Multinuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 8.[1] Base Hydrolysis monitored at Very High Magnetic Field

J. W. Akitt* and Julie M. Elders
The School of Chemistry, The University of Leeds, Leeds LS2 9JT

New studies of base-hydrolysed aluminium(III) solutions were made using high-field ^1H and ^{27}Al n.m.r. spectroscopy. The increased sensitivity of the modern equipment has allowed data to be obtained at concentrations as low as 1×10^{-3} mol dm^{-3}, some of it quantitative, and the ^1H n.m.r. spectra of solutes transferred to non-aqueous solvents has provided new structural data. The results enable it to be stated quite unequivocally that the tridecameric cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ is the principal species formed at lower concentrations, and is virtually the only one formed below 20×10^{-3} mol dm^{-3}. At concentrations higher than this, and at intermediate levels of hydrolysis, an oligomeric mixture is formed with a stoicheiometry close to $\{[Al(OH)_{2.5}]^{\frac{1}{2}+}\}_n$ and which could be composed of species such as $[Al_2(OH)_5]^+$, $[Al_3(OH)_8]^+$, $[Al_4(OH)_{10}]^{2+}$, and $[Al_5(OH)_{13}]^{2+}$. Partial deuteriation produces isotopic splitting of the proton resonances of bound water which allows these to be distinguished from the resonances of OH-bridge protons. An indication of fine structure due to hydrogen–deuterium substitution on AlO_6 fragments is also obtained which favours the more condensed structures and this is in accord with the ease with which the oligomer is converted into the tridecamer on simple dilution. It is now certain that the dihydroxo-bridged dimer found in the solid state is not a significant constituent of these solutions. Oxygen-17 n.m.r. data are also briefly reported.

The previous paper in this series[1] described the self hydrolysis of aluminium salt solutions in which $[Al(H_2O)_6]^{3+}$ dissociates to form $[Al(H_2O)_5(OH)]^{2+}$. In part 4 of the series[2] we described the reactions which take place when hydrolysis is forced by adding base, sodium carbonate being used because this provides a particularly clean hydrolysis at the higher concentrations deemed necessary for n.m.r. spectroscopic studies. While there is no doubt that the monomeric self-hydrolysed cation is formed in such solutions, it is always a minor component and the principal products are polymeric species whose constitution has been a cause of controversy for decades. The degree of forced hydrolysis is described by the hydrolysis ratio m, which is defined as the ratio $[OH^-]$ added/total [Al]. As m is increased the concentration of $[Al(H_2O)_6]^{3+}$ can be monitored satisfactorily by ^{27}Al n.m.r. spectroscopy and it was shown that this fell linearly with increasing m to zero at $m = 2.5$. At the aluminium concentration used of 1.0 mol dm^{-3}, a second resonance was observed at about $m = 1.5$ which was assigned to the tridecameric cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, which has a structure with a formal OH/Al ratio of 2.46. The AlO_4 unit of this cation, whose structure is known,[3] gives a sharp ^{27}Al resonance at 62.5 p.p.m. while the resonance of the octahedral aluminium is very broad and can only be observed at elevated temperatures. A reasonably integrable spectrum is obtained in a high-field instrument and this confirms that the known crystal structure almost certainly exists in solution.[4] Another species exists at lower m, which has a broad resonance 500 Hz wide at *ca.* 4 p.p.m. This is hidden in the skirt of the narrow Al^{3+} resonance in 23.45-MHz spectra and cannot be assessed quantitatively, though it has been observed in a continuous-wave (c.w.) differential saturation experiment,[5] and is easily observed at high field.[4] We have assumed it was the dimeric cation which has been found as a solid sulphate with the structure $[(H_2O)_4Al(\mu\text{-}OH)_2Al(H_2O)_4]^{4+}$,[6] since it contains octahedrally co-ordinated aluminium in an environment sufficiently distorted to explain the breadth of its resonance. Despite the lack of quantitative data, the fact that the system takes up 2.5 mol of base per mol of Al^{3+} lost should have warned us that the above formulation might not have been correct and one of the purposes of this paper is to provide the quantitative data and the correct formulation of this oligomer. The system has also been studied at lower concentrations by Bottero *et al.*[7–9] who made quantitative measurements of Al^{3+} and tridecamer resonances for total aluminium concentrations of 0.1, 0.01, and 0.001 mol dm^{-3}. This was a remarkable achievement in a low-magnetic-field spectrometer and indicated that the proportion of oligomer formed was small if not zero. Recent potentiometric studies come to much the same conclusion and suggest that the oligomer is a trimer rather than a dimer.[10] Following this work, we have shown that the speciation in this system is very concentration dependent and that dilution of a partially hydrolysed solution causes a rapid fall in the concentration of the oligomer and a slow rise in that of the tridecamer,[11] and it is our second objective here to give a full description of this work. Finally, it has become apparent as we have applied high-field ^{27}Al n.m.r. spectroscopy to these hydrolysed solutions that the amount of information available is limited and has to be supplemented by other means, and we also describe the application of proton n.m.r. spectroscopy coupled with partial deuterium substitution to the resolution of some of the structural problems.[12] We also summarise the results of some ^{17}O n.m.r. data obtained with ^{17}O-enriched samples.

