COMPOSITION AND STRUCTURE OF ALUMINUM FLUOROCOMPLEXES IN AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AND INORGANIC ACIDS

V. V. Kon'shin, B. N. Chernyshov,
and E. G. Ippolitov

UDC 543.422.25:541.49:546.623:546.16

In aqueous solutions, aluminum forms octahedral aquo- and aquoacidocomplexes having the composition $[AlF_n(H_2O)_{6-n}]^{3-n}$ (n = 0-6), but unambiguous experimental evidence for the existence of all six fluoroaluminate complexes in solution is lacking. According to the accepted interpretation of the ^{19}F NMR data, individual signals of the fluoroaluminate complexes $[AlF(H_2O)_5]^{2+}$–$[AlF_4(H_2O)_2]^{1-}$ are registered in aqueous solutions at mole ratios of F/Al between 1 and 3 [1, 2]. Analysis of the ^{19}F NMR spectra at a F/Al ratio >6 led to the conclusion [3] that the complex $[AlF_6]^{3-}$ could be present in the aqueous solution. Data supporting the formation of aquofluorocomplexes of aluminum obtained using ^{27}Al and ^{1}H NMR are not available.

For the purpose of seeking direct data on the formation and unambiguous identification of all the aluminum fluorocomplexes in solutions, we used ^{19}F, ^{27}Al, and ^{1}H NMR to investigate the aluminum compounds in solutions of hydrogen peroxide, which was selected as a solvent capable of stabilizing the first coordination sphere of Al^{3+}, and in solutions of inorganic acids.

EXPERIMENTAL

The F/Al ratio in solutions of Al(III) nitrate or chloride solutions was varied using NH_4F, KF, RbF, or HF. The concentration of the salts in the solution was varied over the range 0.1-0.5 M for 1000 g of solution. The ^{1}H, ^{19}F, and ^{27}Al NMR spectra were recorded on a Bruker WP-80SY spectrometer with thermostabilization.

RESULTS AND DISCUSSION

At F/Al mole ratios of 1-3, individual signals are registered in the ^{19}F spectra that on the basis of [1, 2] can be attributed to the aquofluoroaluminate complexes $[AlF(H_2O)_5]^{2+}$, $[AlF_2(H_2O)_4]^{+}$, $[AlF_3(H_2O)_3]$, and $[AlF_4(H_2O)_2]^{-}$. On increasing the mole ratio of F/Al from 4 to 6, signals are also registered from $[AlF_5(H_2O)]^{2-}$, $[AlF_6]^{3-}$ and the free fluorine ion in the ^{19}F NMR spectra of the aqueous–peroxide systems. In aqueous solutions, signals from these complexes are not detected. A direct experimental criterion for the formation of the the $[AlF_6]^{3-}$ complex in the solution is the multiplicity of NMR signals caused by the ^{27}Al–^{19}F spin–spin interaction. In aqueous solutions, the multiplicity of the NMR signals of the fluoroaluminate complexes is not detected [3]. In an aqueous-peroxide solution at 253 K and a F/Al ratio ≥ 6, two signals are recorded: a sextet and a singlet of F^-.

In the general case, without taking into account the effects of quadrupole relaxations of the ^{27}Al, the sextet signal shape should be typical of any fluoroaluminate complex $[AlF_n(H_2O)_{6-n}]^{3-n}$ as a result of the spin–spin interactions in them between the isotopes of ^{27}Al (I = 5/2) and ^{19}F (I = 1/2). The multiplicity of the signals of the ^{27}Al NMR signals is determined by the number N of equivalent F atoms in the complex as 2NI + 1. For this reason, when only one signal is observed in the ^{27}Al NMR spectra of the same solutions at 233-253 K, a multiplet of seven lines, it is clear that the number of equivalent F atoms in the complex formed is N = 6. When the spin–spin interactions due to ^{19}F are suppressed, the multiplicity of the ^{27}Al signal disappears, unambiguously indicating that these signals are due entirely to the $[AlF_6]^{3-}$ complex [4], in accordance with the theoretically calculated multiplet for systems AX_6 for a ^{27}Al–^{19}F spin–spin interaction of 19 ± 1 Hz.

Institute of Chemistry, Far East Science Center, Academy of Sciences of the USSR, Vladivostok. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1707-1711, August, 1987. Original article submitted January 31, 1986.

0568-5230/87/3608-1577$12.50

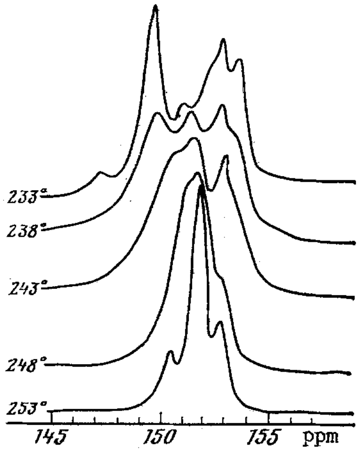


Fig. 1. ^{19}F NMR spectra of a 30% peroxide solution of $AlF_3 \cdot 9H_2O$ as a function of temperature.

