

Oxygen-17 and Aluminium-27 Nuclear Magnetic Resonance Spectroscopic Investigations of Aluminium(III) Hydrolysis Products

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We report the ^{17}O and ^{27}Al nuclear magnetic resonance (n.m.r.) spectra of the products of aluminium(III) hydrolysis by base. Our results indicate that combined use of solution (chemical shift, linewidth, and spin-lattice relaxation time) and solid-state (static, 'magic-angle' sample spinning, and cross-polarization 'magic-angle' sample spinning) n.m.r. techniques permits determination of nuclear quadrupolar coupling constants (e^2qQ/h , in solution and solid state) for both ^{17}O and ^{27}Al nuclei, and in suitable cases, measurement of rotational correlation times in solution. Cross polarization allows differentiation between AlO_4 and Al-O-H oxygens in solid-state n.m.r. spectra of tridecamer crystals. The ^{17}O e^2qQ/h value for AlO_4 is in good agreement with predictions based on electronegativity considerations. The AlO_4 oxygens in the tridecamer are essentially inert to substitution, while the others are quite labile. The rotational correlation time of the tridecamer in solution at 23 °C is *ca.* 1.3×10^{-10} s.

The hydrolysis of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ has been a subject of interest for more than a century, and very considerable progress in understanding the mechanisms of hydrolysis has been made recently by Akitt *et al.*,¹ using nuclear magnetic resonance (n.m.r.) spectroscopy. We are interested² in supplementing these ^{27}Al studies in solution with ^{17}O n.m.r. studies in solution, as well as ^{27}Al and ^{17}O studies in the solid state, of both the crystalline and amorphous products formed in such hydrolyses. In this article, we discuss recent results in which we have investigated the lability and rotational mobility (correlation times) of the various species involved, as well as determining their ^{27}Al and ^{17}O nuclear quadrupole coupling constants and asymmetry parameters.

Experimental

We monitored the hydrolysis of aluminium(III) by the fast hydrolysis process.¹ An aqueous solution of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ was heated to 90–95 °C, and then a hot aqueous solution of sodium carbonate was added stepwise, with 'vortex' mixing. Such a preparation takes about 15–20 min, and vortex mixing aids in redissolving the white precipitate that appears (due to formation of aluminium hydroxide). On some occasions a permanent white colouration occurred; such samples were discarded.

The crystalline dimer, $[(\text{H}_2\text{O})_4\text{Al}(\text{OH})_2\text{Al}(\text{OH})_2]_2[\text{SO}_4]_2 \cdot 2\text{H}_2\text{O}$, was obtained using the method reported in the literature.³ The ^{17}O -labelled crystalline selenate salt, $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SeO}_4]_4 \cdot 13\text{H}_2\text{O}$, was obtained essentially as described by Johansson,⁴ except that ^{17}O -labelled water was used for the hydrolysis. Solid-state n.m.r. spectra were recorded on 'home-built' n.m.r. spectrometers at magnetic field strengths of 11.7 T, 8.45 T, and 3.52 T, as described elsewhere.⁵ Aluminium-27 and ^{17}O solution spectra were obtained only at 11.7 T. Most of the ^{17}O solution n.m.r. spectra were recorded using a gated solvent-suppression pulse technique, in order to attenuate the large water resonance. The chemical shifts for ^{27}Al are reported with respect to an external standard of $1 \text{ mol dm}^{-3} [\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ in H_2O , and for ^{17}O with respect to an external sample of tap water. Low field, high-frequency, deshielded or paramagnetic shifts are reported as positive values on the δ scale.

Results and Discussion

Our strategy has been to use ^{27}Al solid-state n.m.r. to yield values of the nuclear quadrupole coupling constants for ^{27}Al in well defined crystalline aluminium(III) hydrolysis products, and to use these e^2qQ/h values, together with ^{27}Al T_1 and T_2 values (from linewidths), to obtain correlation time (τ_c) information for the various species, in aqueous solution. The τ_c values are compared with reasonable estimates based on the Stokes-Einstein approach.^{6,7} Once τ_c is known for the hydrolysis product, measurement of the ^{17}O T_1 and T_2 values (from linewidths) yields the ^{17}O e^2qQ/h value, which can then be compared with that for the crystalline solid. Such an approach yields, we believe, useful information on e^2qQ/h values, rotational correlation times in solution, specific assignments, and on chemical exchange processes. Further assignment information is provided by the use of cross polarization with hydrogen, which helps differentiate protonated from non-protonated oxygens in the ' $\text{Al}_{13}\text{O}_{40}$ ' polyanion.

