^{27}Al Nuclear Magnetic Resonance Studies of the Hydrolysis and Polymerisation of the Hexa-aquo-aluminium(III) Cation

By **J. W. Akitt, N. N. Greenwood,*† B. L. Khandelwal,** and **G. D. Lester,** Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

The hydrolysis of aluminium salt solutions has been studied using ^{27}Al and ^{1}H n.m.r. and this has led to reliable values for the concentrations of the species of $Al(H_2O)_6^{3+}$, $Al_2(OH)_2(H_2O)_8^{4+}$, and $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ at different degrees of hydrolysis. These ions do not account for all the aluminium in solution and another species, probably $Al_8(OH)_{20}(H_2O)_x^{4+}$ is thought to be present. It is shown that previous controversy over the constitution of these solutions arose because of the different methods used for preparing the solutions: only the first two species exist when hydrated aluminium(III) chloride is dissolved in water whereas the highly polymeric species appear only after considerable hydrolysis has occurred at higher pH. The cations, particularly the dimer, may also be more hydrolysed than the above formulae indicate and this has probably confused the previous interpretation of the potentiometric results.

THE hydrolysis of aluminium salts has been extensively studied for over a century using numerous techniques and the literature contains many conflicting views of the nature of the cationic species produced by hydrolysis. Our preliminary results [1,2] have shown that the ^{27}Al n.m.r. is sensitive to the degree of hydrolysis in these solutions and, in particular, that it is possible to measure unequivocally the quantity of unhydrolysed $Al(H_2O)_6^{3+}$ present, a figure which it had never previously been possible to obtain. We can thus test the many models postulated for these solutions by comparing calculated and measured concentrations of $Al(H_2O)_6^{3+}$. In addition, there is the promise that we might detect some of the other cationic species present [2] and so resolve the long standing controversy regarding the size of the ionic clusters formed during hydrolysis.

EXPERIMENTAL

Solutions of hydrolysed aluminium salts have been prepared in various ways by previous workers. Evidence presented later in this paper indicates that such variations may well affect the nature of the equilibria being studied and accordingly we give here in some detail the apparently trivial methods used in the present work.

(*a*) AnalaR aluminium wire was refluxed in three mole equivalents of concentrated hydrochloric acid. Copious acid fumes were evolved initially and further acid was removed by boiling for periods up to 24 h. Solutions containing a ratio of only 2·2 atoms of chloride per atom of aluminium could be prepared in this way. Solutions of varying degrees of hydrolysis were made by adding hydrochloric acid to aliquots of the stock solution at room temperature. The chlorine and aluminium concentrations of the stock solution of $AlCl_{2\cdot 2}$ were determined gravimetrically and by standard titration techniques. An alternative and more rapid method is to distil the hydrogen chloride and water from the solutions whilst simultaneously replacing the lost liquid with a continual feed of pure water. It was noted that nitric acid could also be removed in this way from aluminium nitrate solutions and that a stream of nitrogen will purge hydrogen chloride from a warmed solution.[3] These techniques are based on work by Ordway.[4]

(*b*) The salt $AlCl_3,6H_2O$ has recently become commercially available. Sodium hydroxide solution (1·0M) was added to aqueous solutions of the salt and the initial precipitate was dissolved near the boiling point. The solutions were aged at *ca.* 90° prior to making measurements and the solution volume was kept approximately constant during the ageing process by addition of water. Provided that the concentration of aluminium was kept below 0·3M,

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† *Present address:* Department of Inorganic and Structural Chemistry, University Leeds, LS2 9JT.

[1] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *J. Chem. Soc.* (*A*), 1969, 803.

[2] J. W. Akitt, N. N. Greenwood, and G. D. Lester, *Chem. Comm.*, 1969, 988.

[3] J. W. Akitt, N. N. Greenwood, and B. L. Khandelwal, *Spect. Letters*, 1971, **4**, 139.

[4] J. Ordway, *Amer. J. Sci.*, 1858, **26**, 203.

clear solutions could be prepared containing up to 2·4 mol of sodium hydroxide per mol of aluminium.[5] At higher concentrations of aluminium a precipitate was obtained which dissolved on heating and re-precipitated on cooling.

(*c*) Solid sodium carbonate was added to aluminium nitrate solution, the precipitate dissolved near the boiling point, and the solution was then aged for 1 h. The majority of the carbonate is lost as carbon dioxide during this process. Solutions 0·75M in aluminium were prepared with up to 2·5 mol of hydroxide per mol of aluminium, though even higher concentrations can be reached.[6] Solutions could also be prepared in this manner using aluminium chloride.

(*d*) A few solutions were also prepared by dissolving freshly precipitated aluminium hydroxide in $AlCl_3,6H_2O$ solution to give a stock solution of having a solute stoicheiometry of $AlCl_{2\cdot 2}$. Varying degrees of hydrolysis were obtained by adding concentrated hydrochloric acid to aliquots of the stock solution at room temperature.

