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Nuclear Magnetic Resonance Studies of Aluminum(III) Fluoride Ion Complexes in Aqueous Solutions[1]

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Separate ^{19}F nmr signals have been distinguished for the AlF_4^-, AlF_3, AlF_2^+, and AlF^{2+} complex ions present in aqueous solutions of AlF_3 and $Al(NO_3)_3$. From the relative signal areas the concentration equilibrium quotients, Q_n, have been calculated for the reactions $2AlF_n^{+3-n} \rightleftarrows AlF_{n+1}^{+2-n} + AlF_{n-1}^{+4-n}$ ($Q_1 = 0.15$, $Q_2 = 0.14$, and $Q_3 = 0.038$). The equilibrium quotients are temperature independent and are remarkably insensitive to the solution composition. Below −15°, the ^1H nmr signal of water coordinated to Al(III) can be distinguished from that for bulk water. The relative ^1H signal areas are consistent with the formulation of the Al–F complexes as $(H_2O)_5AlF^{2+}$, $(H_2O)_4AlF_2^+$, and $(H_2O)_3AlF_3$. The Q values and the trends in the ^{19}F chemical shifts are discussed.

Introduction

In the several previous ^{19}F nmr studies of Al(III)–F^- ion complexes in aqueous solutions,[2,3] it was possible to characterize directly only the species AlF^{2+} and AlF_2^+. The range of solution compositions throughout which the fluoride ion complexes could be directly detected was limited in those studies by the use of $NaF–Al(NO_3)_3$ or $HF–Al(NO_3)_3$ solutions. For the former solutions, the Al(III) concentration is restricted by the slight solubility of $NaAlF_4$ in water and, for the latter, the useful $[F^-]/[Al(III)]$ ratios are restricted by the acid catalysis of F^- ion exchange from Al(III)–F^- complexes and by the affinity of the proton for F^- ion.

We have found that the salt $AlF_3 \cdot 9H_2O$ is very soluble in water and herein we report the direct characterization, by ^1H and ^{19}F nmr spectroscopy, of the complexes $AlF_4(aq)^-$, $(H_2O)_3AlF_3$, $(H_2O)_4AlF_2^+$, and $(H_2O)_5AlF^{2+}$ in aqueous solutions of mixtures of $Al(NO_3)_3 \cdot 9H_2O$ and $AlF_3 \cdot 9H_2O$. Also described in this report is a study of the equilibria among these complexes, the results of which indicate that the ratios of the activity coefficients of the complexes are remarkably insensitive to the solution composition.

Experimental Section

Materials.—The salt $Al(NO_3)_3 \cdot 9H_2O$ (Baker and Adamson reagent) was recrystallized from distilled deionized water and the crystals obtained were dried *in vacuo* for 8 hr at 25°. In a typical preparation of the salt $AlF_3 \cdot 9H_2O$, 5.00 g of Al powder (Baker and Adamson reagent) was added gradually over a period of 3 hr to 75.0 g of 15% aqueous HF (obtained by dilution of Aristar 42% HF) contained in a Teflon beaker immersed in an ice–water bath. The reaction of Al with HF is highly exothermic and it is essential that the temperature of the reaction mixture be kept below 50°. If the Al powder is added to HF too rapidly, the slightly soluble α and β phases of $AlF_3 \cdot 3H_2O$[4] precipitate from the hot solution. After the last portion of the slight excess of Al powder had been added, the solution (pH 5) was filtered and the filtrate was allowed to stand in a −10° bath for 2 hr. The crystals which had deposited were then collected by filtration and dried by drawing air through the filter for 1 hr. It was found that the crystals slowly deliquesced after being dried in this manner for more than 2 hr (at 25° and a relative humidity of 30%). The crystals were stored at −20° in a tightly sealed container. *Anal.* Calcd for $AlF_3 \cdot 9H_2O$: Al, 10.98; F, 23.2. Found: Al, 11.0; F, 22.9. Calcd for $Al(NO_3)_3 \cdot 9H_2O$: Al, 7.20. Found: Al, 7.21.

Analyses.—Aluminum was determined by titration with a standard solution of ethylenediaminetetraacetic acid using Eriochrome Black T as the indicator.[5] For the determination of aluminum in $AlF_3 \cdot 9H_2O$, it was necessary to separate Al(III) from F^- ion by precipitating hydrous Al_2O_3 from aqueous solutions of the fluoride salt with aqueous NH_3. The hydrous oxide was then dissolved in nitric acid and Al(III) was determined in the conventional manner.[5]

In the determination of fluoride, a weighed sample of $AlF_3 \cdot 9H_2O$ was pyrohydrolyzed at 850–900° and the condensate containing HF was caught in a plastic beaker containing 1 *M* aqueous NaOH. The F^- ion concentration of the resulting solution was then determined by Mr. Ivan Kressin of this laboratory using a fluoride ion specific electrode.[6]

Measurements.—Proton and ^{19}F nmr spectra were recorded by the use of a Varian DP-60 spectrometer operated at 56.45 MHz and equipped with a Varian variable-temperature probe insert. The temperature was controlled and the systems were calibrated in a conventional manner.[7] The ^{27}Al spectra were obtained at 15.65 MHz by modifying the DP-60 spectrometer with the V-4280A sweep unit, the Varian variable-frequency V-4210A radiofrequency unit, and a variable-frequency V-4230 probe. The areas of the nmr peaks were obtained by planimetry of the recorded signals and are accurate to within ±7%. In the spectra of some solutions, the ^{19}F nmr signals of the complexes, AlF_4^-, and AlF_3 overlapped. In the determination of the relative areas of these signals, the signals were first resolved by analyzing each of them as a pure Lorentzian curve.

