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A calorimetric study of some metal ion complexing equilibria

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Abstract

The cumulative enthalpies of formation of Sc(III)–F^- and Ag(I)–NH_3 complexes were determined using a conventional isothermally-jacketed solution calorimeter with a solid gold inner can.

The stepwise enthalpies of formation of $ScF_n^{(3-n)+}$ ($n = 1$–4) from HF(aq) in 0.5 M $(Na^+,H^+)ClO_4^-$ at 25 °C are -2.156 ± 0.402, -4.413 ± 1.081, -3.467 ± 1.190, and -11.880 ± 0.977 kcal mol^{-1}, respectively. The entropy of formation of the ScF^{2+} complex is $+29.0$ cal $°C^{-1}$ mol^{-1}. Correcting this value for the substitution of a fluoride ion for a coordinated water molecule gives an entropy change of $+14.18$ cal $°C^{-1}$ mol^{-1} and shows the expected trend of the dependence of the entropy change on ionic radius when it is compared to corrected values of $\Delta S^{\ominus}$ for the formation of AlF^{2+}, FeF^{2+} and InF^{2+} from the metal 3+ ion and aqueous fluoride ion in 0.5 M ClO_4^-.

The cumulative enthalpies of formation of $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ are -5.134 ± 0.492 and -13.536 ± 0.137 kcal mol^{-1}, respectively, in 1 M NH_4NO_3(aq) at 25 °C. The associated cumulative entropy changes are -2.07 ± 1.68 and -12.58 ± 0.470 cal $°C^{-1}$ mol^{-1} and correspond to the sum of the changes for removing a coordinated water molecule in each step and coordinating an ammonia molecule in its place, plus the statistical entropy change for coordinating an ammonia molecule in the two available positions in the coordination sphere of the Ag(I) ion.

INTRODUCTION

It is of interest to extract the contributions of the enthalpy and entropy terms from the free energies of formation of metal ion complexes by appropriate experiments. The determination of the free energies of formation at several temperatures which are not too far apart allows the calculation of the enthalpy terms assuming that the heat capacity does not change very much within a short temperature interval. Nevertheless, even

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very good equilibrium constant data collected at several temperatures do not give as accurate results as calorimetric data with the use of accurate equilibrium constants [1].

Some complexing equilibria are difficult to study because additional reactions may occur which make it impossible or hard to determine the necessary experimental data. Silver ion complexing equilibria and fluoride ion complexing equilibria sometimes fall in this category. A conventional isothermal solution calorimeter with an inner can coated with epoxy resin could not be used to obtain the stepwise enthalpies of formation of the silver–ammine and scandium–fluoride complexes. A gold- or teflon-coated inner calorimeter can also prove to be inadequate. This paper reports the results of direct calorimetry on silver–ammine complexes in 1 M ammonium nitrate and scandium–fluoride complexes in 0.5 M (Na^+, H^+) perchlorate aqueous solutions using a solid gold inner calorimeter can [2].

EXPERIMENTAL

Apparatus

A solid brass can which housed a vacuum-thermostatted inner gold cylindrical can of about 130 ml capacity was fitted in the open circle in the cover of a large constant temperature bath which was kept at 26 ° C. The electrical resistors for the dummy heating circuit and the temperature sensor were housed in an oil-bath nearby which was kept at 25 ° C. The reactions were carried out at exactly 25 ° C by breaking a thin-walled glass ampoule against the platinum tip on a short gold rod at the bottom of the inner can. This allowed about one milliliter of the metal ion solution in the ampoule (held in a stirrer) to mix with the ligand solution in the inner can. The heating element, made of manganin wire, was inside the inner gold can. The thermometer consisted of 50 feet of copper wire which had been wound around the outside of the gold inner can and coated with epoxy resin. The design of this calorimeter is very similar to Calorimeter D of Sunner and Wadso [3]. Details of the construction of the calorimetric apparatus were described previously [2,4,5].