N.m.r. spectra were obtained at 90 MHz for protons and at 23·45 MHz for ^{27}Al, using a Bruker spectrometer equipped with a variable-temperature probe. The spectrometer was operated in the frequency-sweep mode though it was not found necessary to use the proton lock facility since the field drift could be kept below 4 Hz h^{-1} which is negligible relative to the broad lines observed. The gain and attenuation controls were carefully calibrated. Since we were interested in quantitative data, extreme care was taken to avoid saturation. Spectra were recorded at several power levels and the filter setting was adjusted to a short time constant to avoid distortion of the lines. Both precautions are particularly important where lines of very different widths are being compared. Unfortunately both these precautions resulted in spectra of poor appearance and the rather large signal-to-noise ratio limited the precision of a single area determination of an ^{27}Al line to *ca.* 5%. The spectra shown in the Figures were obtained at higher power levels; these accurately reproduce the qualitative features of the spectra but cannot be used for quantitative area determinations.

Line areas were determined by (i) weighing cut outs, (ii) using a DuPont 310 Curve Analyser or (iii) collecting several spectral traces sequentially in a CAT (Fabritek 1074) and then integrating. The first two techniques were limited to determining the variations in concentration of monomeric $Al(H_2O)_6^{3+}$ since the broad line due to the polymeric species [2] was lost in the baseline noise. With the CAT however it was possible to observe this line in the integrals of the more concentrated solutions so that a value for the concentration of monomer plus polymer could also be obtained. Unfortunately this was not possible in the 0·2M solutions prepared from aluminium chloride by method (*b*); this may reflect either the inherent insensitivity of the method or the small concentrations of dimer in this particular range of solutions.

The proton resonance data are more accurate (*ca.* ±2%) because of the stronger signal available. A single sample tube was used for a given series of determinations (5 mm diameter for proton and 10 mm diameter for aluminium) to avoid possible errors due to differences in tube diameters.

The pH was determined using either an E.I.L. model 23A or a Radiometer model 2306 pH meter, both instruments being standardised with a sodium acetate buffer at pH 4·0 before use. Some difficulty was experienced with these measurements due, apparently, to a reaction involving the glass of the electrode and the concentrated aluminium salt solutions which led to some irreproducibility in the readings. This effect has not yet been resolved but it is possible to avoid it by using the Radiometer 202c electrode. The pH measurements probably constitute the main source of error in Figure 7. A set of results obtained at 2·44 mol l^{-1} of Al gave a strongly anomalous plot.

RESULTS

Measurements of monomer ion concentration and, where possible, of monomer plus polymer, were made using the ^{27}Al resonance for solutions of all degrees of hydrolysis and for solutions containing an excess of acid. It was found that in the latter case the line intensity was constant and that all the aluminium was being observed as $Al(H_2O)_6^{3+}$ monomer. The concentrations of monomer and of monomer plus polymer were then expressed as a proportion of this maximum peak area. These results are summarised in Figure 1. The open circles represent solutions prepared by methods (*a*) and (*d*) where [Al] = 3·0, 1·36, 1·33, 1·21, or 0·5M. The × signs represent solutions prepared by method (*b*) [Al] = 0·2M, and closed circles those prepared by method (*c*) [Al] = 0·75M. In addition to the sharp monomer and broad polymer lines previously reported a third sharp line was observed in the most highly hydrolysed solutions well downfield at −62·5 p.p.m. from the resonance due to $Al(H_2O)_6^{3+}$. The area of this line is also plotted in Figure 1 and labelled as Al_{13} species. A range of spectra and their integrals are shown in Figures 2—4.

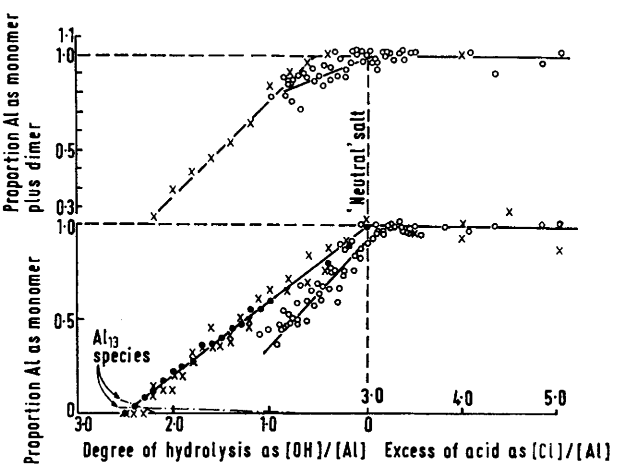

FIGURE 1 Proportion of aluminium in the various ^{27}Al resonances as a function of the degree of hydrolysis. The open circles refer to solutions prepared by methods (*a*) and (*d*), closed circles to method (*b*), and crosses to method (*c*). The dashed lines at high degrees of hydrolysis indicate the data for the low field line; experimental points are omitted for clarity. The concentrations of aluminium used range from 3·0 to 0·2M

The results in Figure 1 fall into two groups, depending on the method of preparing the solution. Solutions prepared by method (*a*) or (*d*) exhibit lower monomer concentrations than those prepared by method (*b*) or (*c*). The method of preparation is thus significant in the hydrolysis

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[5] G. Johansson, G. Lundgren, L. G. Sillén, and R. Soderquist, *Acta Chem. Scand.*, 1960, **14**, 769, 771.