Solutions were prepared by weight. Standard 5-mm o.d. glass nmr tubes (Wilmad) were used in the ^{19}F and ^1H studies and 15-mm o.d. test tubes were used in the ^{27}Al studies. No etching of the glass was detected and no time dependence of the spectra was noted even for concentrated solutions which had been stored for 3 months. To some of the solutions HNO_3 was added to the extent of 0.01 or 0.10 *m*. Nitric acid at these concentrations had no effect either on the number of signals in the ^{19}F nmr spectra or on their relative areas, but it broadened (by ≤40%) the signals for the AlF_4^- and AlF_3 complexes. This broadening is probably due to proton catalysis of F^- ion exchange. The pH

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[1] Work performed under the auspices of the USAEC.

[2] (a) R. E. Connick and R. E. Poulson, *J. Am. Chem. Soc.*, **79**, 5153 (1957); (b) R. E. Connick and R. E. Poulson, *J. Phys. Chem.*, **63**, 568 (1959).

[3] M. Yamazaki and T. Takeuchi, *Kogyo Kagaku Zasshi*, **70**, 656 (1967).

[4] W. F. Ehret and F. J. Frere, *J. Am. Chem. Soc.*, **67**, 64 (1945).

[5] G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, Inc., New York, N. Y., 1957.

[6] J. J. Lingane, *Anal. Chem.*, **39**, 881 (1967).

[7] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966).

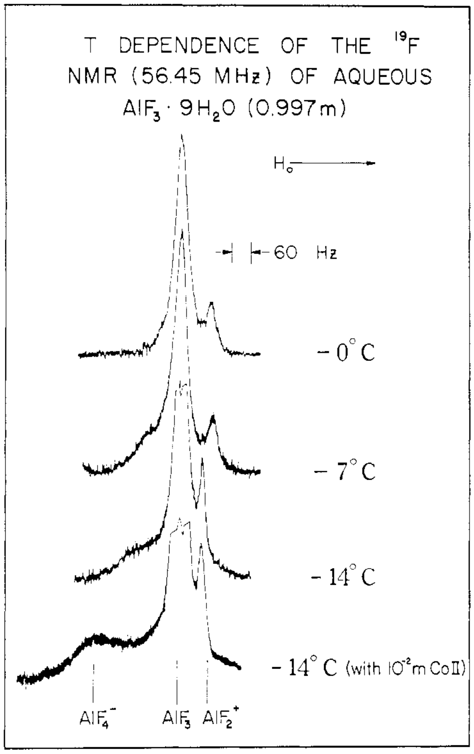

Figure 1.—Temperature dependence of the ^{19}F nmr spectra of a 0.997 *m* solution of $AlF_3 \cdot 9H_2O$ in water. The magnetic field increases from left to right.

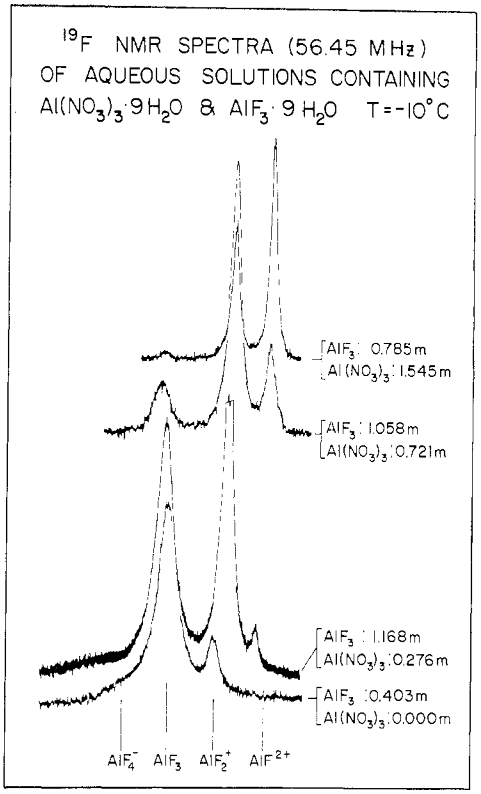

Figure 2.—The ^{19}F nmr spectra of representative aqueous solutions of AlF_3 and $Al(NO_3)_3$ at −10°. The magnetic field increases from left to right.

was not controlled in these studies: 1 *m* $AlF_3 \cdot 9H_2O$ exhibited pH 5 and 2 *m* $Al(NO_3)_3 \cdot 9H_2O$ exhibited pH 1.4.

Results

1. Assignment of the ^{19}F Nmr Signals.—In Figure 1 the temperature dependence of the ^{19}F nmr spectra of an aqueous solution of $AlF_3 \cdot 9H_2O$ is summarized. Representative spectra obtained at −10° for aqueous solutions of mixtures of $AlF_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ are reproduced in Figure 2. As indicated in the figures, the lowest field ^{19}F resonance is assigned to the AlF_4^- ion and the remaining resonances, in the order of their occurrence at increasing field strengths, are assigned to the species AlF_3, AlF_2^+, and AlF^{2+}.