Calorimetric solutions

In eight experiments involving silver–amine complexes, the concentrations of silver(I) ranged from 6.1568×10^{-3} M to 8.2357×10^{-3} M and the amounts of a 0.02286 M aqueous ammonia stock solution which were placed in the inner can gave $\bar{n}$ values which ranged from 0.652 to 1.974 [2].

In eight experiments involving scandium(III)–fluoride complexing, the concentrations of scandium(III) ranged from 5.3223×10^{-3} M to 1.1308×10^{-3} M in the reactions of the sample of the 1.066 M scandium perchlorate hexahydrate aqueous stock solution in 2.158 M perchloric acid with varying amounts of a 0.5618 M hydrofluoric acid aqueous stock solution in 0.09901 M perchloric acid and 0.3993 M sodium perchlorate. In these reactions the values of $\bar{n}$ ranged from 0.521 to 3.559. Precipitation of scandium fluoride occurred at the highest $\bar{n}$ values [2].

The heats of dilution of Ag(I) and Sc(III) in the complexing solution media were determined in two separate experiments in each case. In the case of the Sc(III) ion these dilution experiments were carried out in an epoxy-coated inner can prior to the substitution of the gold inner can into the calorimetric apparatus.

CALCULATIONS

The stepwise formation constants of the silver–ammine complexes and the protonation constant of the ammonium ion as determined by Lundeen were used [2]. In the scandium-fluoride system, the stepwise formation constants reported by Kury et al. [6], refined by a non-linear least-squares analysis by Hugus [7], were employed. The equilibrium constant used for the formation of hydrofluoric acid from $H^+(aq)$ and $F^-(aq)$ in the same medium as the calorimetric experiments was as reported by Connick and Tsao [8] and the values of its enthalpy of formation and entropy of formation in this medium were corrected from values given by Kury et al. [6] and Hepler et al. [9]. The hydrolysis equilibria of Sc(III) were calculated with the equilibrium constants of Biedermann et al. [10] to include the species $Sc(OH)^{2+}$ and $Sc_2(OH)_2^{4+}$ in the calculations; the concentrations of these species were negligibly small in the calorimetric experiments.

The concentrations of the complex ion species present in solution were calculated using the appropriate formation constants by a program of iteration in which the initial concentrations were estimated to be equal to the stoichiometric concentrations [11,12]. Susccessive approximations were obtained by the Newton–Raphson method using a Taylor series expansion about the initial or earlier values [12]. The iteration was stopped when successive calculated concentrations agreed within 10^{-5} %.

The heat change which is observed in a particular experiment is a cumulative enthalpy change for the formation of the various complex ion species which are present in the solution

$$q(\text{observed}) = \sum_{n=0}^{n=N} \alpha_n q_n$$

where n is 0 or an integer, N is the maximum coordination number, q_n the cumulative enthalpy of formation of the nth complex and α_n the fraction of the nth complex present in the solution. The observed heats of reaction were treated by a non-linear least-squares program to obtain the best values of the cumulative enthalpies of formation of the complexes that are presumed to be present in solution:

$$\sum_{i=1}^{i=m} [q(\text{observed}) - q(\text{calculated})]^2$$

for m data points. The sum of the squares of the differences between the observed and calculated values of the heats of reaction for each data point i are minimized by setting the partial derivative of q with respect to each cumulative enthalpy of formation q_1 to q_N equal to zero.

