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Water Exchange in Fluoroaluminate Complexes in Aqueous Solution: A Variable Temperature Multinuclear NMR Study

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An ^{17}O, ^{19}F, and ^{27}Al NMR study of fluoroaluminate complexes ($AlF_n(H_2O)_{6-n}^{(3-n)+}$, $n = 0$, 1, and 2) in aqueous solution supports the idea that for each substitution of a bound water molecule by a fluoride anion, the exchange rate of bound water with free water increases by about 2 orders of magnitude. New rate coefficients for exchange of inner-sphere water molecules in $AlF(H_2O)_5^{2+}$ are $k_{ex}^{298} = 230(\pm 20)$ s^{-1}, $\Delta H^‡ = 65(\pm 3)$ kJ mol^{-1}, and $\Delta S^‡ = 19(\pm 10)$ J mol^{-1} K^{-1}. The corresponding new values for the $AlF_2(H_2O)_4^+$ complex are: $k_{ex}^{298} = 17\,100(\pm 500)$ s^{-1}, $\Delta H^‡ = 66(\pm 2)$ kJ mol^{-1}, and $\Delta S^‡ = 57(\pm 8)$ J mol^{-1} K^{-1}. When these new results are combined with those of our previous study,[4] we find no dependence of the solvent exchange rate, in either $AlF(H_2O)_5^{2+}$ or $AlF_2(H_2O)_4^+$, on the concentration of fluoride or protons over the range of $\sum F = 0.06-0.50$ M and $[H^+] = 0.01-0.44$ M. A paramagnetic shift of ^{27}Al resonances results from addition of Mn(II) to the aqueous solution as a relaxation agent for bulk waters. This shift allows resolution of the $AlF_n(H_2O)_{6-n}^{(3-n)+}$ species in ^{27}Al NMR spectra and comparison of the speciation determined via thermodynamic calculations with that determined by ^{27}Al, ^{19}F, and ^{17}O NMR.

Introduction

The reactivity of aqueous aluminum complexes is particularly important to the earth and environmental sciences because the cycling of aluminum in soil affects the health of forests,[1] the stratification of soils[2] and the toxicity of natural waters.[3] In previous work,[4] we reported that substitution of F^- into the inner-coordination sphere of $Al(H_2O)_6^{3+}$(aq) causes a remarkable increase in the lability of inner-sphere water molecules. We found that the lifetimes of inner-sphere water molecules decreased by approximately a factor of 10^2 with each substitution of fluoride in the inner-coordination sphere and provided estimates for the rate parameters for solvent exchange on $AlF(H_2O)_5^{2+}$ and $AlF_2(H_2O)_4^+$, based on a very limited set of data.

Recently Bodor et al.[5] employed ^{19}F NMR methods to estimate the rates of fluoride exchange in these complexes and noted an apparent paradox; the rate of exchange of dissolved fluoride with bound fluoride in the $AlF_2(H_2O)_4^+$ complex is much faster than our reported rate for exchange of bound water molecules with solvent. They also found evidence that the mechanism of exchange of free fluoride with bound fluoride was an associative interchange (I_a) and not the dissociative interchange mechanism (I_d) usually associated with ligand exchange in aluminum complexes. Their results led us to augment our previous experiments and to study rates of solvent exchange in the $AlF(H_2O)_5^{2+}$ and $AlF_2(H_2O)_4^+$ complexes in greater detail. Here we report more extensive data, including experiments on the $AlF_2(H_2O)_4^+$ complex where the proton concentration and the total ligand-to-metal ratio ($\sum F/\sum Al$) were varied at a constant total aluminum concentration. The results allow us to better constrain the average lifetime of a water molecule in the inner-coordination sphere of the complexes and show that solvent exchange is independent of the fluoride and proton concentrations. These results are consistent with an I_d mechanism for solvent exchange but also complement the conclusions of Bodor et al.[5] of rapid exchange of free and bound fluoride in the $AlF_2(H_2O)_4^+$ complex.