The assignments are based upon the fact that the equilibrium quotients, *Q*, calculated for reactions 1–3 from the species concentrations derived from the relative signal areas are constant.

$$2AlF(aq)^{2+} \rightleftarrows Al(aq)^{3+} + AlF_2^+ \qquad Q_1 \qquad (1)$$

$$2AlF_2(aq)^+ \rightleftarrows AlF_3(aq) + AlF^{2+} \qquad Q_2 \qquad (2)$$

$$2AlF_3(aq) \rightleftarrows AlF_4(aq)^- + AlF_2^+ \qquad Q_3 \qquad (3)$$

In deriving the species concentrations two assumptions were made: (1) all the F^- ions in the solutions of AlF_3 and of mixtures of AlF_3 and $Al(NO_3)_3$ are present in the form of aluminum complexes and (2) the ^{19}F resonance observed at the highest field is indeed due to the AlF^{2+} ion. In none of the solutions studied here could a resonance due to the free F^- ion be detected even when the solutions were doped with Cu(II) ion[8,9]—in control experiments using aqueous NaF solutions doped with $Cu(ClO_4)_2$ a free F^- ion resonance at approximately 2000 Hz downfield of the resonances due to the Al–F complexes could be detected for solutions as dilute as 0.03 *m* NaF. Also without recourse to the equilibria involved, we can assume confidently that the highest field ^{19}F resonance is due to the AlF^{2+} ion, because at the highest ratios, [Al(III)]/[F], that resonance was the only one detected both in concentrated solutions containing $Al(NO_3)_3$–AlF_3 and in dilute solutions containing NaF–$Al(NO_3)_3$.

In Table I are listed the species concentrations obtained from the relative areas of the ^{19}F nmr signals in the spectra of representative AlF_3 solutions at −15°. In deriving the concentrations it was assumed that the amount of AlF^{2+} ion in the AlF_3 solutions is negligible—no ^{19}F signal for the AlF^{2+} ion could be detected in these solutions over a wide range of temperatures and spectrometer settings. Considering the wide range of solution composition employed, the constancy of the concentration equilibrium quotients calculated on the basis of reaction 3 (the Q_3 values listed in Table I) provides justification for the assignment of the ^{19}F signals to the complexes AlF_4^-, AlF_3, and AlF_2^+. This assignment requires that the ratio of the area of the low-field signal (AlF_4^-) to that of the high-field one (AlF_2^+) be 2:1. Although that ratio *is* 2:1 within the limits of error of the measurement of the signal areas, the overlap between the

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[8] Because Cu(II) ion drastically shortens the relaxation times of ^{19}F,[9] its presence even at low concentrations ($<10^{-2}$ *M*) allows use of high radiofrequency power levels without causing saturation of the ^{19}F resonance.

[9] M. Eisenstadt and H. L. Friedman, *J. Chem. Phys.*, **48**, 4445 (1968).

TABLE I

CONCENTRATIONS AND EQUILIBRIUM QUOTIENTS FOR THE FORMATION OF ALUMINUM FLUORIDE COMPLEXES IN REPRESENTATIVE AQUEOUS SOLUTIONS OF AlF_3 AT $-15°$ DERIVED FROM THE RELATIVE AREAS OF THE ^{19}F NMR SIGNALS[a]

Formal concn of AlF_3, *m*	—Derived concn of Al–F complexes,[b] *m*— AlF_4^-	AlF_3	AlF_2^+	Q_3[c]
1.165	0.169 (2.10)	0.836 (7.78)	0.161 (1.00)	0.0388
0.997	0.140 (1.93)	0.714 (7.38)	0.145 (1.00)	0.0398
0.495	0.0656 (1.89)	0.360 (7.77)	0.0694 (1.00)	0.0351
0.376	0.0540 (2.05)	0.270 (7.67)	0.0527 (1.00)	0.0390
			Av	0.038 ± 0.008[d]

[a] Since it was assumed that all F^- ions are present in the form of Al–F complexes (see text), the concentrations of the complexes can be calculated readily using these equations: [total formal F^-] = $4[AlF_4^-] + 3[AlF_3] + 2[AlF_2^+]$; [total formal AlF_3] = $[AlF_2^+] + {}^2/_3[AlF_2^+](A_{AlF_3}) + {}^1/_2[AlF_2^+](A_{AlF_4^-})$, where, for example, A_{AlF_3} represents the area of the ^{19}F signal assigned to AlF_3. [b] Relative areas of ^{19}F signals in parentheses ±6%. [c] Q_3 is the equilibrium quotient for reaction 3: $Q_3 = [AlF_2^+][AlF_4^-]/[AlF_3]^2$. [d] Q_3 is the average value obtained using ten different solutions in which the formal AlF_3 concentration was varied between the limits 0.25 and 1.25 *m*.