^{27}Al N.M.R. Spectra.—Dimer and tridecamer crystals. The ^{27}Al n.m.r. spectrum of the static dimer consists of a single, featureless, broad resonance. 'Magic-angle' sample spinning (m.a.s.s.) sharpens the peak and enables a measurement of the field-dependent second-order quadrupole-induced shifts from the isotropic value. These shifts are related to the quadrupole coupling constant by equation (1) (see ref. 2 and refs. therein),

$$\delta(\text{p.p.m.}) \approx 6(1 + \eta^2/3)(e^2qQ/h\nu_0)^2 10^3 \quad (1)$$

where ν_0 is the Larmor frequency, e^2qQ/h the nuclear quadrupole coupling constant in Hz, and η is the asymmetry parameter.⁶ The observed chemical shifts of the dimer resonance (spectra not shown) are: 1.5 ± 1 , 0 ± 1 , and -7 ± 4 p.p.m. at 130.3, 93.8, and 39.2 MHz, respectively. A weighted least-squares analysis of these results yields $e^2qQ/h = 1.4 \pm 0.2$ MHz (assuming $\eta = 0$). Such an assumption on η introduces a maximum error of 16% in the e^2qQ/h values.

The ^{27}Al n.m.r. spectra of the tridecamer crystals have recently been published.² The tridecamer sulphate (' $\text{Al}_{13}\text{O}_{40}$ '- SO_4) and the tridecamer selenate (' $\text{Al}_{13}\text{O}_{40}$ '- SeO_4) salts both have e^2qQ/h values for the tetrahedral $[\text{Al}(4)]$ and octahedral

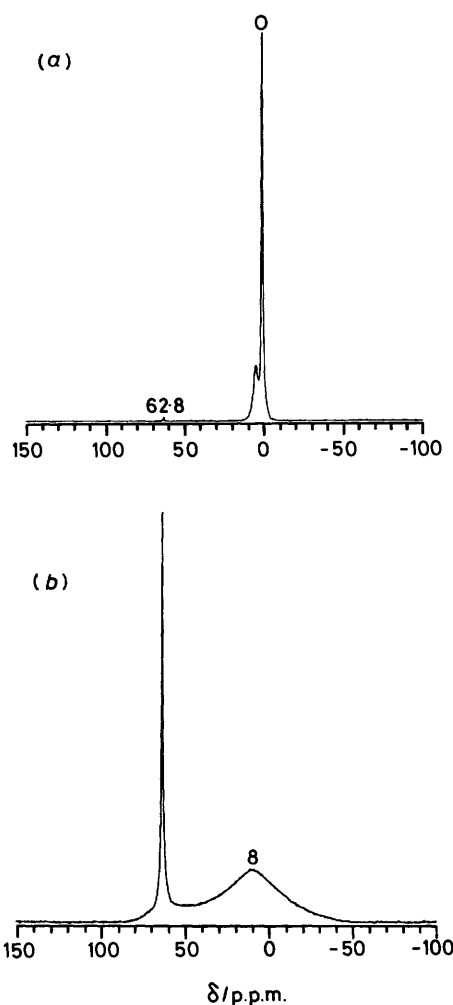


Figure 1. Aluminium-27 solution n.m.r. spectra at 11.7 T (130.3 MHz) and 26 °C of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ hydrolysed by base $\{\delta$ relative to external $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. The degree of hydrolysis is denoted by m (see text); (a) $m = 1.0$, (b) $m = 2.5$

$[\text{Al}(6)]$ co-ordinated aluminium atoms of *ca.* 1 and 10 MHz, respectively. Values of η are close to zero, and are assumed to be zero in the following discussion.

Hydrolysis products. It is customary to denote the ratio $[\text{OH}]/[\text{Al}] = m$ as the degree of hydrolysis. With the fast hydrolysis method, it has been shown from previous ^{27}Al n.m.r. studies¹ that around $m = 1$ solutions contain three species, having the following chemical shifts: monomer, $[\text{Al}(\text{OH}_2)_6]^{3+}$, at 0; dimer, $[(\text{H}_2\text{O})_4\text{Al}(\text{OH})_2\text{Al}(\text{OH}_2)_4]^{4+}$, at 5; and a very small amount of the tridecamer, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{OH}_2)_{12}]^{7+}$, at 62.8 p.p.m. [Figure 1(a)]. The possibility that the line assigned to the dimer is in fact a trimer, $[\text{Al}_3(\text{OH})_4]^{5+}$, is discussed further below. As the hydrolysis proceeds (m increases), more of the monomer is converted into dimer and tridecamer. At around $m = 1.3$, the dimer has its maximum concentration. This decreases as m increases further, and in the vicinity of $m = 2.5$ the only observable species in solution is the tridecamer (polymeric species probably are also present, however).