The effect of the temperature on the possibility of recording signals from these complexes is more conveniently investigated using AlF_3, which has been well-studied in aqueous solutions. From Fig. 1 it follows that in H_2O/H_2O_2 solutions, the signals separate in two stages. The activation energy of these steps, on the basis of ^{19}F NMR, are the same within the limits of error and are equal to 2.9 kcal/mole·deg. At the first step (∿273 K), both in aqueous and in aqueous—peroxide solutions, three signals are registered in ^{19}F NMR spectra that are attributed to the complexes $[AlF_2(H_2O)_4]^+$, $[AlF_3(H_2O)_3]$, and $[AlF_4(H_2O)_2]^-$. Lowering the temperature leads to a broadening and subsequent separation (∿233 K) of these signals (cf. Fig. 1), and at the second step they are transformed into six signals. In order to assign these signals we used the change in the integrated intensities of the lines of the spectrum as a function of the F/Al ratio at 233 K (Fig. 2).

The fine structure of the signal in the weak field at 253 K collapses as the temperature is reduced, so that this signal can be assigned only to $[AlF_6]^{3-}$. The remaining signals shown in Fig. 2 were assigned taking into consideration the redistribution of the integrated line intensities with change in the F/Al mole ratio. The correctness of the assignments of the lines in the spectrum was confirmed by the equality of the calculated and the assigned F/Al ratio. Taking into account the assignments of the signals of the two steps in the resolution, the content of the corresponding aluminum fluorocomplexes and the magnitudes of their chemical shifts as a function of the F/Al molar ratio (Fig. 3) were determined. From the dependence shown (cf. Fig. 3a) it follows that the values of the chemical shifts for anionic and neutral complexes in the first and second stages are similar, while the chemical shifts of the cationic complexes at the different steps differ appreciably. Furthermore, in the first and the second stages both the composition and content of the individual Al fluorocomplexes are different (cf. Figs. 3b and 3c).

As a consequence of the ionic nature of the Al—F bond, there are strong H-bonds in the solutions studied with both free water molecules (Al—F...H_2O) and with coordinated water molecules of various aquo- and aquofluorocomplexes of Al. As a result, association complexes form that contain one or more Al—F...H_2O—Al fragments, the number of which depends on the F/Al ratio. For this reason, when the intermolecular exchange of F^- is retarded, individual signals from association complexes of the composition $\{Al_mF_{mn}(H_2O)_{(6-n)m}\}$, n = 1-5, $m \geq 2$ are registered. Further lowering of the temperature of the solution also retards the intramolecular exchange of ligands, which causes the F^- to be redistributed among the individual aluminum ions in the association complexes. This type of redistribution disrupts the statistical distribution of F^- in the system and shifts the equilibrium toward the formation of those aluminum complexes higher in fluorine registered in the ^{19}F NMR spectra.

Consequently, at the first stage of the separation of the ^{19}F NMR exchange signal, aquofluoroaluminate association complexes with a statistical distribution of F atoms in them in terms of the F/Al ratio are detected. The actual composition and distribution of the aluminum fluorocomplexes in the solution can be established by the ^{19}F NMR method only when ligand exchange, to which the second stage of the signal separation corresponds, is slow.

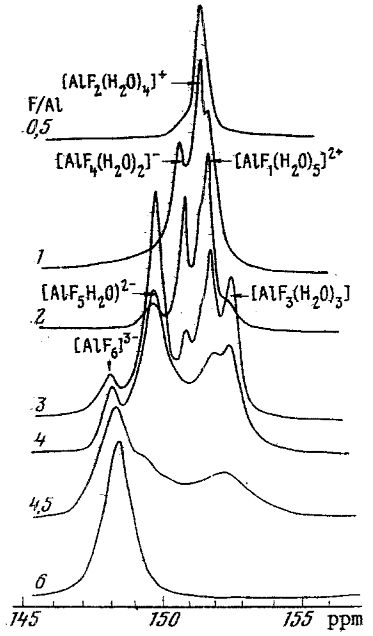


Fig. 2

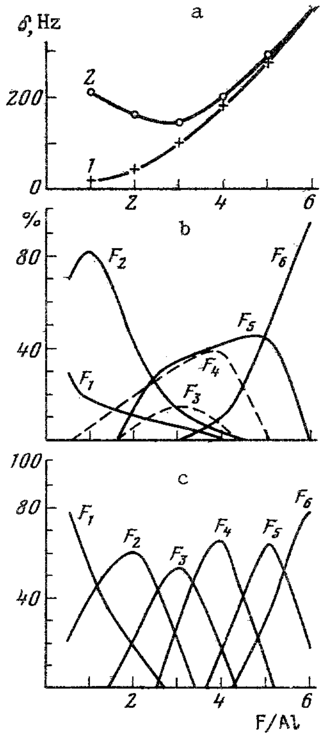


Fig. 3

Fig. 2. ^{19}F NMR spectra of solutions of $Al(NO_3)_3 \cdot 9H_2O + NH_4F$ in 30% H_2O_2 at 233 K as a function of the F/Al ratio.