Experimental Methods

Materials. For ^{27}Al and ^{19}F NMR experiments, stock solutions were prepared by dissolving reagent grade $AlCl_3(H_2O)_6$, KF, HCl, KCl, and $MnCl_2(H_2O)_4$ (Fisher Chemical, Fair Lawn, NJ) in distilled and deionized water. The compositions of these solutions were checked by coulometric titration for chloride. Samples for ^{27}Al and ^{19}F NMR experiments (Table S1) were prepared from these stock solutions, and the apparent ionic strength was increased to 3 M by adding KCl. We used potassium fluoride instead of sodium fluoride to avoid the precipitation of Na_3AlF_6. For the variable-composition ^{27}Al NMR experiments at room temperature, the aluminum concentration was kept at 0.1 M and the $\sum F/\sum Al$ ratio was varied between 0.5 and 2.4. To examine the effect of paramagnetic Mn(II) species on the spectra, a second set of experiments were conducted at otherwise identical conditions with $MnCl_2$ being replaced with dissolved $ZnCl_2$. The solution (#812) for ^{27}Al NMR experiments at variable temperatures was chosen to have a $\sum F/\sum Al$ ratio of 2.0 and $[H^+] = 1.0$. For ^{19}F

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NMR experiments at room temperature, solutions with $0.5 \leq \sum F/\sum Al \leq 2.4$ and variable proton concentrations ($0.01 \leq [H^+] \leq 0.10$ M) were prepared with and without either $ZnCl_2$ or $MnCl_2$.

Solutions for ^{17}O NMR experiments were prepared by dissolving appropriate amounts of solid reagents directly into ^{17}O-enriched water (~15%) and HCl solution. The range of the $\sum F/\sum Al$ ratios available to the ^{17}O NMR measurements is limited by the solubility of K_3AlF_6 (ref 5) and by the necessity of maintaining relatively high concentrations of the $AlF_2(H_2O)_4^+$ complex. Precipitation of a solid occurred at $\sum F/\sum Al > 2.4$. At $\sum F/\sum Al < 1.6$, the concentrations of $AlF_2(H_2O)_4^+$ became too low, relative to $Al(H_2O)_6^{3+}$ and $AlF(H_2O)_5^{2+}$, to detect by ^{17}O NMR.

NMR Spectroscopy. The NMR measurements were made using a Bruker Avance spectrometer that is based on an 11.7 T magnet ($\nu_o = 67.8$ MHz for ^{17}O; $\nu_o = 130.3$ MHz for ^{27}Al; and $\nu_o = 470.6$ MHz for ^{19}F) and fitted with different probes for each nucleus. A 10 mm broadband probe (Doty Scientific, Colombia, SC), which yields very low background intensity for aluminum, was used for ^{27}Al NMR. Typical ^{27}Al NMR experiments were conducted using a 20 μs pulse ($\pi/2$ pulse = 42 μs), a relaxation delay of 0.5 s, and a digitization rate of 50 kHz. Prior to Fourier transform of the time-domain data, the first five points were recalculated by linear-prediction methods to remove a baseline roll. An external standard was included as 0.1 M $Al(OH)_4^-$ in a coaxial insert to give a peak at 80 ppm. Chemical shifts are referenced to δ $^{27}Al = 80$ ppm for $Al(OH)_4^-$(aq). The integrated intensities of the ^{27}Al NMR signals for all of the samples were normalized to the signal for the 0.1 M $Al(OH)_4^-$ reference.

The ^{19}F spectra were collected with a 5 mm Bruker probe with a 7 μs pulse ($\pi/2$ pulse = 9 μs) and a relaxation delay of 1 s. Typically, 100 acquisitions were collected to achieve adequate signal-to-noise ratio in the spectra.