[6] W. V. Rausch and H. D. Bale, *J. Chem. Phys.*, 1964, **40**, 3391.

reaction. Further, the scatter of results is larger in the former group; it exceeds the accuracy of the determination and may also reflect a preparative effect.

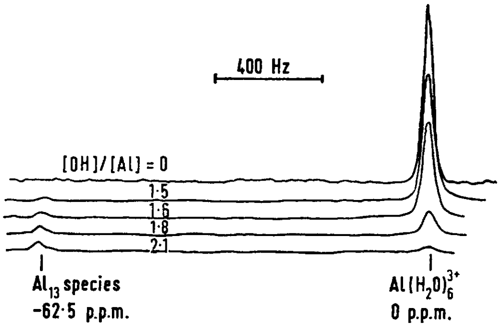

FIGURE 2 ^{27}Al Spectra at 23·45 MHz of 0·2M aluminium solutions at various degrees of hydrolysis

The point at which the new low-field peak first appeared during hydrolysis was also studied qualitatively. If *ca.* 2·3 mol of hydroxide is added per mol of aluminium then a solid is immediately precipitated and the resonance due to $\mathrm{Al(H_2O)_6}^{3+}$ is much diminished. No low-field peak is visible and this only appears if the solution is heated so as to dissolve the precipitate. This procedure however has little further effect on the $\mathrm{Al(H_2O)_6}^{3+}$ resonance. Addition of acid to this solution results in a rapid reaction and after *ca.* 1 min only the $\mathrm{Al(H_2O)_6}^{3+}$ resonance can be observed.

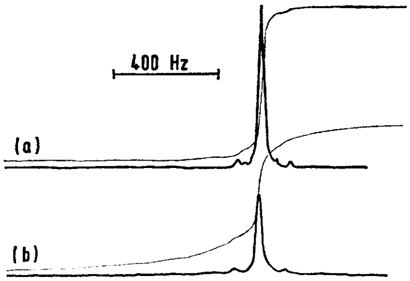

FIGURE 3 ^{27}Al Spectra (23·45 MHz) and integrals of 1·33M aluminium chloride solutions (a) non-hydrolysed and (b) hydrolysed. The presence of the dimer peak can be seen clearly in the integral of (b). The small peaks are spinning side bands

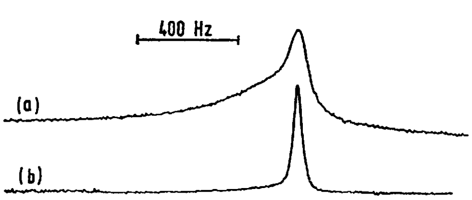

FIGURE 4 The ^{27}Al spectra (23·45 MHz) of a highly hydrolysed aluminium salt solution at different power levels and same gain (a) 10 dB, (b) 30 dB showing differential saturation of the two lines

The fact that a line due to a polymeric species can be seen just to low-field of the $\mathrm{Al(H_2O)_6}^{3+}$ resonance indicates that the two species, if exchanging, are only exchanging slowly. If a partly hydrolysed solution is heated the rate of exchange is increased and the narrow $\mathrm{Al(H_2O)_6}^{3+}$ resonance broadens and decreases in intensity.[1] The point of full spectral collapse is not reached by 100° and one can estimate that the lifetime of the aluminium in the two environments is *ca.* 6 ms at that temperature.

Recent work [7-9] has shown that concentrated aqueous aluminium chloride solutions can be cooled to temperatures as low as $-60°$ at which temperature proton exchange on the monomer $\mathrm{Al(H_2O)_6}^{3+}$ ion is slowed sufficiently for separate proton resonances to be seen for the bulk water and for complexed water. We have made similar measurements on cooled solutions in the hope that it would prove possible to observe the protons co-ordinated to polymeric species. These solutions prepared by method (*a*), had a constant total concentration of aluminium but varying degrees of hydrolysis. However only two resonances were observed, namely those assigned to bulk water and to water in $\mathrm{Al(H_2O)_6}^{3+}$; the intensity of the latter resonance decreased as the degree of hydrolysis was increased while that of the bulk water increased correspondingly (Figure 5). We conclude that the polymer protons are exchanging rapidly with the bulk water and that their signal is included in the bulk water line. This result agrees with recent pulse echo measurements in such solutions which indicate the presence of a very fast proton exchange mechanism.[10] It is possible, knowing the monomer concentration, the total water content, and the proportion of water bound to the aquo-ion, to calculate the hydration number of monomer throughout the range of compositions studied. The results are shown graphically in Figure 6, which demonstrates that the ion maintains a constant hydration number in the presence of the hydrolysis products. The slope of the line gives the hydration number as 6·01 ± 0·05 with correlation coefficient of 0·999.