TABLE II

CONCENTRATIONS AND EQUILIBRIUM QUOTIENTS FOR THE FORMATION OF ALUMINUM FLUORIDE COMPLEXES IN REPRESENTATIVE AQUEOUS SOLUTIONS OF AlF_3 AND $Al(NO_3)_3$ AT $-15°$ DERIVED FROM THE RELATIVE AREAS OF THE ^{19}F NMR SIGNALS[a]

No.	Formal concn of initial solute, *m* AlF_3	$Al(NO_3)_3$	Derived concn of Al^{3+} complexes,[b] *m* AlF_4^-	AlF_3	AlF_2^+	AlF^{2+}	Al^{3+}[c]	Q_2[d]	Q_1[d]
1	1.168	0.276	0.080 (2.00)	0.528 (9.90)	0.723 (9.03)	0.160 (1.00)	...	0.16	...
2	1.058	0.721	...	0.213 (1.20)	1.003 (3.77)	0.532 (1.00)	...	0.12	...
3	1.480	1.220	...	0.252 (0.75)	1.340 (2.65)	1.010 (1.00)	0.10	0.14	0.13
4	1.058	1.743	...	0.051 (0.10)	0.740 (0.96)	1.541 (1.00)	0.469	0.14	0.15
5	0.403	0.670	...	...	0.294 (0.95)	0.620 (1.00)	0.159	...	0.12
6	0.785	1.545	...	0.021 (0.05)	0.502 (0.78)	1.287 (1.00)	0.52	0.11	0.16
7	0.933	3.460	...	...	0.306 (0.28)	2.187 (1.00)	1.900	...	0.12
8	0.445	1.740	...	...	0.180 (0.37)	0.974 (1.00)	1.031	...	0.19
9	0.231	2.086	...	...	0.031 (0.10)	0.630 (1.00)	1.656	...	0.13

[a] See footnote *a*, Table I. [b] Relative areas of ^{19}F signals in parentheses ±6%. [c] Al^{3+} concentration obtained by difference: $[Al^{3+}] = [\text{total formal Al(III)}] - \Sigma_n[AlF_n]$. [d] Q_2 and Q_1 are the concentration equilibrium quotients for reactions 2 and 1, respectively. $Q_2(\text{av}) = 0.14 \pm 0.03$; $Q_1(\text{av}) = 0.15 \pm 0.03$.

intense AlF_3 signal and the weak AlF_4^- one leads to a large error in the estimated area of the latter (see Experimental Section, Measurements). To exclude systematic errors in the data analysis, we have taken advantage of the large chemical shifts in the ^{19}F signals of anionic fluoride ion complexes induced by cobalt(II) ion.[10] In Figure 1 is reproduced an ^{19}F nmr spectrum of a representative aqueous solution of AlF_3 doped with $Co(ClO_4)_2$. Because the contact interaction between the Co(II) and AlF_4^- ions induces a large separation between the AlF_3 and AlF_4^- resonances, an accurate area, 2.00 ± 0.05, of the AlF_4^- ion resonance relative to that of the AlF_2^+ ion in all solutions employed was obtained.

On the basis of the relative ^{19}F signal areas of the AlF_3 solutions alone, one could argue that the chemical events monitored in nmr spectroscopy are those summarized in eq 4 which would lead to equilibrium quotients different from these calculated for the reaction in eq 3 but which are, nonetheless, constant

$$cis\text{-}AlF_3 \rightleftharpoons trans\text{-}AlF_3 \qquad (4)$$

as a function of solution composition. For *cis*-AlF_3, the F atoms would be equivalent and should give rise to a single ^{19}F signal, whereas for *trans*-AlF_3 the two equivalent equatorial ^{19}F atoms should give rise to a ^{19}F signal twice as intense as that for the unique axial ^{19}F atom of the *trans*-AlF_3 isomer. We can exclude this interpretation because it requires that the relative areas of the signals we have assigned to AlF_4^- and AlF_2^+ be 2:1 even for solutions containing $Al(NO_3)_3$. That this requirement is not fulfilled is evident from the spectra reproduced in Figure 2 and the data collected in Table II.[11]

In Table II are collected the species concentrations obtained from the relative areas of the ^{19}F nmr signals in the spectra of representative aqueous solutions containing AlF_3 and $Al(NO_3)_3$. Again, the constancy of the equilibrium quotients, Q_1 and Q_2, calculated on the basis of reactions 1 and 2, respectively, confirms the assignment of the ^{19}F signals.

A test of the validity of the treatment of the data discussed above is provided by the requirement that the solutions to which the species concentration listed in Table II apply be electrically neutral. A comparison between the actual NO_3^- ion concentration and the NO_3^- ion concentration required to balance the charge of the cations is provided in Table III for a few representative solutions. Considering the errors involved in deriving the cation concentrations, the agreement between the actual NO_3^- ion concentration and that required to maintain electroneutrality is surprisingly good.

The calculated equilibrium constants are independent of the temperature within the ranges studied: Q_1, -15 to 90°; Q_2, -15 to 40°; Q_3, -20 to 0°. Depending upon the solution composition, coalescence of the ^{19}F nmr signals of the various Al(III)–F^- ion complexes occurs within the following temperature

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(10) N. A. Matwiyoff, unpublished observations.