At room temperature, only the tetrahedral aluminium $[\text{Al}(4)]$ resonance from the tridecamer (' $\text{Al}_{13}\text{O}_{40}$ ') has been previously observed in solution n.m.r. spectra.¹ However, in our hydrolysis experiments with $m \geq 2$, a new broad resonance around 8

p.p.m. can be observed, which most probably arises from the octahedral aluminium atoms $[\text{Al}(6)]$ in the $\text{Al}_{13}\text{O}_{40}$ cluster. At approximately $m = 2.5$, our ^{27}Al n.m.r. spectra show the presence of only the tridecameric species, consisting of a very sharp resonance ($\Delta\nu_{\frac{1}{2}} \approx 15$ Hz) at 62.8 p.p.m., due to the tetrahedral aluminium, and a very broad resonance ($\Delta\nu_{\frac{1}{2}} \approx 4$ kHz) at 8 p.p.m., due to octahedral aluminium [Figure 1(b)]. As has been discussed by earlier workers,¹ such preparations are not particularly reproducible. However, despite certain small differences between preparations, all of our spectra show essentially the same n.m.r. behaviour. Quantitative analysis of the spectrum of Figure 1(b) using a Nicolet curve-fitting routine (NMRCAP), and after accounting for loss of signal due to spin-spin relaxation during the spectrometer 'dead-time,' yields a tetrahedral-to-octahedral ratio of 1:11 (at high temperatures: ~ 86 °C) in close agreement with the theoretical expectation of 1:12.

In solution, e^2qQ/h influences n.m.r. spectra through relaxation processes, and under conditions of rapid, isotropic tumbling, in the extreme narrowing limit, the spin-lattice (T_1) and spin-spin (T_2) relaxation times for ^{27}Al (or any spin $\frac{5}{2}$ nucleus) are given by equation (2),⁷ where τ_c is the rotational

$$1/T_1 = 1/T_2 = (12\pi^2/125)(1 + \eta^2/3)(e^2qQ/h)^2 \tau_c \quad (2)$$

correlation time. Using the fact that T_2 is related to the width at half-height ($\Delta\nu_{\frac{1}{2}}$) by $T_2 = 1/\pi\Delta\nu_{\frac{1}{2}}$, we find the T_2 values for $\text{Al}(4)$ and $\text{Al}(6)$ in the $m = 2.5$ solutions to be 2.0×10^{-2} and 8.0×10^{-5} s, respectively, at 26 °C. Measurements of T_1 on such solutions have also been performed (data not given) and yield a T_1 value of $(1.9 \pm 0.4) \times 10^{-2}$ s for $\text{Al}(4)$, in good agreement with the T_2 value ($T_1 = T_2$). However, for $\text{Al}(6)$, T_1 was too short to be measured accurately. Using the e^2qQ/h value for $\text{Al}(6)$ of 10 MHz, $\eta = 0$ (see ref. 2), and the values of T_1 and T_2 given above we find e^2qQ/h for $\text{Al}(4)$ to be ~ 0.65 MHz and $\tau_c = 1.3 \times 10^{-10}$ s, again from equation (2). The e^2qQ/h value for $\text{Al}(4)$ obtained in this way agrees quite well with those obtained from previous solid-state measurements,² and again supports the assignment of the broad resonance at 8 p.p.m. to $\text{Al}(6)$ in the tridecamer.

Furthermore, an independent estimate of τ_c is also possible from the Stokes-Einstein-Debye equation (3),^{6,7} where η' is the

$$\tau_c = 4\pi\eta' a^3 f / 3kT \quad (3)$$

viscosity of the medium, a is the radius of the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster, k is the Boltzmann constant, T is the absolute temperature, and f is the 'microviscosity coefficient.' The microviscosity coefficient varies as a function of the size of the solute and solvent molecules.⁸ If the radius of the solvent (water) is taken as 1.0 Å then $f = 0.60$. Using $\eta' = 10^{-2}$ poise (10^{-3} Pa s, for water at room temperature), $a = 5.5$ Å (from the X-ray geometry⁴), and $T = 300$ K, we obtain a value of $\tau_c = 1.0 \times 10^{-10}$ s. This is in very good agreement with the value of 1.3×10^{-10} s obtained using equation (2), as described above. Equation (2) is used again later in the discussion to deduce the ^{17}O nuclear quadrupole coupling constant for the AlO_4 oxygens in the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster using the measured $\Delta\nu_{\frac{1}{2}}$ (or T_1) and the τ_c value derived above.