RESULTS

Silver ion–ammonia complexing equilibria in aqueous 1 M ammonium nitrate solutions

The value of $\bar{n}$, the heats of reaction observed in the experiment, and the heats of reaction as calculated by the non-linear least-squares algorithm are listed in Table 1. From the data, the cumulative enthalpies of formation of the two silver–ammine complexes were calculated to be -5.134 ± 0.492 kcal mol^{-1} for the $\text{Ag(NH}_3)^+$ ion and -13.536 ± 0.137 kcal mol^{-1} for the $\text{Ag(NH}_3)_2^+$ ion. The squares of the variances in the cumulative enthalpies of formation were obtained from the least-squares

TABLE 1A

The observed and calculated heats of reaction, q(observed) and q(calculated), and $\bar{n}$ values in eight Ag(I)–NH_3(aq) complexing experiments in 1 M NH_4NO_3(aq) at 25 °C [2]

$\bar{n}$	$-q$(observed) (kcal mol^{-1})	$-q$(calculated) (kcal mol^{-1})
1.974	11.5321	11.4803
1.934	11.1332	11.0629
1.822	10.4416	10.4115
1.474	8.3944	8.3087
0.841	4.5755	4.5687
0.804	4.3338	4.3578
0.776	4.1730	4.1540
0.652	3.4753	3.4899

TABLE 1B

The cumulative free energies ΔG_n (kcal mol^{-1}), enthalpies ΔH_n (kcal mol^{-1}) and entropies of formation ΔS_n (cal $°\text{C}^{-1}$ mol^{-1}) of the complexes $\text{Ag(NH}_3)_n^+$ in 1 M NH_4NO_3(aq) at 25 °C.

ΔG_1	-4.518 ± 0.008	ΔG_2	-9.786 ± 0.003
ΔH_1	-5.134 ± 0.492	ΔH_2	-13.536 ± 0.137
ΔS_1	-2.07 ± 1.68	ΔS_2	-12.58 ± 0.470

sum shown above divided by the number of degrees of freedom, which is equal to the total number of data points minus the number of heats of reaction that are being calculated. The dilution experiments, a plot of the molar heat evolved against $\bar{n}$, and the least-squares value of q_0 all indicate that the molar enthalpy of dilution of an approximately 0.01 M silver nitrate aqueous solution in 1 M $NH_4NO_3(aq)$ solution is close to zero and can be neglected.

Bjerrum [13] reported the values of the stepwise formation constants of Ag(I)–ammine complexes in 0.5, 2 and 5 M $NH_4NO_3(aq)$ solutions at 22 and 30 °C. We obtained new cumulative formation constants, K_1 and K_2, from his pH data by a non-linear least-squares algorithm [14]. These values are $K_1 = 1.514 \times 10^3 \pm 0.035 \times 10^3$ and $K_2 = 1.070 \times 10^7 \pm 0.005 \times 10^7$ and do not differ very much from the values reported by Bjerrum [13]. (His reported values are $K_1 = 1.585 \times 10^3$ and $K_2 = 1.070 \times 10^7$ in 2 M $NH_4NO_3(aq)$ at 30 °C.) Using Bjerrum's [13] K_1 and K_2 values, we calculated the following values for the cumulative enthalpies of formation: $\Delta H_1^\ominus = -9.7$ and $\Delta H_2^\ominus = -14.3$ kcal mol^{-1}. These enthalpies of formation can be compared to the values obtained by Johansson [15] and quoted by Paoletti et al. [16] ($\Delta H_1 = -4.9$ and $\Delta H_2 = -13.5$ kcal mol^{-1}) and to those obtained by the present authors ($\Delta H_1 = -5.134 \pm 0.492$ and $\Delta H_2 = -13.536 \pm 0.137$ kcal mol^{-1}) using direct calorimetry [2]. Though the overall enthalpy of formation obtained from the free energy changes at 22 and 30 °C agrees within a half kilocalorie per mole with our work [2] and Johansson's [15] calorimetric work, Bjerrum's [13] first enthalpy of formation is about four kilocalories per mole higher than either value obtained by direct calorimetry [2,15]. If we calculate the cumulative entropy changes $\Delta S_1^\ominus$ and $\Delta S_2^\ominus$ from the free energies and enthalpies of formation using the formation constants reported by Bjerrum [13], given above, we obtain the following entropy changes in 1 M $NH_4NO_3(aq)$ solutions at 25 °C when the formation constants are corrected for the change in temperature and the concentration of the salt medium using Bjerrum's [13] formula: $\Delta S_1^\ominus = -14.9$ and $\Delta S_2^\ominus = -13.9$ cal °C^{-1} mol^{-1}. According to these data the entropy of formation of the $Ag(NH_3)_2^+$ complex from the $Ag(NH_3)^+$ complex is +1.0 cal °C^{-1} mol^{-1}. However, using our own data for the formation constants and for the enthalpies of formation we calculate that $\Delta S_1 = -2.07$ and $\Delta S_2 = -12.58$ cal °C^{-1} mol^{-1} in 1 M $NH_4NO_3(aq)$ at 25 °C and, therefore, the entropy of formation of the second silver(I)–ammine complex from the first complex is equal to -10.5 cal °C^{-1} mol^{-1}. The formation constants of the silver(I)–ammine complexes in 1 M $NH_4NO_3(aq)$ at 25 °C were also reported by Lloyd [17] but we find that his calculated value for the first formation constant shifts considerably when a non-linear least-squares calculation is carried out on his data. Lloyd [17] reported $K_1 = 2.33 \times 10^3$ and $K_2 = 1.41 \times 10^7$; we calculated K_1 1.010×10^3 and $K_2 = 1.422 \times 10^7$ with associated errors of $\pm 0.525 \times 10^3$ and