(11) Each of the complexes, AlF_4^-, AlF_3, and AlF_2^+, can exist as *cis* and *trans* isomers. In none of the spectra could we detect separate signals for these isomers. Either the more symmetrical isomer is formed exclusively in this system or, more likely, the ^{19}F chemical shift between isomers is very small.

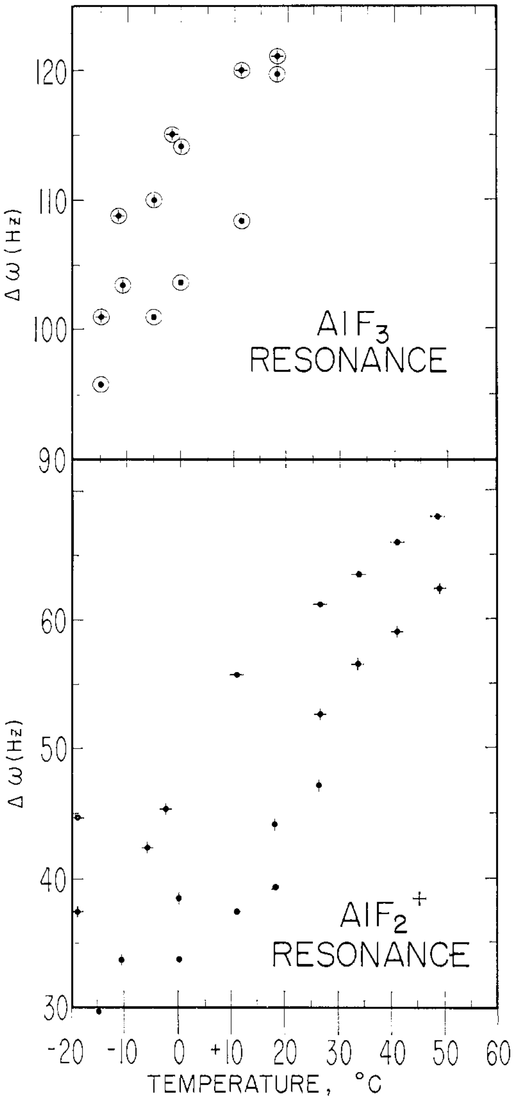

Figure 3.—Temperature and solution composition dependence of the ^{19}F chemical shifts of the AlF_2^+ (●) and AlF_3 (⊙) complexes downfield relative to those of the internal standard AlF^{2+}. Formal solution compositions: 1.168 *m* AlF_3 and 0.276 *m* $Al(NO_3)_3$ (● and ⊙); 1.058 *m* AlF_3 and 0.721 *m* $Al(NO_3)_3$ (♦ and ϕ); 1.480 *m* AlF_3 and 1.220 *m* $Al(NO_3)_3$ (-♦- and -⊕-); 0.933 *m* AlF_3 and 3.460 *m* $Al(NO_3)_3$ (-●- and -○-).

ranges: AlF_4^- with AlF_3, −5 to +5°; AlF_3 with AlF_2^+, 35 to 40°; and AlF_2^+ with AlF^{2+}, >90°.[12]

In the calculation of Q_3 from data obtained above the coalescence temperature of the AlF_4^- and AlF_3 resonances, it was assumed that for solutions containing only the initial solute AlF_3, the concentration of AlF_4^- is equal to the concentration of AlF_2^+ (for which a separate ^{19}F resonance was distinguished). For these solutions, the concentration of AlF_3 was obtained by difference using the area of the coalesced AlF_4^-–AlF_3 resonance relative to that of AlF_2^+ (see, for example, footnote *a* of Table I).

TABLE III

COMPARISON BETWEEN THE ACTUAL NO_3^- ION CONCENTRATION AND THE CONCENTRATION REQUIRED TO MAINTAIN ELECTRONEUTRALITY FOR REPRESENTATIVE SOLUTIONS OF AlF_3 AND $Al(NO_3)_3$ AT −15°

Formal concn of initial solute,[a] *m* AlF_3	Formal concn of initial solute,[a] *m* $Al(NO_3)_3$	Actual concn of NO_3^-, *m*	Concn of NO_3^- required to maintain electroneutrality[b]
1.058	0.721	2.163	2.07
1.480	1.220	3.660	3.66
1.058	1.743	5.229	5.23
0.403	0.670	2.010	2.12
0.231	2.086	6.258	6.24

[a] These solutions correspond to entries 2, 3, 4, 5, and 9 of Table II, respectively. [b] The concentration of NO_3^- ion required to maintain electroneutrality is obtained from $[NO_3^-] = \Sigma_i m_i z_i$, where m_i and z_i represent the derived molality and charge of a given cation.

2. **Relative Chemical Shifts of the ^{19}F Nmr Signals.**—The ^{19}F chemical shifts of the Al^{3+}–F^- ion complexes depend markedly upon the composition of the solution and the temperature. In Figure 3, that dependence is summarized for a representative set of solutions. It should be emphasized that the shifts summarized in Figure 3 are relative to that of the internal standard AlF^{2+}. Representative chemical shifts of the AlF^{2+} complex at 33° *upfield* with respect to the external standard trifluoroacetic acid are: 79.5 ppm for a solution 1.058 *m* in AlF_3 and 0.721 *m* $Al(NO_3)_3$; 79.5 ppm for 1.480 *m* AlF_3 and 1.220 *m* $Al(NO_3)_3$; 79.6 ppm for 0.785 *m* AlF_3 and 1.545 *m* $Al(NO_3)_3$; 79.5 ppm for 0.445 *m* AlF_3 and 1.740 *m* $Al(NO_3)_3$. The temperature coefficient of the ^{19}F shift of the AlF^{2+} complex in each of these solutions is small: ~0.01 ppm/deg.