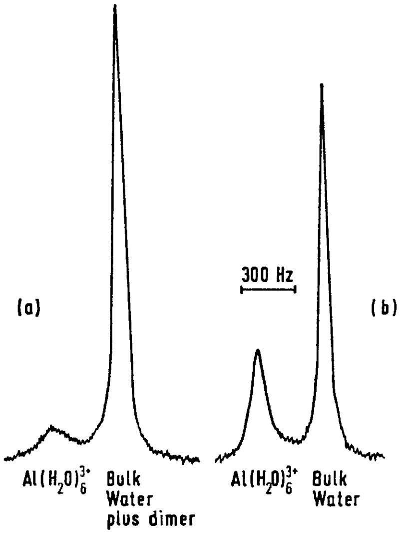

FIGURE 5 The ^{1}H spectra (90 MHz) of cooled 3M-$\mathrm{AlCl_3}$ (a) hydrolysed, (b) non-hydrolysed

It was also noticed that the temperature at which the two proton signals coalesced varied throughout the range

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[7] A. Fratiello, R. E. Lee, V. M. Nishida, and R. E. Schuster, *J. Chem. Phys.*, 1968, **48**, 3705.

[8] N. A. Matwiyoff, P. E. Darley, and W. S. Movius, *Inorg. Chem.*, 1968, **7**, 2173.

[9] A. Takahashi, *J. Phys. Soc. Japan*, 1970, **28**, 207.

[10] Dodd-Wing Fong and E. Grunwald, *J. Amer. Chem. Soc.*, 1969, **91**, 2413.

and was at its highest in the least hydrolysed solutions where coalescence occurred at −8° compared with −39° when 70% of the aluminium monomer was polymerised. The coalescence temperature can also be increased by adding an inert salt such as calcium nitrate.[11] The reduction in exchange rate which is indicated thus appears to be related to the bulk water concentration, which is reduced both by the addition of a salt and by the formation of $Al(H_2O)_6^{3+}$, though increases in viscosity which occur as acid or salt is added must also play some part.

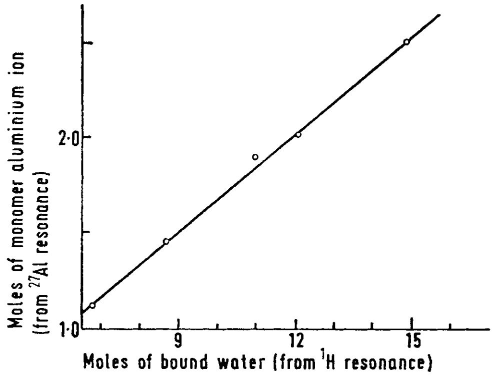

FIGURE 6 The relation between moles of bound water calculated from ^{1}H spectra and moles of monomer ion as calculated from ^{27}Al spectra at different degrees of hydrolysis

DISCUSSION

The majority of studies of the hydrolysis of aluminium salts has been made by potentiometric techniques. The work can be classified into two groups depending upon the way the solutions were prepared for measurement and, not surprisingly, two conflicting interpretations have arisen.

On the one hand [12–20] it has been noted that as alkali is added to a dilute aluminium salt solution there is only a slow change in pH until 2·5 mol of alkali have been added per mol of aluminium. Equilibrium is attained slowly in these solutions and ageing must be allowed to take place before meaningful pH values can be obtained. This behaviour has been interpreted as indicating the formation of the ions $Al_n(OH)_{2\cdot5n}{}^{+0\cdot5n}$ where n can have numerous (mostly even) values from 2—13, higher values being preferred. This view has received considerable support from X-ray crystallographic analysis of the crystals obtained from highly hydrolysed solutions which have been shown to contain the polymeric cation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. The ion is built up of twelve AlO_6 octahedra with shared edges and apices arranged regularly around an AlO_4 tetrahedron.[5] X-Ray data obtained in solution indicate that this ion exists in solution also.[6] Indeed in some of this literature the presence of significant quantities of monomer and dimer hydrolysed ions was specifically discounted.