As can be seen in Figure 1(a), the resonance due to the dimer overlaps with that of the monomer, hence linewidths in the $m = 1$ solution were obtained by spectral simulation, a value of $\Delta\nu_{\frac{1}{2}} = 400$ Hz being obtained for the dimer, corresponding to $T_2 = 8 \times 10^{-4}$ s. Using equation (2) and the e^2qQ/h value for ^{27}Al of 1.4 MHz obtained above, gives an apparent value of $\tau_c = (5 \pm 1) \times 10^{-10}$ s (the error here takes into account only the uncertainty in the asymmetry parameter, and does not include the error in e^2qQ/h and $\Delta\nu_{\frac{1}{2}}$). The anomalously large τ_c supports

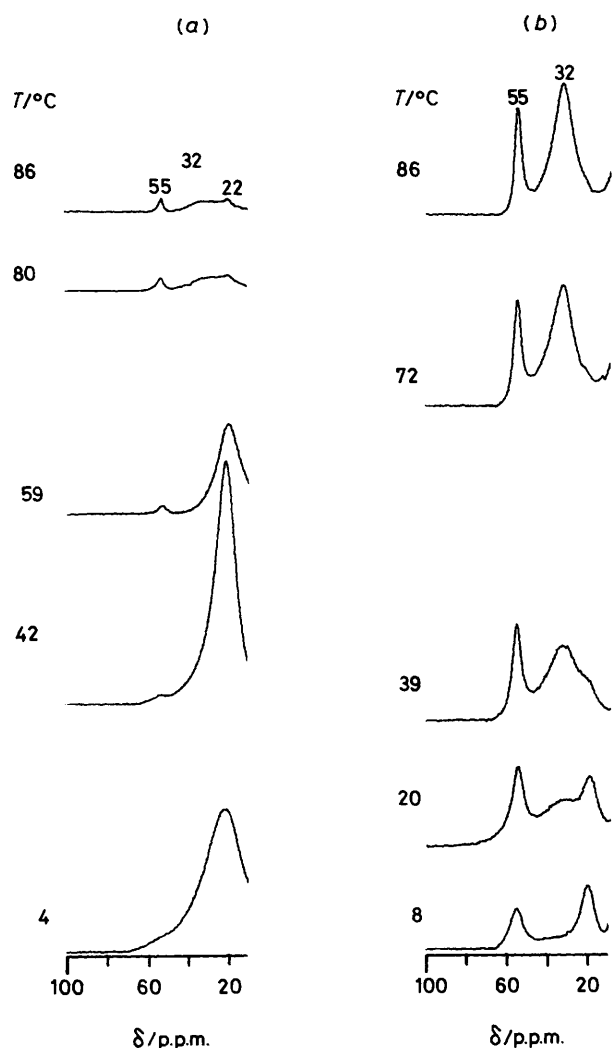


Figure 2. Oxygen-17 solution n.m.r. spectra at 11.7 T (67.8 MHz) of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ hydrolysed by base, in H_2^{17}O , as a function of temperature ($^\circ\text{C}$) (δ relative to external H_2O); (a) $m = 1.0$, (b) $m = 2.5$

the assertion made previously by Akitt *et al.*⁹ that the dimer exchanges with other species, resulting in an exchange-broadened resonance and the inapplicability of such a τ_c determination.

Some of the solutions used above were lyophilized and investigated in the solid state by ^{27}Al n.m.r. The $m = 1$ hydrolysed mixture showed a strong signal from the monomer, which made it difficult to observe the dimer resonance that would otherwise appear close to the monomer resonance, at *ca.* 0 p.p.m. The static n.m.r. spectrum of the $m = 2.5$ lyophilized solid has other resonances in addition to those from the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster. The m.a.s.s. n.m.r. spectrum gave a reasonably sharp resonance due to the Al(4) (but not as narrow as for the crystals) in ' $\text{Al}_{13}\text{O}_{40}$ ' at 63 p.p.m., a broad resonance of width *ca.* 20 kHz (at $\nu_0 = 130.3$ MHz) from Al(6) in ' $\text{Al}_{13}\text{O}_{40}$ ', and another broad resonance at *ca.* 0 p.p.m. which did not sharpen appreciably. This additional resonance most probably arises from the polymeric species which do not give observable ^{27}Al resonances in solution.¹ When the lyophilized material was redissolved in water, the ^{27}Al n.m.r. spectrum was the same as that obtained from the original solution.

It has been observed that high-temperature ageing of these solutions results in the production of species that yield broad

n.m.r. resonances in solution.¹ When $m = 2.5$ hydrolysed solids were heated at 100°C for various periods of time, the peak (due to polymeric species) at 0 p.p.m. grew in size, and the solutions obtained from redissolving the heated material in water gave additional resonances in the vicinity of 10 p.p.m. The structures of the species formed during the ageing process are unknown.