The ^{17}O NMR spectra were collected using a 10 mm broadband probe with 20 μs pulses ($\pi/2$ pulse = 40 μs), recycle delays of 6 ms, and a 100 kHz digitization rate; 80 000 acquisitions were recorded to establish an adequate signal-to-noise ratio. Recalculation of the first 50 μs of the FID by linear-prediction methods prior to Fourier transform gave a flat baseline. A coaxial insert of 0.3 M $TbCl_3$ in isotopically normal water was included in all ^{17}O NMR experiments. This insert gives a peak near 100 ppm in the ^{17}O NMR spectra that corresponds to bulk waters and waters bound to the Tb^{3+} ion that are in rapid-exchange equilibrium.[6]

Rate Coefficients. The average lifetime of a water molecule in the inner-coordination sphere of the complexes was estimated using the dynamic ^{17}O NMR line-broadening technique.[7-14] In this method ^{17}O NMR transverse relaxation times (T_2) were obtained directly from the NMR line width: $T_2 = 1/(\pi \times \text{fwhm})$, where fwhm is the full width at half-maximum of the ^{17}O NMR resonance. The ^{17}O NMR resonance from bulk water is broadened beyond detection by interaction with Mn(II) species present in the solution.

The relaxation rate includes contributions from both chemical exchange and quadrupolar relaxation

$$\frac{1}{T_2} = \frac{1}{\tau} + \frac{1}{T_{2,q}} \qquad (1)$$

where τ is the mean lifetime of a water molecule in the inner-coordination sphere of the $AlF_n(H_2O)_{6-n}^{(3-n)+}$ complex and $1/T_{2,q}$ is the intrinsic quadrupolar relaxation rate. An Arrhenius-like relation is used to model the temperature dependence of quadrupolar relaxation

$$\frac{1}{T_{2,q}} = W_{q,298}e^{(E_q/R)[(1/T)-(1/298)]} \qquad (2)$$

where E_q and $W_{q,298}$ are fitting parameters.[4]

The temperature dependence of k_{ex} (s^{-1}), the pseudo-first-order rate coefficient for exchange of water molecules from the inner-coordination sphere to the bulk solution, takes the form of the Eyring equation

$$\frac{1}{\tau} = k_{ex} = \frac{k_bT}{h}\, e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H^{\ddagger}/RT} \qquad (3)$$

where k_b is Boltzmann's constant and the exponential terms include the activation entropy [$\Delta S^{\ddagger}$] and activation enthalpy [$\Delta H^{\ddagger}$] for chemical exchange. The parameters T, R, and h are absolute temperature, the gas constant, and Planck's constant, respectively.

Line shape parameters were obtained from least-squares fits of the frequency-domain data to a sum of Lorentzian curves. In estimating rate coefficients, we propagated uncertainties of 10% in the raw peak widths through the calculations. These values comfortably span the range of values that are consistent with reasonable adjustments in spectrum phasing and baseline correction. Presence of the narrow peak from the Tb^{3+}(aq) insert, upfield from the bound water peaks, enabled the accurate phase adjustments necessary for measuring the width of broad resonances.

Temperature Control. Temperature control was maintained by the standard Bruker controller, which was calibrated by placing a copper–constantan thermocouple into the coaxial insert of a sample tube and inserting this apparatus into the spectrometer. The accuracy of the spectrometer temperature setting is equal to, or better than, ±0.5 K. To calculate rate coefficients, we use a conservative value of ±0.5 K as a standard deviation (1σ) for temperature.

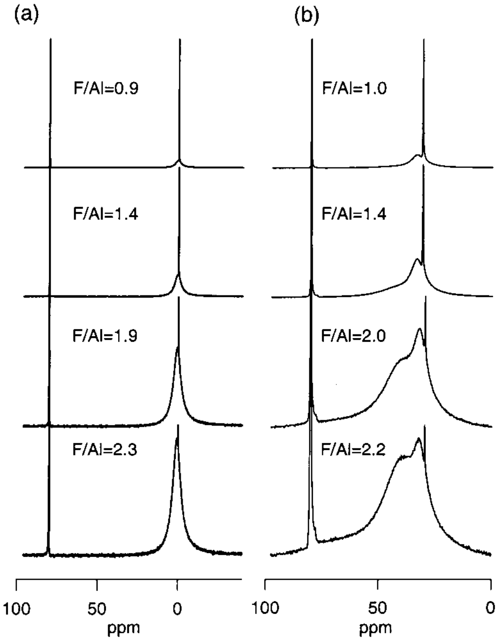

Figure 1. ^{27}Al NMR spectra of Al–F–Cl–H solutions at 298 K with the indicated $\sum F/\sum Al$ ratio and $[H^+] = 0.10$ M. (a) without Mn(II) and (b) with 0.50 M Mn(II). The signal at 80 ppm is from $Al(OH)_4^-$ in the insert.