On the other hand experiments in which the effect of adding acid [21,22] or of progressive dilution of the pure salt solution [23–28] is measured led to the conclusion that the monomer hydrolysate $[Al(OH)(H_2O)_5{}^{2+}]$ is the only species formed [27–30] or that this and the dimer are the only species present.[22,25,26,31,32] This apparent paradox is resolved by Figure 1 which shows that, provided the broad ^{27}Al line is due to a dimer ion, then both conclusions are in fact correct within the appropriate regions studied, with the caveat that the monomer $Al(H_2O)_6{}^{3+}$ and its hydrolysate are definitely still present at high degrees of hydrolysis.

Because of the apparent controversy over the nature of the hydrolysis, these solutions have been studied by numerous other techniques. Freezing-point depression measurements made as alkali is added suggest that high molecular weight species do not form until 2·5 mol of alkali have been added.[33,34] Extraction experiments using 8-hydroxyquinoline have detected $Al(H_2O)_6{}^{3+}$, $Al(OH)(H_2O)_5{}^{2+}$, and a polynuclear species of unknown complexity.[35] Centrifugation experiments show that the degree of polymerisation increases as alkali is added, from 1 to *ca.* 11 and in conjunction with potentiometric measurements it has been shown that this is consistent with the presence of monomer, dimer, and the Al_{13} species.[36] Electrophoretic results suggest that in the region in question the charge of the species is between 1·6 and 0·9, a conclusion which presumably reflects the existence of polymeric species.[37] Coagulation studies have also given information about hydrolysis, the active component of aluminium solutions for coagulation of silver iodide sols apparently being a hydrolysed cation

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[11] J. F. Stephens and G. K. Schweitzer, *Spect. Letters*, 1968, **1**, 373.

[12] C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.*, 1954, **8**, 1917.

[13] W. D. Treadwell and J. E. Boner, *Helv. Chim. Acta*, 1934, **17**, 774.

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[15] L. K. Lepin and A. Ya. Vaivade, *Zhur. fiz. Khim.*, 1953, **27**, 217.

[16] C. Brosset, *Acta Chem. Scand.*, 1952, **6**, 910.

[17] S. Lacroix, *Ann. Chim.*, 1949, **4**, 5.

[18] H. W. Kohlschutter, P. Hautelmann, K. Diener, and H. Schilling, *Z. anorg. Chem.*, 1941, **248**, 319.

[19] J. K. Ruff and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 1523.

[20] L. G. Sillén, *Quart. Rev.*, 1959, **13**, 146.

[21] W. D. Treadwell and O. T. Lien, *Helv. Chim. Acta*, 1931, **14**, 473.

[22] E. Grunwald and Dodd-Wing Fong, *J. Phys. Chem.*, 1969, **73**, 650.

[23] J. G. Denham, *J. Chem. Soc.*, 1908, 93.

[24] E. Corriere and P. Faure, *Bull. Soc. chim. France*, 1942, 809.

[25] J. Faucherre, *Bull. Soc. chim. France*, 1954, 253.

[26] J. Faucherre, *Compt. rend.*, 1948, **227**, 1367.

[27] R. K. Schofield and A. W. Taylor, *J. Chem. Soc.*, 1954, 4445.

[28] C. R. Frink and M. Peech, *Inorg. Chem.*, 1963, **2**, 473.

[29] J. H. Sullivan and J. E. Singley, *J. Amer. Water Assoc.*, 1968, **60**, 1280.

[30] L. P. Holmes, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 1968, **72**, 301.

[31] J. Kenttamaa, *Ann. Acad. Sci. Fennicae*, 1955, *A***2**, 67.

[32] H. Kubota, Ph.D. Thesis, University of Wisconsin, 1956.

[33] P. Souchay, *Bull. Soc. chim. France*, 1948, 148.

[34] K. F. Jahr and A. Brechlin, *Z. anorg. Chem.*, 1952, **270**, 257.

[35] R. C. Turner, *Canad. J. Chem.*, 1969, **47**, 2521.

[36] J. Aveston, *J. Chem. Soc.*, 1965, 4438.

[37] A. L. Reesman, E. E. Pickett, and W. D. Keller, *Amer. J. Sci.*, 1969, **267**, 49.

with a quadruple charge. Either a dimer or an octamer have been suggested as possible species.[38-40]

We have observed two ^{27}Al resonances in addition to that of $Al(H_2O)_6{}^{3+}$ whose relative intensities vary with the degree of hydrolysis. It is necessary to assign them to different ionic species and consider how the results may then reconcile the above somewhat varied set of observations.

We have previously suggested that the broad line 3·3 p.p.m. down field of and overlapping the $Al(H_2O)_6{}^{3+}$ resonance is due to a dimer ion.[2] Since the existence of such an ion has been challenged by some workers it is important that this assignment should be established as fully as possible and we give our arguments in some detail below, based on the linewidth of the resonance and upon changes in area which occur during hydrolysis.