Fig. 3. Dependence of the chemical shifts of ^{19}F (a) and the percentage of the complexes $[AlF_n(H_2O)_{6-n}]^{3-n}$ (n = 1-6) in 30% H_2O_2 on the F/Al ratio (a, b) at a(2), b, 233, and a(1), c, 253 K.

The possibility of lowering the temperature of H_2O/H_2O_2 solutions to 223-213 K makes PMR spectra informative, since it makes it possible to resolve signals from the hydration shells of cationic aluminum aquofluorocomplexes. Over the range of F/Al mole ratios of 0-2.5, three signals are registered in PMR spectra from the water in the complexes $[Al(H_2O)_6]^{3+}$, $[AlF(H_2O)_5]^{2+}$, and $[AlF_2(H_2O)_4]^+$. Reduction of the charge to unity leads to a shift of ~0.5 ppm in the proton signals of the water of the hydration shell of these complexes in the strong field direction. Signals from the hydration shells of aluminum aquofluorocomplexes higher in F are not observed due to the great lability of the water in the anionic complexes. The ^{27}Al NMR spectra of aqueous and aqueous–hydrogen peroxide solutions of aluminum (F/Al = 0-2.5) contain a narrow signal from $[Al(H_2O)_6]^{3+}$ and a broad signal from the aquofluoroaluminate complexes, which cannot be resolved even by lowering the temperature of the solution.

Since H_2O_2 is a weak field with a dissociation constant of about 10^{-4} mole^{-1}, the complexation of aluminum in the strong inorganic acids HCl and H_2SO_4, the anions of which are weak donors compared to fluorine, were also considered. The substantial difference in the dissociation constant of HCl, H_2SO_4, and H_2O_2 affects the state of the "excess" fluorine, which is found in the form of HF or F^-, respectively. In the acids there is intense intermolecular exchange between the fluorocomplexes and the HF which can be retarded on the NMR scale below 243 K. Here, as the F/Al mole ratio changes, signals of all six aquofluoroaluminate complexes are also registered in the ^{19}F NMR spectra, just as in H_2O_2. However, hydrogen peroxide (~30%) is a more convenient solvent than the inorganic acids for studying complexation and solvation of aluminum fluorocomplexes.

The processes of complexation of fluoroaluminates in H_2O_2 (80-90%) over the range of F/Al molar ratios of 4-5 differ considerably from those in nonconcentrated solutions. In the concentrated solutions, signals from fluoroaluminate complexes other than the aluminum aquofluorocomplexes are also registered (Fig. 4). In the ^{27}Al NMR spectra, signals from the individual aluminum aquofluorocomplexes are not registered except for signals from the symmetrical ions $[AlF_6]^{3-}$ and $[Al(H_2O)_6]^{3+}$. From a comparison of the ^{19}F and the ^{27}Al

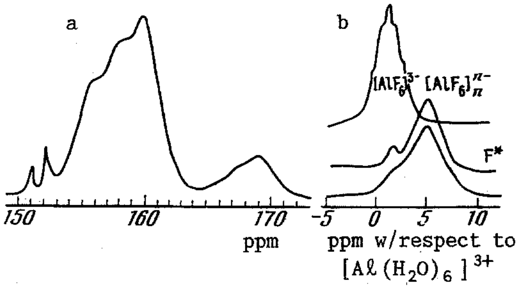
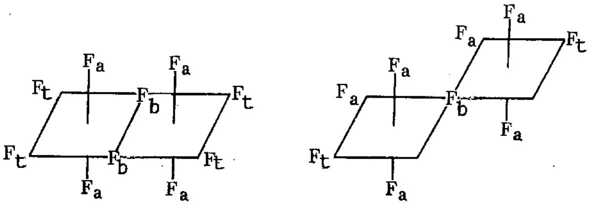


Fig. 4. ^{19}F (a) and ^{27}Al (b) NMR spectra of $AlCl_3$ + NH_4F (F/Al = 4.5) in 98% H_2O_2 at 253 K. F* – broadband suppression of ^{19}F.