Results and Discussion

^{27}Al NMR. For solutions without Mn(II), the ^{27}Al NMR spectra contain a narrow peak at 0 ppm and a broad peak centered at 2 ppm (Figure 1a) that changed in relative intensity depending upon the $\sum F/\sum Al$ ratio of the aqueous solution. It is well-accepted that the signal at 0 ppm arises from $Al(H_2O)_6^{3+}$,

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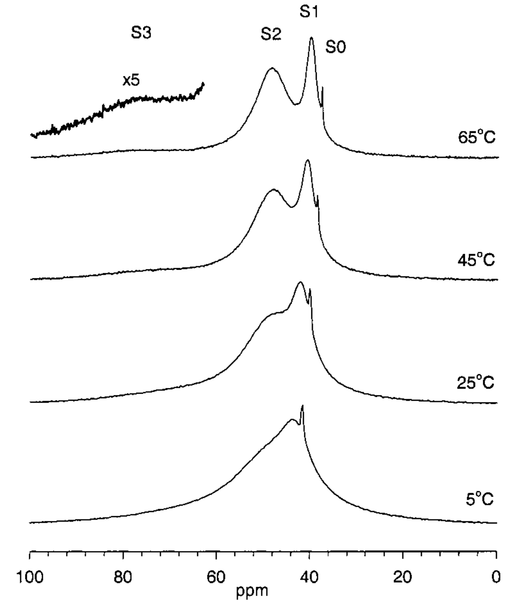

Figure 2. ^{27}Al NMR spectra of Al−F−Mn−Cl−H solutions with $\sum$F/$\sum$Al = 2.0 (sample 812) at the indicated temperatures. S0, S1, S2, and S3 are tentatively assigned to the $Al(H_2O)_6^{3+}$, $AlF(H_2O)_5^{2+}$, $AlF_2(H_2O)^{4+}$, and $AlF_3(H_2O)_3^0$ complexes, respectively.

and the broad downfield signal is due to one or more of the fluoroaluminate complexes.[15,16] The relative intensity and width for the broad peak increase with increasing $\sum$F/$\sum$Al ratio, but the position of this signal does not change significantly. These results are consistent with an interpretation[15] that the broad peak is a composite that corresponds to several fluoroaluminate complexes that exhibit very small differences in chemical shifts. The ^{27}Al NMR resonances for $AlF_2(H_2O)_4^+$ and $AlF_3(H_2O)_3^0$ are probably broader than for $AlF(H_2O)_5^{2+}$, which explains the increased peak width at higher $\sum$F/$\sum$Al ratio (Figure 1a), consistent with previous work.[15,16] Identical spectra to those shown in Figure 1a are observed if the solution contains 0.5 M $ZnCl_2$ (not shown) at constant apparent ionic strength.

The addition of $MnCl_2$ to the solution, however, adds considerable detail to the ^{27}Al NMR spectra (Figure 1b). The spectra of aluminum fluoride solutions with $MnCl_2$ contain at least four resolvable components (Figure 1b) that exhibit systematic changes in relative intensities with the $\sum$F/$\sum$Al ratio, consistent with assignment to distinct $AlF_n(H_2O)_{6-n}^{(3-n)+}$ complexes. Furthermore, the peaks are much broader than the single broad peak assigned to fluoroaluminate complexes in solutions without $MnCl_2$ (Figure 1a). Both the peak positions and widths vary with temperature. (Figure 2). The four signals are tentatively assigned to $Al(H_2O)_6^{3+}$, $AlF(H_2O)_5^{2+}$, $AlF_2(H_2O)_4^+$, and $AlF_3(H_2O)_3^0$ (the signals S0, S1, S2, and S3, respectively, in Figure 2). On the basis of these assignments and the integrated relative intensities of the corresponding peaks, the speciation of Al with a variable $\sum$F/$\sum$Al ratio can be calculated and compared to that calculated from thermodynamic data (Figure S1a). The thermodynamic calculations are based on the compilation from ref 17 after an ionic strength correction based on Davies equation. The data in Figure S1 indicate that addition of Mn(II) does not greatly alter the speciation of Al in the solutions.