$\pm 0.118 \times 10^7$, respectively. It is necessary to have good formation constant data to calculate the concentrations of the species present in solution in the calorimetric experiments. We subjected our own data to the pit-mapping procedure of Sillen [18] in addition to using our own non-linear least-squares algorithm [2,11,12]. Sillen's pit-mapping procedure gave the following results with our data: $K_1 = 2.051682 \times 10^3 \pm 2.8015 \times 10^1$ and $K_2 = 1.494101 \times 10^7 \pm 8.1535 \times 10^4$, in total agreement with our algorithm [2].

It has been suggested by Orgel [19] that the Ag(I) ion may not have a coordination sphere of two water molecules around it in aqueous solution. The presence of two short and four long silver–nitrogen bonds was indicated by the Raman spectral work of Lundeen and Tobias [20] in liquid ammonia. A tetragonally elongated octahedral coordination sphere around the Ag(I) ion would have a center of inversion symmetry. Aqueous salt solutions of the Ag(I) ion appear to have bands in the ultraviolet region corresponding to the $(4d)^{10}(^1S) \rightarrow (4d)^9(5s)^1(^1D)$ transition with oscillator strengths that are independent of temperature according to Texter et al. [21]. This transition is parity forbidden but appears to become partially allowed because of the non-rigidity of the primary coordination sphere of the water molecules. Because the oscillator strength does not appear to depend on the temperature, the molecule may not have a center of inversion and, therefore, it may be tetrahedrally coordinated by four water molecules [21]. On a purely statistical basis the entropies of formation of the first and second Ag(I)–ammine complexes may be taken to be equal to $R \ln 2$, which is equal to 1.38 cal $°C^{-1}$ mol^{-1}, and $R \ln 0.5$, equal to -1.38 cal $°C^{-1}$ mol^{-1}, and the entropy of formation of the second complex from the first complex is given by $R \ln 4$, which is equal to 2.76 cal $°C^{-1}$ mol^{-1}, according to Bjerrum's [13] statistical formula. We compared the statistical entropies of formation to our reported entropy changes corrected for cratic effects. These unitary entropies of formation are: $\Delta S_1 = 5.90$, $\Delta S_2 = 3.36$, $\Delta S_{1,2} = 2.54$ cal $°C^{-1}$ mol^{-1} [2]. Thus, positive entropy changes are obtained at each step and this may suggest that the first ammonia molecule is not replacing one of the two water molecules which are coordinated to the Ag(I) ion in aqueous solution. There would have to be eight to ten water molecules around the Ag(I) ion to account for the unitary entropy change of 5.90 cal $°C^{-1}$ mol^{-1} in the first step.