^{17}O N.M.R. Spectra.—The ^{17}O n.m.r. spectra of $m = 1$ and $m = 2.5$ hydrolysed solutions were investigated as a function of temperature. These solutions gave a very large signal from solvent water, which we attenuated significantly by using a gated solvent-suppression pulse technique. The $m = 1$ hydrolysed solution, which is composed of monomer, dimer, and a small amount of tridecamer, yields only two other ^{17}O resonances below $\sim 50^\circ\text{C}$ [Figure 2(a)]: a weak one at 55 p.p.m. and a broader, more prominent one at 22 p.p.m. These results suggest that water molecules (with ^{17}O) co-ordinated to the monomer, dimer, and tridecamer are in fast exchange with free water, and do not show up as separate, well defined peaks. Such a conclusion was made in regard to the bound water protons in ^1H n.m.r. studies of ' AlCl_3 ' in aqueous solutions.¹⁰ The resonance at 22 p.p.m. in the $m = 1$ hydrolysed solution is *very tentatively* assigned to the hydroxyl oxygens of the dimer (the most abundant species present, since water co-ordinated to the monomer and dimer are not distinguishable from the solvent water resonance due to the postulated fast chemical exchange), while the 55 p.p.m. peak (more prominent in the $m = 2.5$ hydrolysed solution) is tentatively assigned to the 'tetrahedral' oxygen, O(4), of the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster (this assignment is supported by water-exchange studies, as discussed below).

The $m = 2.5$ hydrolysed solutions have only the tridecamer species that yields an observable ^{27}Al n.m.r. spectrum, while at room temperature (20°C) the ^{17}O n.m.r. spectrum yields three resonances [Figure 2(b)]; two relatively sharp ones ($\Delta\nu_{\frac{1}{2}} \approx 400$ Hz) at 55 and 20 p.p.m. and a third fairly broad one at *ca.* 32 p.p.m. The 20 and *ca.* 32 p.p.m. peaks in the $m = 2.5$ hydrolysed solution are tentatively assigned to OH groups in the tridecamer. The behaviour of the spectra as a function of temperature is shown in Figure 2. When the temperature of the $m = 2.5$ hydrolysed solution is increased, the 20 p.p.m. peak broadens (most probably due to an increased rate of OH exchange with water), and the 55 and 32 p.p.m. peaks narrow, due to reduced correlation times [resulting from reduced viscosity and increased temperature in equation (3)]. At the highest temperature examined (86°C), the $m = 2.5$ solution has only two resonances (apart from the partially saturated H_2^{17}O signal at 2 p.p.m.): one at 55 and another at *ca.* 32 p.p.m. (the 20 p.p.m. peak has now broadened beyond detection). A very similar trend is seen in the $m = 1$ hydrolysed solution spectra, shown as a function of temperature in Figure 2(a). The *ca.* 22 p.p.m. peak from the dimer decreases in intensity, and the 55 p.p.m. peak narrows, upon increasing temperature. In addition, a new peak at *ca.* 32 p.p.m. (arising from the tridecamer) begins to appear at *ca.* 80°C . From the similarity of their chemical shifts, and the behaviour of the dimer hydroxyl resonance at 22 p.p.m. and of the tridecamer at 20 p.p.m. upon heating, we suggest that the latter is from the hydroxyl groups in the tridecamer which are co-ordinated as in the dimer (*i.e.* two hydroxyl groups are shared by the same two octahedra, as in $\text{Al} \langle \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \rangle \text{Al}$). If this view is correct, then the resonance at 32 p.p.m. may arise from the hydroxyl oxygens in the tridecamer which are shared by two different octahedra ($\text{Al} \langle \begin{smallmatrix} \text{OH}-\text{Al} \\ \text{OH}-\text{Al} \end{smallmatrix} \rangle \text{OH}$).