The effect of Mn(II) on the ^{27}Al peak positions and widths can be attributed to a pseudocontact interaction between the unpaired electrons in the paramagnetic Mn(II) species and ^{27}Al in the fluoroaluminate complexes.[18] Although virtually all of the Mn(II) species in these acidic solutions are present as $Mn(H_2O)_6^{2+}$(aq), which is electronically isotropic, small concentrations of $MnF(H_2O)_5^+$ complexes with short lifetimes[19,20] are also likely to be present and this fluoridation can induce magnetic anisotropy. Dipolar interactions between the unpaired electrons on this Mn(II) complex, and perhaps others, and the fluoroaluminate complexes can cause both a paramagnetic shift and line broadening. A similar effect was noticed by Matwiyoff et al.[21] who found that Co(II) affected the ^{19}F NMR spectra of the fluoroaluminate complexes.

The dipolar interactions between the unpaired electrons in the Mn(II) species and the ^{27}Al nucleus in the $AlF_n(H_2O)_{6-n}^{(3-n)+}$ complexes require a preferred direction of approach of the ^{27}Al nucleus to the Mn(II) species with respect to its magnetic anisotropy. Correlation of the ^{27}Al shift and width with charge on the fluoroaluminate complex is consistent with electrostatic control of the properties of ion-pair formation. For example, the distances of approach must reflect the electrostatic repulsion so that the Mn(II) species can more closely approach the fluoroaluminate complexes that have a lower charge, such as $AlF_3(H_2O)_3^0$, yielding widths and shifts that are greater than those for complexes with a higher net charge, such as $Al(H_2O)_6^{3+}$.

^{19}F NMR. For a series of samples with constant aluminum concentration, a variable $\sum$F/$\sum$Al ratio from 0.5 to 2.4, and constant proton concentration ($[H^+] = 0.1$ M), the ^{19}F NMR spectra exhibit distinct signals assignable to $AlF(H_2O)_5^{2+}$, $AlF_2(H_2O)_4^+$, and $AlF_3(H_2O)_3^0$. We use the intensities of these peaks to derive speciation information (Figure S1b). The ^{19}F NMR spectra for solutions with constant $\sum$Al = 0.1 M and $\sum$F/$\sum$Al = 2.2 but variable proton concentrations were also collected, and the results were comparable with those reported previously.[4,5] The free F^- signal was observed only for samples with very high proton concentrations ($[H^+] = 0.313$ M) and high $\sum$F/$\sum$Al ratios (>2.2). No signal was observed for $AlF_4(H_2O)_2^-$, as was expected, because the samples had a $\sum$F/$\sum$Al ratio that was too low for measurable concentrations of this species. The fraction of $AlF_2(H_2O)_4^+$ and $AlF_3(H_2O)_3^0$ increases with the increasing $\sum$F/$\sum$Al ratio, as expected. As discussed by Bodor et al.,[5] the peak width of the signal assigned to the $AlF(H_2O)_5^{2+}$ complex does not change with changes in the $\sum$F/$\sum$Al ratio, while we observe a slight increase in the line width for $AlF_2(H_2O)_4^+$ and significant increases for $AlF_3(H_2O)_3^0$ with increasing $\sum$F/$\sum$Al ratio. The fluoride speciation based on ^{19}F NMR data compares well with the speciation calculated from published thermodynamic data (Figure S1b), and we found no changes in aluminum speciation upon addition of $ZnCl_2$ to the aqueous solution. No ^{19}F NMR signal is detectable for solutions containing $MnCl_2$.