Latimer and Jolly [22] have said that the process in which a water molecule bound to a silver(I) ion which is replaced by a neutral ammonia molecule and returned to the bulk solvent water, will have an entropy change of about -5.5 cal $°C^{-1}$ mol^{-1}. Thus, the desolvation of the silver(I) ion and the addition of two ammonia molecules to its coordination sphere in their place may lead to observed entropy changes of -4.12 and -11.00 cal $°C^{-1}$ mol^{-1} cumulatively when these processes are added on to the statistical entropy term. These estimated entropy changes of -4.12 and -11.00 cal $°C^{-1}$ mol^{-1} agree within a little more than two entropy units with the observed entropy change of −2.07 and −12.58 cal °C^{-1} mol^{-1} reported in Table 1B. (There is no change in the number of species involved in the reaction in this calculation and the cratic correction to the entropy term is zero.) The Raman spectral work of Lundeen and Tobias [20] and the UV spectroscopic studies of Texter et al. [21] referred to above suggest that the coordination number of the Ag(I) ion is at least four or higher. A hydration number of four was assumed for the Ag(I) ion in a study of Ag(I)–thiocyanate complex formation by the solubility method [23]. Adiabatic compressibility data in salt solutions appear to indicate a hydration number of 3.1–4.0 at 25 °C [24]. A third ammonia molecule may be added to the coordination sphere of the Ag(I) ion in very concentrated aqueous ammonia solutions according to a recent UV spectroscopic study by Bjerrum [25]. If the aquated Ag(I) ion were to have a fairly non-flexible pseudo-octahedral $2+4$ coordination geometry, it would have an axis of inversion, and the parity forbidden $(4d)^{10}(^1S) \rightarrow (4d)^9(5s)^1(^1D)$ transition observed by Texter et al. [21] would have an oscillator strength that would vary with temperature, which is contrary to their observation.

Direct calorimetric work on the copper(II)–ammine and nickel(II)–ammine complexes indicate that the average enthalpy of formation of a transition metal(II) ion–ammine nitrogen bond is of the order of 4–5 kcal mol^{-1} [4,5,26,27]. The enthalpy of formation of the first Ag(I)–ammine complex is −5.134 kcal mol^{-1} according to our results [2]. The enthalpy of formation of $Ag(NH_3)_2^+$ from $Ag(NH_3)^+$ is equal to −8.402 kcal mol^{-1} and indicates that much stronger bonds form in the linear $Ag(NH_3)_2^+$ complex so that the average enthalpy of formation per bond becomes −6.768 kcal mol^{-1}. The cumulative enthalpy of formation of the $Cu(NH_3)_2^+$ complex is quoted [28] as −16.0 kcal mol^{-1} at 18 °C in 2 M $NH_4NO_3(aq)$ solutions [1]. In this linear diammine complex also, the average enthalpy of formation is more negative than in the square pyramidal penta-ammine–copper(II) complex ion or in the octahedral hexa-ammine–nickel(II) complex ion [4,5]. (The coordination geometry of the penta-ammine–copper(II) ion may be described as $4+1$ and the stepwise enthalpy of formation of the fifth Cu(II)–ammine complex is quite small (−2.70 kcal mol^{-1}) [4].)

In conclusion, we suggest that the presence of a flexible shell of several water molecules in the first coordination sphere of the Ag(I) ion does not allow maximum overlap of the atomic orbitals of Ag(I) with the atomic orbitals of the nitrogen donor in the first complex which forms. Desolvation allows maximum overlap in the $Ag(NH_3)_2^+$ complex ion which forms subsequently.