At room temperature, the central AlO_4 oxygen resonance in the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster has a T_1 value of 1.8×10^{-3} s in the $m = 2.5$ hydrolysed solution (data not given). Using equation (2)

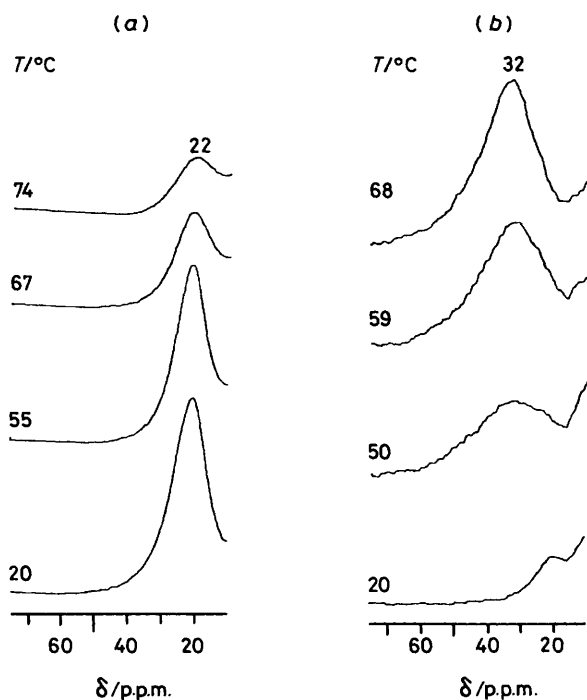


Figure 3. Oxygen-17 solution n.m.r. spectra at 11.7 T (67.8 MHz) of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ hydrolysed by base, lyophilized, then reconstituted in H_2^{17}O , as a function of temperature ($^\circ\text{C}$) (δ relative to external H_2O); (a) $m = 1.0$, (b) $m = 2.5$

and $\tau_c = 1.3 \times 10^{-10}$ s derived from the ^{27}Al n.m.r. data, we obtain an e^2qQ/h value between 2.2 and 1.8 MHz, depending upon the variation of η from 0 to 1, respectively. However, for the OH oxygens, because of exchange with water, it is very difficult to derive any quadrupole coupling constant information.

We have also performed experiments which involve ^{17}O exchange between water and the hydrolysis products. Solutions hydrolysed to $m = 1$ and $m = 2.5$ were made with unenriched water (H_2^{16}O), then lyophilized, and the solids redissolved in ^{17}O -labelled water. This procedure, as well as permitting investigation of chemical-exchange processes, provides more concentrated solutions, which increases the quality of the spectra by reducing the relative intensity of the solvent resonance. The $m = 2.5$ hydrolysed solution [Figure 3(b)] yields only a single resonance at room temperature, at ca. 20 p.p.m. The resonance due to the AlO_4 oxygens, at 55 p.p.m., is not observed. Upon increasing the sample temperature, the resonance at 20 p.p.m. 'disappears' while a new peak, at 32 p.p.m., starts to appear. Above ca. 50°C the 20 p.p.m. peak has disappeared, and the resonance at 32 p.p.m. continues to narrow. These observations suggest that the OH groups in ' $\text{Al}_{13}\text{O}_{40}$ ' clusters readily exchange with water, but the AlO_4 oxygens do not. Results on an $m = 1$ hydrolysed solution [Figure 3(a)] imply the presence of dimer OH oxygens, at 22 p.p.m., which broaden as the temperature is raised, presumably due to exchange with bulk water.

As a corollary to these experiments, we have labelled oxygens which do not readily exchange with solvent water. Thus, a sample was first hydrolysed to $m = 2.5$ with oxygen-17 enriched water, to make a uniformly labelled ' $\text{Al}_{13}^{17}\text{O}_{40}$ ' species. The solution was then lyophilized, and back exchanged with water depleted in oxygen-17, three times. The solvent resonance is now comparable in intensity to that of the ' $\text{Al}_{13}\text{O}_{40}$ ' resonances (Figure 4), and there are no other features near the solvent water peak. Notably, the feature at 55 p.p.m. is now quite intense, due

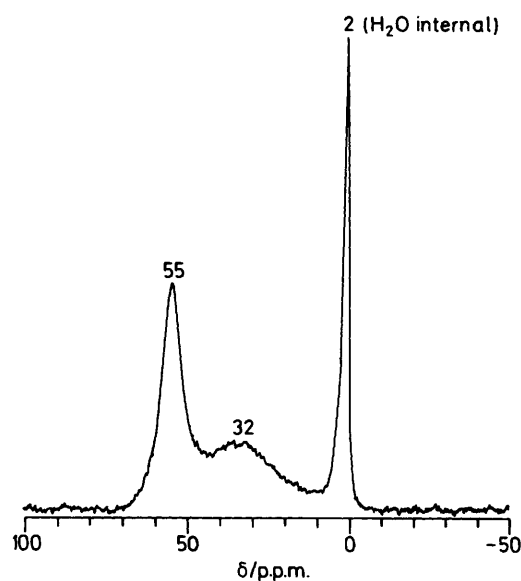


Figure 4. Oxygen-17 solution n.m.r. spectrum at 11.7 T (67.8 MHz) of $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ hydrolysed by base in H_2^{17}O , then lyophilized, and back exchanged three times with H_2^{16}O (δ relative to external H_2O)