The linewidth of the resonance is about 11 times that of the $Al(H_2O)_6{}^{3+}$ (monomer) resonance which on the basis of the Debye model for the correlation time of spherical molecules in a viscous medium suggests that the maximum molecular radius is 2·2 times that of the monomer. The line is narrower than those of most alkylaluminium dimers[41] which suggests it does not arise from a higher polymer. It cannot arise from $Al(OH)(H_2O)_5{}^{2+}$ since the concentration of this species is very small. Dimer ions have been characterised by *X*-ray crystallography[42] and have the structure $Al_2(OH)_2(H_2O)_8{}^{4+}$ with each aluminium at the centre of an octahedron of oxygen atoms, hence the chemical shift should be similar to that of the monomer. In the solid the octahedra are considerably distorted with the bridging oxygens closer than the remainder. If this structure persists in solution the distortion will of course contribute to line broadening.

Line areas also provide evidence for the dimer assignment as follows. Using Figure 1, we can pick out a region of low degree of hydrolysis where only monomer and ' dimer ' are present with no detectable amount of higher polymers. In this region we can then write the following equilibria:

$$Al(H_2O)_6{}^{3+} + H_2O \overset{Q_1}{\rightleftharpoons} Al(OH)(H_2O)_5{}^{2+} + H_3O^+$$

$$Al(H_2O)_6{}^{3+} + Al(OH)(H_2O)_5{}^{2+} \overset{Q_2}{\rightleftharpoons} Al_2(OH)_2(H_2O)_8{}^{4+} + H_3O^+ + H_2O$$

We prefer this two step process since the concentration of monomer is large in these solutions. We can then write for the formation of dimer from monomer, omitting solvation water:

$$[Al_2(OH)_2{}^{4+}] = Q_1Q_2[Al^{3+}]^2/[H^+]^2$$

whence

$$\log\,[Al_2(OH)_2{}^{4+}] = \log Q_1Q_2 + 2\log[Al^{3+}] + 2\ pH.$$

A plot of $\log\,[Al^{3+}] + pH$ against $\log\,([Al_{total}] - [Al^{3+}])$ is shown in Figure 7. It will be seen that so far as pH has any meaning in these solutions this plot is consistent with dimer formation. In view of all the other evidence obtained for dimer formation we feel that assignment of the broad line to a dimer ion is reasonable.

We have also observed a narrow line 62·5 p.p.m. down field from the resonance of $Al(H_2O)_6{}^{3+}$. This line is 42·5 p.p.m. to low field of the resonance of the lowest field octahedral complex so far reported, $Al(EtNCS)_6{}^{3+}$,[43] but is only 17·5 p.p.m. to high field of the resonance ascribed to $Al(OH)_4{}^-$.[44] This strongly suggests that it arises from an aluminium complex where the metal is surrounded tetrahedrally by four oxygen atoms. The anion is not involved since chloride or nitrate solutions give essentially the same results. It is significant that this line appears in solutions where the $Al_{13}O_4(OH)_{24}{}^{7+}$ polymer is known to exist and that this polymer contains an AlO_4 tetrahedron.[5,6] The detailed structure of the polymer[45] indicates that this consists of a highly symmetrical AlO_4 tetrahedron with three distorted AlO_6 octahedra grouped around each apex and interconnected by their edges and vertices. The Al–O distances vary from 185 to 205 pm and the inter-oxygen edge distances vary from 234 to 285 pm (1 pm = 10^{-2} Å). Thus the electric field gradients at the aluminium will be negligible for the central AlO_4 unit but large for the 12 outer octahedra. The relaxation rates and linewidths of these outer aluminium nuclei could therefore be expected to be large whereas that of the central aluminium should be small. The narrow line observed must therefore account for only one thirteenth of the metal in the complex, the remaining signal being very broad and situated near that of dimer and monomer. Unfortunately no such signal has been found but it is presumably too broad to detect.

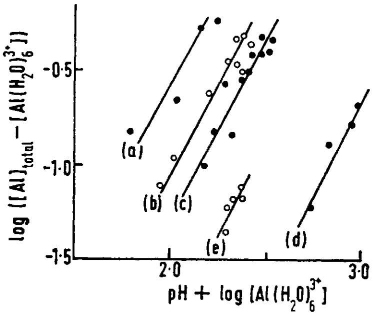

FIGURE 7 Plot of $\log([Al_{total}] - [Al^{3+}])$ *vs.* $\log\,[Al^{3+}] + pH$ for several values of $[Al_{total}]$ (a) 1·65M, (b) 1·33M, (c) 1·2M, (d) 0·6M, (e) 0·2M. The lines are drawn with slope = 2·00

Based on these assignments we have calculated the concentrations of each complex present in the 0·75M solutions, which are the only ones for which the results are sufficiently complete. These are shown in Figure 8

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[39] E. Matijević, K. G. Mathai, R. H. Ottewill, and M. Kerker, *J. Phys. Chem.*, 1961, **65**, 826.