Scandium(III) ion–fluoride complexing equilibria in aqueous 0.5 M perchlorate solutions

Table 2 lists the calculated values of $\bar{n}$, the observed heats of reaction and the calculated heats of reaction for eight Sc(III)–F^- complexing

TABLE 2

The observed and calculated heats of reaction, q(observed) and q(calculated), and $\bar{n}$ values in eight Sc^{3+}–HF(aq) complexing experiments and two dilution experiments of Sc^{3+}(aq) in 0.5 M $(Na^+,H^+)ClO_4^-$ at 25 ° C [2]

$\bar{n}$	$-q$(observed) (kcal mol^{-1})	$-q$(calculated) (kcal mol^{-1})
3.559	15.10200	15.06932
3.539	14.68500	14.72947
3.090	10.39200	10.35459
2.648	9.18300	9.13628
2.561	8.72500	8.80921
1.195	4.57700	4.51470
0.523	2.86800	2.90126
0.521	2.84200	2.89780
0.000	1.99800	1.94319
0.000	1.92700	1.94319

experiments and two dilution experiments of the Sc(III) ion in the same medium [2]. The cumulative enthalpies of formation of the $ScF_n^{(3-n)+}$ complexes from HF(aq) were calculated to be: $\Delta H_1 = -2.156 \pm 0.402$, $\Delta H_2 = -6.569 \pm 0.679$, $\Delta H_3 = -10.036 \pm 0.511$ and $\Delta H_4 = -21.916 \pm 0.466$ kcal mol^{-1} at 25 °C in 0.5 M ClO_4^-. The stepwise enthalpies of formation for the complexing of the Sc(III) ion with F^-(aq) are: $\Delta H_1 = +0.444$, $\Delta H_2 = +0.787$, $\Delta H_3 = +4.333$ and $\Delta H_4 = -1.480$ kcal mol^{-1} using the enthalpy of formation of HF(aq) from F^-(aq) in 0.5 M ClO_4^- medium at 25 ° C given by Kury et al. [6]. The calculated value of the molar heat of dilution q_0 is -2.490 ± 0.139 kcal according to the non-linear least-squares results. The two dilution experiments suggest a value of -2.3 to -2.4 kcal mol^{-1} for q_0 and the plot of molar heat evolved against $\bar{n}$ gives a smooth curve for the total range of $\bar{n}$ values [2]. The value of the fourth molar enthalpy of formation was obtained at an $\bar{n}$ value of about 3.5 because precipitation of ScF_3 started at this $\bar{n}$ value in 0.5 M ClO_4^- at 25 ° C.

It has been suggested that a Coulombic model could give a good description of the bonding in the monofluoro complexes of the +2- and +3-charged metal ions [8]. The Sc(III) ion is given an ionic radius of 0.68 Å by Kittel [29] but many compilations suggest a value as large as the ionic radius of In(III) (0.81 Å) based on the original assignment by Pauling [30–32]. It may be argued that the ionic radius given for Sc(III) by Kittel [29] is too small, because the ionic radii of other first-row transition metal 3+ ions range from 0.76 to 0.62 Å from Ti(III) to Ni(III), according to Pauling [30]. It may be expected that the ionic radius of Sc(III) which has no 3d electrons is close in size to the ionic radius of Ti(III) and not as large as the ionic radius of In(III) which has a closed 4d shell. Thus, the Sc(III) ion is expected to form less stable monofluoro complexes than Al(III) (which has an ionic radius of 0.50 Å) [32] and Fe(III) (which has an ionic radius of 0.64 Å) [30–32] and a more stable monofluoro complex than either In(III) or Y(III). (The latter ion is assigned a value as large as that of In(III) by Wycoff [33] who assigns a value of 0.95 Å to both ions, with a somewhat smaller value (0.93 Å) being given by Pauling [30].)