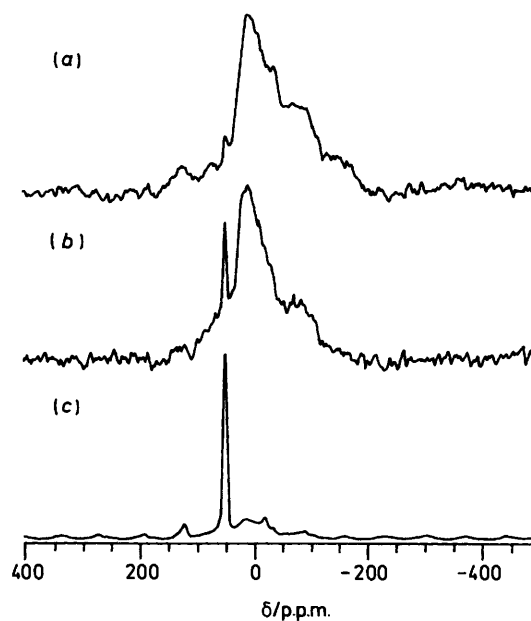


Figure 5. Oxygen-17 solid-state n.m.r. spectra at 11.7 T (67.8 MHz) of $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SeO}_4]_4 \cdot 13\text{H}_2\text{O}$, preferentially labelled in ^{17}O at the AlO_4 sites (δ relative to external H_2O). All spectra were recorded using the same number of accumulations; (a) c.p. m.a.s.s. with 15- μs mix-time, (b) c.p. m.a.s.s. with 1-ms mix-time, (c) m.a.s.s. only

to the inertness of the central AlO_4 sub-unit to oxygen exchange.

While these results all tend to confirm our ideas about chemical exchange, and spectral assignments, they are not particularly good proof for such assignments. In particular, strong evidence for the presence of AlO_4 or OH groups is lacking. We have thus turned to solid-state n.m.r. methods, which in suitable cases may be capable of giving such evidence.

Solid-state ^{17}O m.a.s.s. n.m.r. spectra were first recorded on an $m = 2.5$ lyophilized powder (AlO_4 enriched). The width of the resonance at 55 p.p.m. was compatible with the e^2qQ/h value

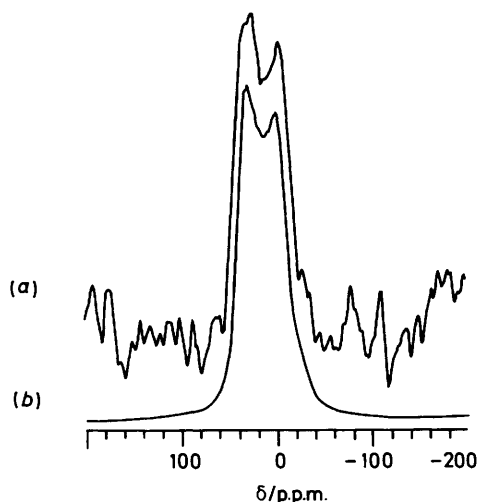


Figure 6. (a) Oxygen-17 solid-state m.a.s.s. n.m.r. spectrum at 3.52 T (20.8 MHz) of $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SeO}_4]_4 \cdot 13\text{H}_2\text{O}$ preferentially labelled with ^{17}O at the AlO_4 sites, together with (b) its computer simulation; $e^2qQ/h = 1.2$ MHz, $\eta = 0$, $\delta_i = 50$ p.p.m.

determined from solution n.m.r., but no well resolved second-order quadrupole splitting was observed. This lack of structure is analogous to the observations of broader resonances for ^{27}Al n.m.r. when lyophilized, rather than crystalline, materials are employed. We have thus prepared a crystalline ^{17}O -labelled sample, as described below.

Taking advantage of the fact that there is no fast exchange between the AlO_4 sites and all of the other oxygens, we prepared $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}][\text{SeO}_4]_4 \cdot 13\text{H}_2\text{O}$ crystals, preferentially labelled at the AlO_4 site. An aluminium(III)-containing solution was hydrolysed with oxygen-17 enriched water to $m = 2.5$, then diluted with natural abundance water, before addition of Na_2SeO_4 . Tetrahedral crystals were harvested after approximately 1 week. These crystals provided high quality spectra at all three magnetic field strengths employed (the spectrum at 3.52 T was obtained by employing a spin-echo sequence¹¹ to remove acoustic ringing).

