17.4 ± 0.2	39 ± 8	190 ± 30
NiF$^+$	water	−4.4 ± 0.1	5.9 ± 0.4	33 ± 2
	methanol	−16.6 ± 0.3	37 ± 2	181 ± 6
CuF$^+$	water	−6.0 ± 0.1	13.4 ± 0.8	65 ± 4
	methanol	−25.8 ± 0.2	69 ± 3	320 ± 10
ZnF$^+$	water	−4.98 ± 0.04	9.2 ± 0.4	48 ± 2
	methanol	−19.2 ± 0.2	35 ± 4	180 ± 13

[a] Calculated from β_1 (determined potentiometrically). [b] Aqueous values determined calorimetrically; methanol values estimated via temperature dependence of β_1. [c] Taken from ref 6, $\mu = 3.0$ via NaClO$_4$. [d] Present work, $\mu = 0.05$ via TEAP. [e] See text. [f] Assuming $\Delta S_1 = -\Delta G_1/T$.

We have obtained some information concerning the magnitude of ΔH_1 and ΔS_1 by temperature-variation studies of β_1 for the monofluoride complexes of the Irving–Williams acceptors in methanol containing 0.05 M TEAP. Sample plots of log β_1 vs. the reciprocal of Kelvin temperature are shown in Figure 2 for two of the complex systems. A summary of estimated ΔG_1, ΔH_1, and ΔS_1 values is presented in Table IV along with some literature values for the corresponding aqueous systems. The uncertainties quoted for ΔS_1 and ΔH_1 in methanol are conservative estimates obtained from linear least-squares calculations, rather than by propagation of experimental uncertainties. The stability constant for MnF$^+$ in methanol was temperature independent, within experimental uncertainty, in the 15–25 °C temperature range where these stability measurements can be made. This indicates that ΔH_1 is nearly zero and that ΔS_1 can be estimated as $-\Delta G_1/T$ for this complex. Thus, both ΔH_1 and ΔS_1 are markedly smaller for MnF$^+$ than for the remaining monofluoride complexes of the Irving–Williams acceptors.

A comparison of aqueous and methanolic solution values in Table IV indicates that, for these acceptors, the reactions are even more strongly entropy controlled in methanol than in water. This is true in spite of the less favorable enthalpy terms in methanol. This same marked effect was previously observed for MgF$^+$ and SrF$^+$, for which ΔS_1 goes from 71 and 59 J K^{-1} mol^{-1} in water to 200 and 140 J K^{-1} mol^{-1} in methanol, respectively, while ΔH_1 goes from 13 and 17 kJ mol^{-1} in water to 35 and 28 kJ mol^{-1} in methanol.[7] Similarly, Ahrland has reported that ΔS_1 for ZnCl$^+$ increases from 15 J K^{-1} mol^{-1} in water to 112 J K^{-1} mol^{-1} in dimethyl sulfoxide and attributes this increase to desolvation effects.[16] It is interesting to note that, with the exception of CuF$^+$ and MnF$^+$, the ΔS_1 values for methanol in Table IV are all within experimental uncertainty of each other. The much higher value of ΔS_1 for CuF$^+$ could arise for some type of rearrangement in coordination, since copper is notable for such effects. Thus, ΔS_1 does not exhibit the distinctive trend associated with Irving–Williams behavior in either water or methanol.

The expectation for an electrostatic model would be an increasing stability order from MnF$^+$ to ZnF$^+$ corresponding to the decreasing ionic radii of the acceptors. This is the trend observed for the monofluoride complexes in the Mg^{2+}–Ca^{2+}–Sr^{2-}Ba^{2+} series, where the small magnesium ion forms the most stable complex.[7] No such trend associated with size is found for the values of ΔG_1, ΔH_1, or ΔS_1 for these transition-metal complexes in methanol. The Irving–Williams sequence, on the basis of ligand field stabilization considerations, should lead to the stability sequence MnF$^+$ < FeF$^+$ < CoF$^+$ < NiF$^+$ < CuF$^+$ > ZnF$^+$, but neither ΔG_1 nor ΔH_1 follows this trend. Furthermore, the trend seen in ΔH_1 for these complexes is exactly the opposite of what is predicted. However, if one considers experimental uncertainty, the values of ΔH_1 are all essentially the same with the exception of those for MnF$^+$ and CuF$^+$. It is possible that ligand field effects modify the pattern from that based upon a simple electrostatic model and/or that the monofluoride complexes have some characteristics of ion pairs rather than those of inner-sphere

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complexes, but the nature of such interactions is not understood at present.