Experimentally, the free energies of formation of $ScF_n^{(3-n)+}$ from Sc^{+3}(aq) and F^-(aq) are cumulatively: $\Delta G_1 = -8.444$, $\Delta G_2 = -15.643$, $\Delta G_3 = -21.201$ and $\Delta G_4 = -25.074$ kcal mol^{-1} in 0.5 M ClO_4^- at 25 °C using the non-linear least-squares values of the formation constants of Hugus [7] derived from the data of Kury et al. [6] on Sc(III)–fluoride complexing reactions and a value of −3.97 kcal mol^{-1} for the complexing of H^+(aq) and F^-(aq) ions to form HF(aq) in the same medium at 25 °C [34]. The first free energy of formation which is reported above, −8.444 kcal mol^{-1}, is more negative than that for the formation of AlF^{2+} obtained from the work of Latimer and Jolly [22], −8.37 kcal mol^{-1}, as has been noted previously [6].

The free energies of formation of the monofluoro complexes of the metal ions reported in the previous paragraph may include large contributions from desolvation effects [22,24,35]. If we compare the enthalpies of formation of the monofluoro complex ions from aqueous hydrofluoric acid which are reported to be −2.156 (ScF^{2+}) [2], −1.45 (AlF^{2+}) [22], −0.58 (FeF^{2+}) [4] and −0.51 kcal mol^{-1} (InF^{2+}) [36], it is evident that these enthalpies of formation do not fit a Coulombic charge model [6]. If, however, we choose to compare the thermodynamic functions at 25 °C in 0.5 M ClO_4^- for the formation of the MF^{2+}(aq) ion from M^{3+}(aq) and F^-(aq), we see that the value of ΔH_1 for the formation of these M^{3+}(aq) ions are all positive. Thus, it is the large ΔS_1 term which makes the value of ΔG_1 negative for these complexes of the 3 + ions. Latimer and Jolly [22] suggest that the entropy change in desolvating the coordination sphere of an aquated metal ion and replacing the H_2O ligand by a fluoride ligand corresponds to about 15.6 cal $°C^{-1}$ mol^{-1} per F^- ion. The remaining portion of the large experimental entropy change may be called the "charge effect" [22]. The charge effect is equal to about 16.3 for AlF^{2+}, 14.6 for FeF^{2+}, 14.2 for ScF^{2+} and 8.5 for InF^{2+}. The charge effect, then, shows the expected dependence on radius of the monofluoro complexes of Al^{3+}, Fe^{3+} and Sc^{3+} ions. The In^{3+} ion has an ionic radius as large as 0.95 Å, according to Wycoff [33], and appears to show about half as large a charge effect as the Al^{3+} ion which has a radius of 0.50 or 0.55 Å [32,33].

If one considers the cumulative formation of the Sc^{3+}–F^- complexes in 0.5 M ClO_4^- at 25 °C, the charge effect has the values 14.2, 8.0, −0.6 and −81.7 cal $°C^{-1}$ mol^{-1} for ScF^{2+}, ScF_2^+, ScF_3(aq) and ScF_4^-, respectively. Thus, it appears that the first two Sc^{3+}–F^- complexes each display a positive charge effect, but that the formation of the other two Sc^{3+}–F^-

complexes have negative charge effect. The last Sc^{3+}–F^- complex, in particular, has a very favorable free energy of formation (-19.316 kcal mol^{-1}). Notably, the value of ΔH_1 is about $+1$ to $+2$ kcal mol^{-1} for the complexes AlF^{2+}, FeF^{2+} and InF^{2+}, but ScF^{2+} has a rather small enthalpy of formation of 0.444 kcal mol^{-1} in 0.5 M ClO_4^- at 25 °C. The more negative free energy of formation of ScF^{2+} appears to be the sum of a rather large favorable charge effect (which appears to be dependent on the size of the metal ion) and a small unfavorable enthalpy of formation (which may be associated with the electronic configuration of the metal ion). For the Sc^{3+} ion which has no 3d electrons, some charge donation may be occurring from the fluoride ligand to the empty 3d orbitals of Sc^{3+}. If this occurs, charge transfer bands should be detectable in or close to the UV region.

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