All of the oxygens in the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster have directly bonded protons, except for the central AlO_4 sub-unit. We thus recorded cross-polarization (c.p.) 'magic-angle' sample-spinning n.m.r. spectra of the preferentially ^{17}O -labelled crystals, as shown in Figure 5(a) and (b). With a c.p. mix-time of 15 μs , an intense feature at ca. 0 p.p.m. is observed, due to OH oxygens (and some water molecules). On increasing the mix-time to 1 ms [Figure 5(b)] a sharp feature at ca. 50 p.p.m. becomes apparent. The observable magnetization reaches a maximum at ca. 50 μs for the OH groups (with directly bonded protons), but at ca. 1 ms for the AlO_4 oxygens (with only longer range dipolar interactions) as noted elsewhere for a series of related model compounds.¹² This strongly supports assignment of the feature at ca. 50 p.p.m. to AlO_4 oxygens. Further support for our assignments comes from simple m.a.s.s. experiments on the same crystals. As shown in Figure 5(c), under m.a.s.s. conditions only the AlO_4 oxygens, with no directly bonded hydrogens, are readily observable, the other 93% of the oxygen sites being barely noticeable without c.p., which compensates for their lower isotopic enrichment (due to back exchange with $^1\text{H}_2^{16}\text{O}$). Thus, the assignment of the feature at 50 p.p.m. to the central AlO_4 oxygens is confirmed.

Figure 6 shows the low field (3.52 T) n.m.r. spectrum of the ^{17}O -labelled ' $\text{Al}_{13}\text{O}_{40}$ ' selenate crystals, together with its spectral simulation. The spectrum is well simulated using $e^2qQ/h = 1.2$ MHz and $\eta = 0 \pm 0.1$, in moderate agreement

with the value of 2.0 ± 0.2 MHz obtained from the solution n.m.r. data, as described above. We also note that the e^2qQ/h values obtained for the AlO_4 oxygens, in the range $(1.2-2.0) \pm 0.2$ MHz, are in good accord with the expectation based on the electronegativity predictions of Schramm and Oldfield:¹³ Al-O-Al, 2.0; Al-O-H, 4.5 MHz.

Finally, we address the question raised by a referee that the species we and others^{1,14} have attributed to a dimer does in fact originate from the trimer, $[\text{Al}_3(\text{OH})_4]^{5+}$ (see, for example, refs. 15 and 16). While this cannot absolutely be ruled out by the results we have presented, the linear trimer $[(\text{H}_2\text{O})_4\text{Al}(\mu\text{-OH})_2\text{Al}(\text{H}_2\text{O})_2(\mu\text{-OH})_2\text{Al}(\text{H}_2\text{O})_4]^{5+}$ clearly has two chemically non-equivalent aluminium atoms, one central and two terminal. Since only one ^{27}Al peak is observed in our n.m.r. experiments, at all temperatures and compositions in question, the simplest conclusion is that there is in fact only one type of Al, as in the dimer. Similar arguments apply to our analyses of the ^{17}O n.m.r. results.

Conclusions

The results given here are the first determination of the rotational correlation time of the aluminium tridecamer produced by the base-catalysed hydrolysis of aluminium(III) ions in aqueous solution. This was made possible by combined use of solid-state e^2qQ/h determinations, and solution T_1 and T_2 (linewidth) measurements. The τ_c value obtained is in good agreement with estimates based on the Stokes-Einstein formula. Using the τ_c value determined for the cluster, and the experimental ^{17}O T_1 and T_2 values for an ^{17}O -labelled tridecamer, we have also been able to obtain the e^2qQ/h value for the central (AlO_4) oxygens in the cluster. The result obtained is in reasonable agreement with that obtained by spectral simulation of the low-field solid-state ^{17}O n.m.r. spectrum of a polycrystalline tridecamer selenate, and is close to the value expected based on the empirical approach described previously.¹³ The isotope labelling possible with ^{17}O n.m.r. suggests that the ' $\text{Al}_{13}\text{O}_{40}$ ' cluster, once formed, does not readily exchange the AlO_4 oxygens with any other oxygens in the solution. We have confirmed assignment of the ^{17}O n.m.r. spectrum of the tridecamer by using cross-polarization with protons: the AlO_4 oxygens cross-polarize much more slowly than do the AlOH oxygens. Taken together, we believe that combined use of solid-state static, m.a.s.s. and c.p. m.a.s.s., and liquid-state T_1 and T_2 (linewidth) measurements, offers promise for characterizing the products of aluminium(III) hydrolysis. Application of such a combination of spectroscopic techniques should be of general use in studies of various complex oxo anions, both in solution and in the crystalline (or non-crystalline) solid state, including determination of protonation sites in polyoxoanions.

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