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[44] R. J. Moolenaar, J. C. Evans, and L. D. McKeever, *J. Phys. Chem.*, 1970, **74**, 3129.

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which indicates that not all the aluminium is accounted for by these three species at intermediate degrees of hydrolysis; the difference between the total aluminium and the sum of the species detected by n.m.r. is also plotted in Figure 8. This undetected aluminium must be present as a large polymer ion with distorted AlO_6 octahedra since at no time was any absorption noted other than the three already mentioned. If we assume [20] that this polymer has the structure $Al_n(OH)_{2\cdot5n}^{(n/2)+}$ then we can also calculate the quantity of hydroxide ion which should be absorbed upon formation of the polymer. This total does not account for all the hydroxide added and the amount of excess hydroxide is also shown in Figure 8. Since the pH of these solutions is almost independent of the OH : Al ratio this excess of hydroxide must be absorbed by further hydrolysis of the polymeric ions, a process which seems to be particularly pronounced in the region of maximum concentration of dimer. This result supports the suggestion that ions such as $Al_2(OH)_3^{3+}$ are formed [46] possibly up to $Al_2(OH)_6(H_2O)_4$. The existence of such further hydrolysis could well explain the rapid proton exchange involving dimer.[2,10] It would also lead to a considerable buffering effect which would complicate the interpretation of potentiometric titrations in terms of formation of a series of polymer ions.

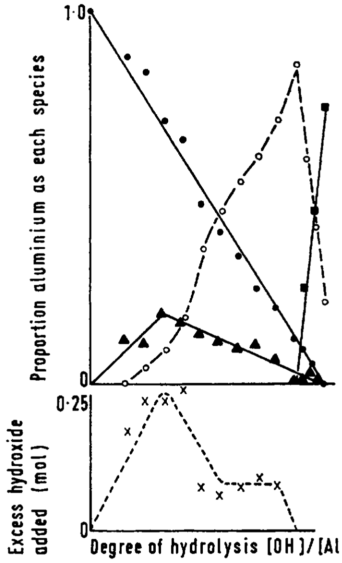

FIGURE 8 Measured and calculated concentrations of species present in a 0·75M $AlCl_3$ solution at different degrees of hydrolysis. The filled symbols are measured values, the open circles and crosses are calculated assuming that the low field line is due to an Al_{13} polymer, only one aluminium atom of which gives a visible resonance, and that the unaccounted aluminium forms a polymer $Al_n(OH)_{2\cdot5n}^{(n/2)+}$

We can obtain some idea of the degree of aggregation of the unknown species by comparing our results with the centrifugation measurements of Aveston.[36] An average degree of polymerisation can be calculated from results for various values of n. The figures for $n = 8$ are plotted as crosses in Figure 9 where it will be seen that they fall very close to the figures given by Aveston. Smaller n does not give so good a correspondence and since n is considered to be either 6, 7, or 8 this suggests that only an octamer species is formed. This conclusion is in accord with the coagulation experiments [38-40] which require a 4+ species to explain the results. Both dimer and octamer carry this charge and exist over a large range of hydrolysis. Unfortunately it is not clear in which region of hydrolysis the coagulation experiments were carried out; information as to the OH : Al ratio achieved might enable a choice of active species to be made.

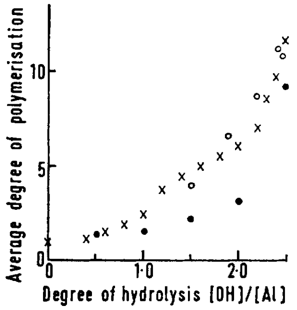

FIGURE 9 Average degrees of polymerisation of hydrolysed aluminium salt solutions, × = present results for Al^{3+}, Al_2^{4+}, Al_8^{4+}, and Al_{13}^{7+}; ○ = Aveston's ultracentrifugal measurements; ● = cryoscopic results of Jahr and Brechlin

The cryoscopic results for the degree of polymerisation are also plotted in Figure 9. These do not correlate well at the intermediate ratios of OH : Al, but it seems likely that the solutions used for these measurements were not in full equilibrium.[33,34] Diffusion measurements, interestingly, show a generally falling diffusivity as OH : Al increases but with two plateaux in the regions of the maxima in dimer and octamer concentrations.[47]

Thus when considered in conjunction with the many other studies of these solutions the present results show the presence of the four cationic species: $Al(H_2O)_6^{3+}$ including $Al(OH)(H_2O)_5^{2+}$, $Al_2(OH)_2(H_2O)_8^{4+}$, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$, and, with less certainty, $Al_8(OH)_{20}(H_2O)_x^{4+}$. The relative concentrations of these species depend markedly upon the method of solution preparation and the concentration. At 0·2M [Al] the Al_{13} polymer exists over a much greater range of OH : Al ratio though its final proportion at OH : Al = 2·5 is only half that obtained at 0·75M [Al]. Solutions prepared by boiling off acid seem to contain more of the Al_8 or similar polymer. Such behaviour makes it very difficult to compare different workers' results meaningfully. The existence of monomer at all OH : Al ratios is particularly striking and would not previously have been accepted.