NMR spectra it follows that the signal of the same width as that from $[AlF_6]^{3-}$, with a chemical shift in the strong field direction of 5 ppm, corresponds to the broad signals of the ^{19}F from the fluoroaluminate complexes in the ^{27}Al NMR spectra. Under ^{19}F broadband suppression, this signal narrows (cf. Fig. 4b). Consequently, this signal is assigned to a complex with a symmetrical distribution of F atoms about the central Al(III) atom. Since in the systems considered the F/Al ratio is less than 6, sufficiently symmetrical complexes can form only as a result of polymerization, for example, such as occurs during the formation of crystals of aluminum tri-, tetra-, and pentafluorides [5]. For this reason, in conc. H_2O_2 at F/Al = 4-5, Al(III) has its highest coordination number for F, namely, six, as the result of dimerization. As $[H_2O_2]$ is reduced, ^{19}F and ^{27}Al NMR indicate that the water molecules replacing the F atoms break the bridging bonds and the dimers change into aquofluoroaluminate complexes with one or two water molecules. Similar to the increase in the concentration of the water, the increase in the F content in the systems leads to its interaction with dimer complexes, and their transformation into monomeric $[AlF_6]^{3-}$.

The H_2O_2 dimers existing in the solutions (polymers) can form from chains of AlF_4 and AlF_5 containing corners or edges of octahedra, depending on the F/Al ratio.



For such complexes, the theoretical ratio of the integrated intensities of the ^{19}F NMR signals should be, if they are completely resolved, 4:4:2 and 8:2:1, or assuming the equal probability of the two dimers, 16:3 for bridging and terminal F atoms, which is what was observed in the experimental spectrum (cf. Fig. 4a).

The ^{19}F NMR spectrum for the system $AlCl_3$ + NH_4F in 98% H_2O_2 (F/Al = 4, 5) contains five overlapping signals (cf. Fig. 4a), the width of which depends only slightly on the temperature in the range 293-253 K. The signals in the strong field (167-169 ppm) can be assigned only to the bridging atoms of F in dimers because of the great ionicity of the bond, which is observed in the analogous dimers Ti_2F_{10}, Sn_2F_{10}, Ti_2F_{11}, and Sn_2F_{11} [6]. The signal with a chemical shift of 160 ppm is assigned to the axial F_a and the terminal F_t atoms of fluorine in the complex Al_2F_{11}, which is not resolved in the ^{19}F spectrum because of the small difference in their screening. Because of the strength of the fluorine bridge in the Al_2F_{10} dimer, its signals, which appear in the 169 ppm region, distinguishes the axial (F_a = 158 ppm) and the terminal (F_t = 156 ppm) fluorine atoms. The spin–spin interaction constants for the Al–F and F–F interactions in these complexes do not appear because of the quadrupole relaxation of the aluminum and the reduction in the symmetry of the environment compared to $[AlF_6]^{3-}$.

For a selective suppression in the ^{19}F of the fluorine bridging atoms in the dimers, the lines corresponding to the axial atoms narrow, confirming the correctness of the signal assignments made. This is also confirmed by the nature of the change in the integrated intensity of the signals with changing F/Al ratio, for which an increase from 4 to 5 results in a monotonic decrease in the strength of the signals assigned to the dimer Al_2F_{10}. On salting out such solutions with ethanol, a finely dispersed white crystalline precipitate forms, the elemental chemical analysis of which corresponds to the compound NH_4AlF_4; its crystal structure consists of an infinite series of $[AlF_6]^{-\infty}_{+\infty}$ octahedra linked in two directions at their corners [5]. The uniqueness of the compound obtained is confirmed by x-ray phase analysis.

CONCLUSIONS

1. Using ^{19}F, ^{27}Al, and ^1H NMR methods, all the fluoroaluminate complexes of composition $[AlF_n(H_2O)_{6-n}]^{3-n}$ (n = 0-6) have been shown to form in aqueous—hydrogen-peroxide solutions, and the F/Al ranges in which they exist have been determined.

2. The fluoroaluminates in the solutions form association complexes that exist as a result of the strong H-bonds between the H_2O and F^- ligands coordinated in the different complexes.

3. The association of the fluoroaluminates in H_2O_2 solutions leads to polymerization as a result of the formation of bridging bonds between the fluoroaluminate complexes.

LITERATURE CITED

1. N. A. Matwiyoff and N. E. Wageman, Inorg. Chem., 9, 1031 (1970).
2. Yu. A. Buslaev and S. P. Petrosyants, Koord. Khim., 5, 163 (1979).
3. D. Khass, S. P. Petrosyants, Yu. A. Buslaev, and I. Hartleb, Dokl. Akad. Nauk SSSR, 269, 380 (1983).
4. V. V. Kon'shin, B. N. Chernyshov, and E. G. Ippolitov, Dokl. Akad. Nauk SSSR, 278, 380 (1984).
5. I. Naray-Szabo, Inorganic Crystal Chemistry, Adler, New York.
6. P. A. W. Dean, Can. J. Chem., 51, 4024 (1973).