3. **^1H Nmr.**—The temperature dependence of the ^1H nmr spectra of a typical aqueous solution of AlF_3 and $Al(NO_3)_3$ is summarized in Figure 4. From the composition dependence of the pmr spectra at the lowest temperatures, the low-field signal can be assigned to H_2O in the first coordination sphere of the AlF_n^{+3-n} complexes and the high-field signal to H_2O in the bulk of the solvent. Although the individual AlF_n^{+3-n} complexes could, in principle, give rise to separate pmr signals, we could detect only a single coordinated H_2O resonance over a wide range of sweep fields and spectrometer settings. Because that resonance is a symmetrical Lorentzian line, it appears that the proton shifts of the various complexes are identical.

Using the solution compositions derived from the ^{19}F spectra, we have calculated the relative areas of coordinated and bulk water to be expected for various values of *q* in the $(H_2O)_qAlF_n^{+3-n}$ complexes. The results, which are summarized in Table IV for a few solutions, show that the complexes are best represented by the formulas $(H_2O)_5AlF^{2+}$, $(H_2O)_4AlF_2^+$, and $(H_2O)_3AlF_3$. In a previous proton nmr study,[13] it was shown

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(12) The ^{19}F line widths of these complexes are dominated by chemical exchange of ^{19}F over a wide temperature range. We have not been able to account for the temperature and solution composition dependence of the ^{19}F exchange rates in terms of a simple dissociation mechanism (*e.g.*, $AlF_n^{+3-n} \rightleftarrows AlF_{n-1}^{+4-n} + F^-$). Instead, the data suggest that the dominant path involves cooperative exchange of ^{19}F among the Al(III) complexes without the intervention of free F^- ion. The low apparent activation energies for the exchange (E_a = 8–10 kcal) and the lack of an effect by added Cu(II) ion on the exchange rates are consistent with the latter mechanism.

(13) N. A. Matwiyoff, P. E. Darley, and W. G. Movius, *Inorg. Chem.*, **7**, 2173 (1968).

TABLE IV

COMPARISON BETWEEN THE CALCULATED AND MEASURED RELATIVE AREAS OF THE PROTON RESONANCES IN BULK WATER AND WATER COORDINATED IN THE $(H_2O)_qAlF_n^{+3-n}$ COMPLEXES[a]

Formal soln compn[b]	R_{exptl}[a]	R_{calcd}[c] (for q = 6 and 4)	Formal soln compn[b]	R_{exptl}[a]	R_{calcd}[c] (for q = 6 and 4)
2	0.162	0.156 (0.074)	4	0.310	0.325 (0.188)
3	0.260	0.268 (0.134)	8	0.274	0.269 (0.205)

[a] Measured area of the coordinated H_2O resonance relative to that for bulk water obtained from spectra recorded at −25°. [b] Entries correspond to those of Table II. [c] Relative area calculated by assuming a distribution of the total amount of water into the bulk environment and into the complex ions $Al(OH_2)_6^{3+}$, $FAl(OH_2)_5^{2+}$, $F_2Al(OH_2)_4^{2+}$, and $F_3Al(OH_2)_3$. Values in parentheses were calculated by assuming coordination of water in the complex ions $Al(OH_2)_6^{3+}$, $FAl(OH_2)_3^{2+}$, $F_2Al(OH_2)_2^{+}$, and F_3AlOH_2.

that the only important Al(III) complex present in concentrated aqueous solutions of $Al(NO_3)_3$ is the $Al(OH_2)_6^{3+}$ ion. Because a coordinated H_2O resonance could be distinguished only for solutions containing small amounts of AlF_4^-, we could not evaluate q for that complex.

4. **^{27}Al Nmr.**—In the temperature range −20 to +33°, the ^{27}Al resonance for each of the solutions studied here consists of a single signal shifted slightly downfield (≤2 ppm) and broadened appreciably with respect to the resonance of the external standard, 1 *m* aqueous $Al(NO_3)_3$. For example, the ^{27}Al chemical shifts and line widths of 1 *m* AlF_3 and 1 *m* $Al(NO_3)_3$ aqueous solutions at +33° are, respectively, −1.5 ppm and 1.8 G and 0.00 ppm and ≤100 mG.

Because the ^{27}Al resonance did not provide any additional direct information about the individual AlF_n^{+3-n} complexes, we did not conduct an intensive study of the composition and temperature dependence of the ^{27}Al shifts and signal shapes. However, we did observe a ^{27}Al resonance having the proper signal area in the absorption mode of detection and the proper signal amplitude in the dispersion mode to account for *all* the Al(III) in each of the solutions of AlF_3 and $Al(NO_3)_3$ (including those of AlF_3 alone in which *all* the Al(III) is present in the form of AlF_3, AlF_2^+, and AlF_4^-). The ^{27}Al chemical shift differences among the individual Al–F complexes are apparently small compared to the signal widths. The signal areas and amplitudes were compared to those of a standard 1 *m* aqueous $Al(NO_3)_3$ solution at the same spectrometer settings (which allowed the detection of a pure Lorentzian signal unbroadened by modulation and saturation effects) of radiofrequency field, modulation amplitude, field sweep rates, etc.