The question of ageing in these solutions is also of interest. The existence of separate dimer and monomer ^{27}Al resonances indicates that the aluminium spends

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considerable time in each environment before exchange occurs. If this is so then addition of acid to a highly dimerised solution should cause the pH to drop immediately and then rise slowly as the dimer is broken up and the acid neutralised. This behaviour can be observed crudely on a pH meter but is outstandingly demonstrated using a stopped-flow apparatus which measures the change with time in indicator absorption after acid and dimerised aluminium solutions are mixed[48] (see Figure 10). The half-life of the dimer is *ca.* 1 s. Since the formation constant Q_2 in the reaction scheme (2) above is *ca.* 10^{-2} mol^{-1} l^{-1} then the rate constant for formation of dimer must be *ca.* 10^{-2} s^{-1}. The reactions involving the higher polymers appear to be slower. Thus when alkali is added to an aluminium salt solution an hydroxide gel is immediately formed since the polymers cannot form rapidly. The gel then slowly dissolves as the polymer species form. This change is accelerated by heating though there is of course no guarantee that the species formed during 1 h at 90° are in the same concentrations, or indeed are the same species as those formed at 20° over six months. The slow formation of dimer also accounts for the slow loss of hydrogen chloride or nitric acid from the salt solutions at 20° and the more rapid loss at 100°. Addition of acid to acid-deficient solutions made by method (*a*) or (*d*) should however result in quite rapid equilibration and it is not understood why they contain less dimer and more of the higher polymers than the alkali hydrolysed ones, unless, after initial addition of acid, the dimer is destroyed more rapidly than the higher polymers and the solutions are in quasi-equilibrium. This could well account also for the large spread of results.

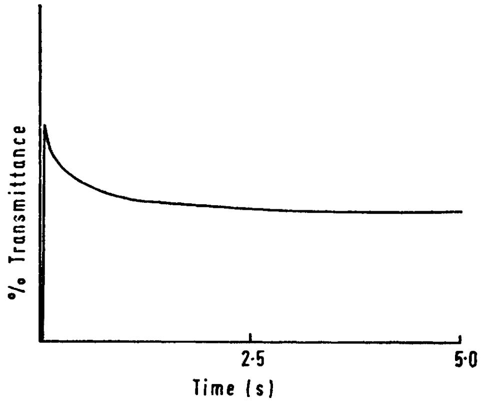

FIGURE 10 Changes in indicator absorption immediately after acid and deaerated, hydrolysed aluminium sulphate are mixed. The indicator was *p*-dinitrobenzene

We have already shown that hydrogen exchange on the dimer and polymers is very fast (*ca.* 10^7 s^{-1}) and it is known that exchange on the monomer is also fast.[7,10,49,50] In contrast, the oxygen exchange on the monomer is slow with a lifetime of *ca.* 7 s.[51-54] The rate of oxygen exchange is comparable with the polymer lifetimes and it follows that these polymers must be oxygen-bridged and cannot be held together by hydrogen bonds as has often been suggested previously. Currently one forms a picture of almost unchanging AlO clusters surrounded by a cloud of protons rapidly jumping between cluster and solvent.

The recognition of large quantities of dimer in solutions prepared by method (*a*) is also significant for our previous results.[1] Thus the increase in the ^{27}Al linewidth of monomer observed as its solutions are heated above 35° is due to an increasing rate of exchange between monomer and dimer, the least acid solutions which contain most dimer showing the greatest broadening. We are also led to modify our results showing ^{27}Al linewidth as a function of $1/[H^+]$ since a proportion of the broadening which occurs as the pH is increased will arise from exchange with increasing amounts of dimer. The effect of this has been calculated according to McConnell's treatment[55] and while it is small, it is sufficient to reduce the slope of the plot, the linewidth of the unknown hydrolysed species causing the broadening becoming *ca.* 700 Hz, a value nearer to that found for the dimer reported here.

The results obtained for the hydration number are also of interest since there is some question of whether this is the integral number 6 or whether the n.m.r. results which give non-integral numbers within $\pm 0{\cdot}2$ of this[7,50,52,56,57] show that the hydration complex is a less definite compound. It is possible (though unlikely) that the presence of small amounts of dimer in this previous work could have led to the results being low. This possibility has been avoided in the present work since we have a direct assay of the amount of aluminium monomer present. The results of Figure 6 indicate that the monomer is associated with the same number of water molecules throughout both a large range of dimer concentrations and a large pH range, and this implies that the deviations observed from a hydration number of 6·0 are merely due to experimental error. These results thus emphasise the integrity of the $Al(H_2O)_6^{3+}$ ion.

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