^{17}O NMR. The solution compositions for solvent exchange measurements were chosen such that the $AlF(H_2O)_5^{2+}$ and $AlF_2(H_2O)_4^+$ species were the dominant fluoroaluminate complexes in the solution, using the ^{27}Al and ^{19}F NMR spectra of similar solutions as a guide (Figure S1). Correspondingly, the ^{17}O NMR spectra of the solutions contain overlapping peaks due to the

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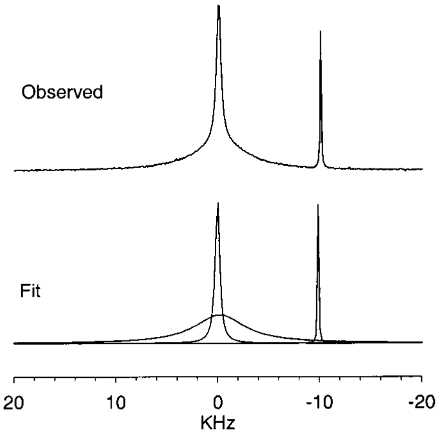

Figure 3. ^{17}O NMR spectrum for solution 3192d at 25 °C, which can be fit with a sum of three Lorentzian peaks. The peak at −10 kHz is due to the $TbCl_3$(aq) insert. Origin of the frequency scale is arbitrary.

bound water on each of the $AlF(H_2O)_5^{2+}$ and $AlF_2(H_2O)_4^{+}$ complexes (plus a small amount of $Al(H_2O)_6^{3+}$(aq)). Interconversion among the $AlF_n(H_2O)_{6-n}^{(3-n)+}$ complexes is slow on the ^{17}O T_2 NMR time scale.[5] The resonances for the different complexes can be distinguished from one another when their peak widths differ by a factor of about 3.

A typical ^{17}O NMR spectrum is shown in Figure 3, along with the results of a least-squares fit to a sum of Lorentzian curves, which yields T_2 and intensity for each component. The narrow peak is assigned to $AlF(H_2O)_5^{2+}$, and the broad peak is assigned to $AlF_2(H_2O)^{4+}$. The ratio of the two complexes, obtained by integrating the fitted ^{17}O NMR intensities, agrees well with the results from ^{27}Al and ^{19}F NMR data (Figure S1). At successively higher temperatures, the peaks for $AlF_2(H_2O)_4^{+}$ and $AlF(H_2O)_5^{2+}$ become too broad to detect, as indicated by loss of intensity, compared to the peak for the Tb^{3+}(aq) standard, which represents a constant number of ^{17}O nuclei throughout the experiments.

The widths of the ^{17}O NMR peaks assigned to each of the three complexes, $AlF(H_2O)_5^{2+}$, $AlF_2(H_2O)_4^{+}$, or $Al(H_2O)_6^{3+}$, vary differently with temperature, but there is consistency for a given complex between different samples. The ^{17}O NMR transverse relaxation times (T_2) for the various peaks were obtained directly from the NMR line width and are plotted in Figure 4 as a function of inverse temperature. We were able to obtain data over a larger range of temperatures than in our previous experiments and now observe a contribution to the line width of the $AlF(H_2O)_5^{2+}$ complex from quadrupolar relaxation (Figure 4). These data allow us to estimate the contribution to the line widths from intrinsic quadrupolar relaxation at all temperatures from values of $W_{q,298}$ and E_q in eqs 1−3.

The resulting value of k_{ex}^{298} for the $AlF(H_2O)_5^{2+}$ complex is 230(±20) s^{-1}, which is within a factor of 2 of our previous estimate (Table 1). The difference between this new value of k_{ex}^{298} for the $AlF(H_2O)_5^{2+}$ complex and that of Phillips et al.[4] is wholly attributable to better correction for the contribution to the line width from quadrupolar relaxation; the raw data are in excellent agreement with the previous results. The activation parameters were obtained by fitting the raw data into eqs 1−3 without any constraints (Table 1).