These observations are important because they refute an earlier proposal that the decrease in the "intensity" of the $^{27}Al^{3+}$ resonance in the presence of F^- ion can be used to calculate the amount of "uncomplexed" $Al(OH_2)_6^{3+}$ ion present in such solutions.[1]

In the latter study, emphasis was placed upon the change induced in the amplitude of the ^{27}Al resonance of $Al(OH_2)_6^{2+}$ ion by the F^- ion. The expectation was that because ^{27}Al has a large quadrupole moment, mixed complexes such as $(H_2O)_qAlF_n^{+3-n}$ would possess a large field gradient at the Al(III) ion and consequently would exhibit broad, nondetectable ^{27}Al resonances. The resonance is indeed broadened but not beyond detection.

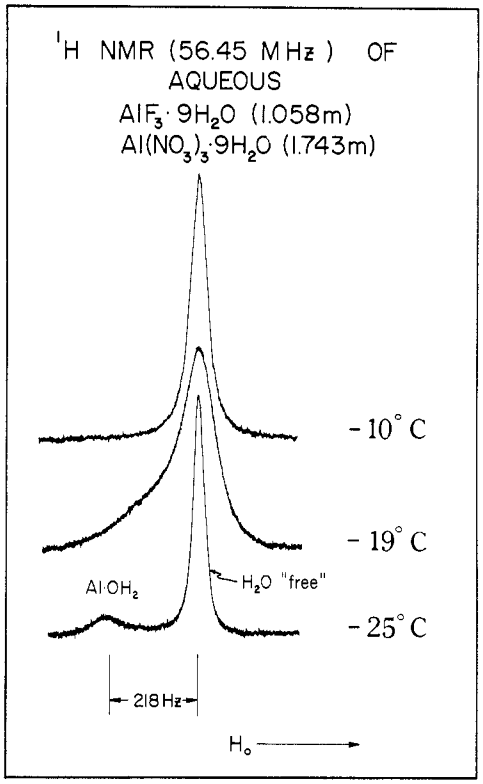

Figure 4.—Temperature dependence of the proton nmr spectrum of an aqueous solution of AlF_3 and $Al(NO_3)_3$.

Discussion

The ^{19}F and ^{1}H nmr spectra demonstrate that the species $Al(OH_2)_5F^{2+}$, $Al(OH_2)_4F_2^+$, $Al(OH_2)_3F_3$, and $AlF_4(aq)^-$ are kinetically well-defined entities in aqueous solutions of AlF_3 and $Al(NO_3)_3$. Although the temperature independence of the Q values for the equilibria among these complexes is consistent with the small enthalpies of formation that have been obtained calorimetrically for the individual Al–F ions,[14] the constancy of the *concentration* equilibrium quotients, Q, over a wide range of solution compositions is surprising.

If the equilibrium constants are to be meaningful thermodynamic parameters, then the ionic activities (γ) must be incorporated; *e.g.*, the thermodynamic equilibrium constant, K, for reaction 1 can be defined

$$K_1 = Q_1 \left[\frac{\gamma_{AlF^{2+}}\gamma_{Al^{3+}}}{(\gamma_{AlF^{2+}})^2}\right]$$

If the activities are formulated properly, then K is a constant and any composition dependence of the activities is compensated by a corresponding composition dependence of the Q values.

Although the nmr technique, as we applied it, cannot be used to distinguish a *small* consistent trend of

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(14) W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 1548 (1953).

equilibrium quotients with solution composition, certainly a *large* change in these quotients would be expected on the basis of extensions of the Debye–Hückel limiting law. For example, the Davies approximation[15] for mean ion activities, extended by others to single ions,[16] eq 5, would require large variations of the Q's over the range of ionic strengths employed—$1 \leq I \leq 19$, where γ_i is the molal ionic activity of

$$-\log \gamma_i = -0.5Z_i^2\{(\sqrt{I}/1 + B''a\sqrt{I}) - C''I\} \quad (5)$$

an ion of charge Z_i, I is the ionic strength, and B'', a, and C'' are "adjustable" constants.

Of course approximations like the Davies equation strictly apply only to dilute solutions and they have not been tested adequately at the high ionic strengths used in this study. Because these approximate equations contain a number of "adjustable" constants which are sensitive both to the ionic strength and nature of the ions involved, such a test would require a wide range of precise experimental data at high ionic strengths. Presently the appropriate data either are not available or are subject to ambiguities in interpretation.[17]

In this regard, it is of interest to point out that the Q values we have measured are much different from those we have calculated from the data of Brosset and Orring:[18] $Q_1 = 0.078$; $Q_2 = 0.068$; $Q_3 = 0.078$. Brosset and Orring used an Fe(II)–Fe(III) electrode to obtain the equilibrium constants for the formation of the individual Al–F complex from F^- ion in $NaNO_3$-NaF-$Al(NO_3)_3$ solutions at 25° and at a constant ionic strength of 0.5. Our measurements were made at much higher ionic strengths *and* Al(III) concentrations. At this time, it is not possible to decide whether the discrepancy is due to a general ionic strength effect or a specific ion effect.[19-21] Such a distinction could be made if the nmr measurements could be extended to dilute Al(III) solutions kept at constant ionic strength. We intend to obtain data for the latter solutions when nmr signal averaging equipment becomes available. It will also be of interest to obtain data for systems in which the "inert" counterion (NO_3^- in this study) is varied.