Conclusions

There remains little, if any, doubt that the monofluoride compexes are a clear and distinct exception to the Irving-Williams sequence. The use of methanol as an alternate solvent plays a crucial role in this conclusion and has proved to be an ideal choice for enhancing the anomalous aqueous sequence. These acceptors are distinctly "a" type in methanol, as in water. The predominance of electrostatic interactions in both solvents facilitates a direct and unambiguous comparison of stability data in these two solvents. Entropy control of these reactions is marked and overwhelms all other considerations.

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The Nature of Selenium Dissolved in Hydrochloric Acid Containing Selenium Dioxide

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Elemental selenium dissolved in solutions of SeO_2 in concentrated hydrochloric acid to a small extent, giving strongly yellow solutions. Gravimetric analysis and spectrophotometric study of these solutions show that the principal species in equilibrium with $SeOCl_2$ is Se_2Cl_2. A completely satisfactory interpretation of the results requires however the presence of $SeCl_2$ also. Formation constants and extinction coefficients at 25 °C for Se_2Cl_2 and $SeCl_2$ are given.

Introduction

It has been known for a long time that elemental selenium dissolves in concentrated hydrochloric acid containing SeO_2.[1] Concentrated solutions of this type are employed in the preparation of diselenium dichloride by a method first developed by Lenher and Kao.[2] Diselenium dibromide is prepared similarly. The nature of the dark yellow species formed when selenium is dissolved in SeO_2-containing solutions in hydrochloric acid was studied by Ullrich and Ditz.[3] They concluded that the species formed at low concentrations was diselenium dichloride on the basis of titration of Se(IV) in hydrochloric acid with tin(II) chloride to the point of precipitation of elemental selenium. However, on the basis of the solubility of selenium in the SeO_2 solutions, they showed that Se_2Cl_2 formation was not complete. The precise nature of the selenium species in these solutions was of interest to us as an extension of our work on solutions of SeO_2 in hydrochloric acid.[4] Of the three known chlorides of selenium, Se_2Cl_2, $SeCl_2$, and $SeCl_4$, only Se_2Cl_2 and $SeCl_4$ are known in condensed form while $SeCl_2$ is known only in the vapor phase[5] although Se(II)-halogen species are apparently stabilized by coordination of additional donor ligands.[6,7] A similar situation is found for the selenium bromides, and several studies of the equilibria between $SeBr_4$, Se_2Br_2, and $SeBr_2$ in nonaqueous solvents have been made.[8,9] In view of the possible existence of Se(II) in Se-SeO_2 mixtures in hydrochloric acid, a more precise study of such solutions by spectrophotometric and gravimetric means was considered of interest.

Experimental Section

Hydrochloric acid (J. T. Baker) was standardized against sodium carbonate by the usual procedures. All HCl solutions were then adjusted to 11.80 M. Selenium dioxide (Ventron) was analyzed for purity, and selenium (Baker AR) was finely ground before use.

Solutions, which were prepared from excess selenium and stock solutions of SeO_2 in hydrochloric acid, were stored in well-sealed flasks to minimize air oxidation. The solutions were shaken for 8 h at room temperature and then equilibrated overnight at 25 °C in a constant-temperature bath before study. Both spectrophotometric and gravimetric analytical methods showed no change in selenium solubility after 24 h of saturation.

Dissolved selenium was determined by simple dilution of 25-mL aliquots of the supernatant of the saturated acid solutions to 250 mL and weighing of precipitated elemental selenium. Analysis of total selenium in the saturated solutions by standard procedures[10] yielded the same value of the sum of original Se(IV) and dissolved elemental selenium, indicating that the dilution method is accurate and that no reduced selenium species, apart from Se(IV), remained dissolved after dilution.

Spectrophotometric measurements were made with a Varian DMS 90 UV-visible spectrophotometer using both 1 cm and 1 mm path length quartz cells. All measurements were blanked against air. The absorbances listed in this work are corrected for the hydrochloric acid background absorbance.

Results and Discussion

The results of the gravimetric determination of dissolved elemental selenium in various solutions of SeO_2 in 11.8 M hydrochloric acid are given in Table I. Elemental selenium

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