The ^{17}O NMR signal for the $AlF_2(H_2O)_4^{+}$ complex appears to be dominated by chemical exchange at temperatures above about 288 K. In estimating the rate and activation parameters for this complex, we assume that the parameters describing quadrupolar relaxation are identical to those obtained for the $AlF(H_2O)_5^{2+}$ complex ($W_{q,298} = 1382$ s^{-1} and $E_q = 23$ kJ mol^{-1}). This assumption makes little difference in the estimated rate parameters because quadrupolar relaxation contributes so little to the observed line width of the $AlF_2(H_2O)_4^{+}$ complex, which exchanges water with solvent about 10^2 times more rapidly than the $AlF(H_2O)_5^{2+}$ complex. The values of k_{ex}^{298} for $AlF_2(H_2O)_4^{+}$ and $AlF(H_2O)_5^{2+}$ fall within the range measured for other Al complexes, for which direct measurements are available (refs 9−13).

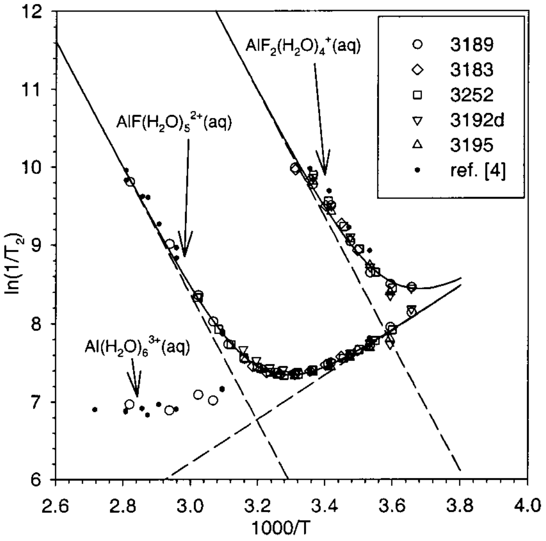

Figure 4. Temperature dependence of ln(1/T_2) of ^{17}O NMR signals for the solutions 3189 (○), 3183 (◇), 3252 (□), 3192d (▽), and 3195 (△) and data from ref 4 (●).

Table 1. A Compilation of Rate Coefficients and Activation Parameters for Exchange of Water Molecules from the Inner-Coordination Sphere of Fluoroaluminum Complexes to the Bulk Solution, As Determined from ^{17}O NMR

species	k_{ex}^{298} [a] (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	source
$Al(H_2O)_6^{+3}$	1.29	85(±3)	42(±9)	ref 7
$AlF(H_2O)_5^{2+}$	230(±20)	65(±3)	19(±7)	comb data
$AlF_2(H_2O)_4^{+}$	17 100(±500)	66(±2)	57(±8)	comb data

[a] The estimated uncertainties for $k_{ex}^{298}$are for a single estimated standard deviation. The data from this study are combined with those of ref 4 to yield the estimates in the table.

Although presence of Mn(II) in the solution has a large effect on the ^{27}Al spectra of the fluoroaluminate complexes, it does not appear to significantly affect the ^{17}O signal from the bound waters, except as a relaxation agent for solvent water. In contrast to the ^{27}Al results, we observed no change in the ^{17}O T_2 values upon changing the Mn(II) concentration from 0.25 to 0.50 M, and the ^{17}O resonances do not display significant relative paramagnetic shifts of the resonances for the different complexes. The lack of paramagnetic effects on the ^{17}O spectra suggests nearly complete averaging of the dipolar interaction to the unpaired Mn(II) electron spins, which can occur by random orientation of the water positions during ion-pair formation.

The data in Figure 4 demonstrate that the average lifetimes of water molecules in the inner-coordination spheres of $AlF(H_2O)_5^{2+}$(aq) and $AlF_2(H_2O)_4^{+}$(aq) do not vary with either proton or fluoride concentrations. The absence of a dependence on proton concentration indicates that hydroxyl ternary complexes, such as $AlF_2OH(H_2O)_3$, are unimportant to the observed ^{17}O NMR relaxation, supporting conclusions of Bodor et al.[5]

and others that fluoride forms simple binary complexes with hydrated aluminum in these solutions.