The ^{19}F resonance for the Al–F complexes as a set occur *upfield* with respect to the resonance of the free $F(aq)^-$ ion. Apparently, paramagnetic deshielding of F^- ion by hydrogen-bonded H_2O molecules[22,23] is reduced in the Al–F complexes due to the dehydration of the $F(aq)^-$ ion which accompanies the formation of the Al–F bond. This dehydration effect on the ^{19}F shielding must be large since it swamps the large deshielding expected for ^{19}F in the Al–F complexes due to the electric field of Al(III). It has been estimated that upon hydration of the hypothetical "free" F^- ion, the ^{19}F resonance shifts downfield by -155 ppm.[23]

Such a large hydration effect can account qualitatively for the puzzling trend in the ^{19}F shifts for the Al–F complexes which decrease in the order $AlF^{2+} > AlF_2^+ > AlF_3 > AlF_4^-$. Both the Saika–Slichter covalency theory[24] and the electric field effect treatments[25] of ^{19}F shifts predict the reverse trend for these complexes. However, if hydration effects on the ^{19}F shifts are predominant, the ^{19}F shielding should decrease as the ease with which $F^-\cdots HOH$ hydrogen bonds are formed increases. On a simple electrostatic basis, one would expect that such hydrogen bonds would be formed most readily between HOH and the AlF_4^- ion and least readily between HOH and the AlF^{2+} ion.

The pronounced effect of electrolytes[22,23,26,27] and temperature[23] changes upon the chemical shift of free $F(aq)^-$ have been attributed to ion-pair formation and dehydration effects. Connick and Poulson[26] have reported that $NaNO_3$ and $NaClO_4$ induce large *upfield* shifts of the ^{19}F resonance of the $AlF_2(aq)^+$ and $AlF(aq)^{2+}$ ions. The direction and concentration dependence of the shifts are consistent with an electrolyte-induced "dehydration" of the coordinated F^- ion. However, as summarized in Figure 3, the ^{19}F resonances of AlF_3 and AlF_2^+ in our systems shift *downfield* with increasing electrolyte $[Al(NO_3)_3]$ concentration and temperature. The direction of the shifts apparently is not consistent with a simple "dehydration" mechanism.[23] To assess anion and water structure effects on the ^{19}F shifts, we intend to obtain data for systems in which the inert anion is varied.

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(15) C. W. Davies, "Ion Association," Butterworth and Co. Ltd., London, 1962, pp 34–60.

(16) See, for example: R. A. Robinson, "The Structure of Electrolyte Solutions," W. J. Horner, Ed., John Wiley and Sons, Inc., New York, N. Y., pp 253–267; *Discussions Faraday Soc.*, **24**, 83 (1957); C. B. Monk, "Electrolytic Dissociation," Academic Press, Inc., New York, N. Y., 1961, p 153.

(17) For example, most of the available thermodynamics data for the formation of complex ions are based upon activity measurements, such as conductivity studies which require the assumption of a limiting equivalent conductivity for the complex ion. Even when a concentration measurement such as electronic absorption spectroscopy can be applied, it often requires the simultaneous evaluation of an equilibrium constant and the molar absorptivity of the complex ion, in addition to the assumption that the molar absorptivities of the free and complex ion are independent of the solution composition.

(18) C. Brosset and J. Orring, *Svensk Kem. Tidskr.*, **55**, 10 (1943).

(19) There is a similar discrepancy between ^{19}F nmr and activity data for the reaction $BeF_3(aq)^- + F(aq)^- \rightleftarrows BeF_4(aq)^{2-}$. Mesmer and Baes[20] used an emf method to obtain $Q = 26.7$ for dilute (10^{-3} M) solutions of Be(II) and F^- in a 1 M NaCl aqneous solution. Feeney, *et al.*,[21] used ^{19}F nmr to obtain $Q = 13$–16 for aqueous solutions 0.2–0.6 m in $(NH_4)_2BeF_4$.

(20) R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 618 (1969).

(21) J. Feeney, R. Haque, L. W. Reeves, and C. P. Yue, *Can. J. Chem.*, **46**, 1389 (1968).

(22) J. N. Shoolery and B. N. Alder, *J. Chem. Phys.*, **23**, 805 (1955).

(23) C. Deverell, K. Schaumburg, and H. J. Bernstein, *ibid.*, **49**, 1276 (1968), and references therein.

(24) A. Saika and C. P. Slichter, *ibid.*, **22**, 26 (1954).

(25) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960), and references therein.

(26) R. E. Connick and R. E. Poulson, *J. Phys. Chem.*, **62**, 1002 (1958).

(27) A. Carrington, F. Dravnicks, and M. C. R. Symons, *Mol. Phys.*, **3**, 174 (1960).