The absence of a dependence on fluoride concentration suggests that solvent exchange around the $AlF_2(H_2O)_4^+(aq)$ complex occurs via a dissociative interchange mechanism (I_d), as is commonly found for ligand-exchange reactions involving other aluminum coordination complexes[22] and for $Al(H_2O)_6^{3+}(aq)$.[7] Because the concentration of free fluoride ions in these experiments is very sensitive to the $\sum F/\sum Al$ ratio and total proton concentration, this 0.16−0.22 M change in total dissolved fluoride concentration would have caused a change of over a factor of 10 in the concentration of a simple outer-sphere ion pair between $AlF_2(H_2O)_4^+(aq)$ and $F^-(aq)$, using the Fuoss equation to estimate an equilibrium constant. Fluoride, in the outer-coordination sphere of $AlF_2(H_2O)_4^+$, apparently does not influence the rates of bond dissociation between aluminum and inner-sphere water molecules.

Bodor et al.[5] indicated an associative interchange mechanism (I_a) for the exchange of bound and free fluoride in the $AlF_2(H_2O)_4^+(aq)$ complex. Their conclusion was reached, in part, because fluoride in the $AlF_2(H_2O)_4^+(aq)$ complex exchanges for free fluoride at a rate ≈40 times faster than the rate of solvent exchange reported in our earlier work,[4] and repeated here. They also found that free fluoride exchanges for a bound water molecule at rates that were too slow to detect via ^{19}F NMR, consistent with our results and an I_d mechanism for solvent exchange.

Water exchange, however, may be involved in cis−trans isomerization in the $AlF_2(H_2O)_4^+(aq)$ complex. Bodor et al.[5] reported coalescence of two peaks in the ^{19}F spectra assigned to cis- and trans-isomers of the $AlF_2(H_2O)_4^+(aq)$ complex at temperatures near 262 K. The rate of isomerization at the coalescence temperature (≈262 K) can be estimated from

$$k = \frac{\pi\,|\Delta\nu|}{2^{1/2}} \qquad (4)$$

where $\Delta\nu$ is the frequency difference (Hz) of peaks in the ^{19}F NMR spectra assigned to the two isomers in the limit of no exchange. The estimation of the values of $\Delta\nu \approx 165(\pm 30)$ Hz at 255 K from Figure 5 of Bodor et al.,[5] yields $k > 350(\pm 70)$ s^{-1}. Extrapolation of the rate of water exchange from the inner-coordination sphere of the $AlF_2(H_2O)_4^+(aq)$ complex to bulk solution to near 262 K yields $k_{ex}^{262} \approx 450(\pm 20)$ s^{-1}, which is close to the rate of isomerization. The result suggests that dissociation of a water molecule from aluminum in the inner-coordination sphere might be directly involved in the rate-controlling step in this isomerization reaction.

Conclusions

The substitution of a fluoride ion for each ligand water molecule in $AlF_n(H_2O)_{6-n}^{(3-n)+}$ complexes ($n = 0$, 1, and 2) in aqueous solution increases the exchange rate of bound water with free water by about 2 orders of magnitude. We observe no dependence of the lifetime of an inner-sphere water molecule on fluoride or proton concentration that might indicate contributions to chemical exchange from ternary hydroxyl complexes or by rapid displacement of a water molecule by a fluoride ion. Interestingly, we find that adding Mn(II) species to the aqueous solution as a relaxation agent for bulk waters induces a shift in the peak positions for the $AlF_n(H_2O)_{6-n}^{(3-n)+}$ species in ^{27}Al NMR spectra, allowing us to compare the intensities with those observed in ^{17}O NMR. The rates of exchange of these monomers compare well with those determined for other aluminum complexes.[9,13,23,24]

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Supporting Information Available: A table providing information about the compositions of solutions for NMR experiments and a figure providing data based on thermodynamic calculation and NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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