Experimental

Hydrolyses of $AlCl_3$ solutions were carried out as described previously,[2] except that a variety of bases were used, namely NH_4OH, NaOH, Na_2CO_3, or K_2CO_3, and the concentrations used were slightly lower, being in the range initially of 0.5—0.8 mol dm^{-3}. Once the importance of concentration became apparent, this range was extended to 0.01—3.0 mol dm^{-3}. The dynamic changes following dilution of partially hydrolysed solutions were followed simply by mixing a solution with water and transferring this to a sample tube which was placed immediately in the spectrometer. In this way it was possible to obtain the first spectrum 3 min after mixing. Hydrolysed solutions were prepared for proton n.m.r. studies by adding K_2CO_3 to $Al(ClO_4)_3$ solutions and cooling in iced water to

precipitate the maximum quantity of $KClO_4$. The filtrate was dried over P_2O_5 to give a solid which contained only a small amount of free water and which was dissolved in $(CD_3)_2CO$. Hydrogen–deuterium exchange occurs in such solutions so that the cations were always appreciably deuteriated in these samples, and the degree of deuterium substitution could be varied by the length of delay between preparation and measurement of the spectrum. Some samples were also prepared in CD_3CN and in this case partial deuteriation has to be achieved by carrying out the initial hydrolysis in a suitable H_2O–D_2O mixture.

Spectra were measured using a Bruker HX400 cryo instrument at frequencies of 400 MHz for ^1H, 104.2 MHz for ^{27}Al, and 54.2 MHz for ^{17}O. The solvent was used as lock for the ^1H spectra whereas for the ^{27}Al spectra two techniques were used, either the samples were held in coaxial cells with the sample in a central 8-mm tube and D_2O in the annulus between this and an outer 10-mm tube, or a 10-mm tube was used with a 5-mm capillary tube held in a coaxial position by a 5-cm long Teflon plug. The capillary in this case was filled with a solution containing $[Al(OD)_4]^-$ in D_2O and served as both lock and quantitative standard, this cell being chosen as being quantitatively more reproducible than the first. Some ^{27}Al n.m.r. measurements were also carried out at 23.45 MHz using a Bruker HFX3 spectrometer. The $[Al(OD)_4]^-$ capillary was not appropriate in this case because of the low chemical shift dispersion and quantitative data were obtained by comparing the initial free induction decay (f.i.d.) intensity of a sample and of a standard $[Al(H_2O)_6]^{3+}$ solution, using an output of the first few f.i.d. data points as described previously.[13] No attempt was made to deconvolute the three components present in the f.i.d. and the information was restricted to the total aluminium content.

The pH was measured on a Radiometer PHM 64 research instrument using electrodes from Russell pH Ltd.

Results

The hydrolysis profile for 0.5—0.8 mol dm^{-3} aluminium salt solutions is shown in Figure 1 which summarises all the results obtained in this concentration range for all the bases used. This differs from earlier data,[2] in that we present a measured value for the oligomer concentration and that the tridecamer concentration does not fall off at the highest values of m, which is almost certainly due to the somewhat lower concentration used. The scatter of points gives an indication of the accuracy with which it is possible to make these measurements, an individual value being determined to no better than perhaps $\pm 10\%$, though sufficient data are presented to permit the overall behaviour to be ascertained to a much better level of certainty than this. There are two principal reasons for the errors in measurement: one is that the narrow monomer and broad oligomer lines overlap, making integration difficult; the other is the fact that the tridecamer is estimated from an albeit narrow resonance but one which represents only 7.7% of its total aluminium content. We believe that within these limits of measurement we are observing all the aluminium present as residing in the three spectroscopically observed species. Indeed, the proton work below will demonstrate that the tridecamer solutions contain a very low level of contamination by other species. We note that, for small m, the oligomer resonance appears with increasing m at the same rate as the monomer is consumed. It thus follows that the oligomer must have a structure which contains 2.5 OH ligands per Al atom, *i.e.* be $[Al(OH)_{2.5}(H_2O)_x]_n^{\frac{1}{2}n+}$ where x will depend upon the actual structure of the cation. This formulation also virtually forces us to accept that n is an even number. For it to be odd two or three OH ligands per Al would be needed and neither of these possibilities seems to be supported by Figure 1. However, if the formulation is not exactly 2.5:1 as is the case for the tridecamer, then structures containing $Al_3(OH)_7$, $Al_3(OH)_8$, $Al_5(OH)_{12}$, $Al_5(OH)_{13}$ become possible and these are easily encompassed within the error of the measurements. There is now no doubt at all that this species is not the dihydroxo dimer. Its high formal hydroxide content also indicates that it must contain some singly co-ordinated OH as well as OH (or O) bridges.

In order to examine the effect of aluminium concentration on the nature of the species present, a series of solutions were prepared with $m = 1$ and total aluminium concentrations varying from 0.01 to 3.0 mol dm^{-3}. The results are plotted in Figure 2 which shows two clear features. At the higher concentrations, not all the aluminium is detectable in the spectra, and below 0.5 mol dm^{-3} the oligomer species decreases

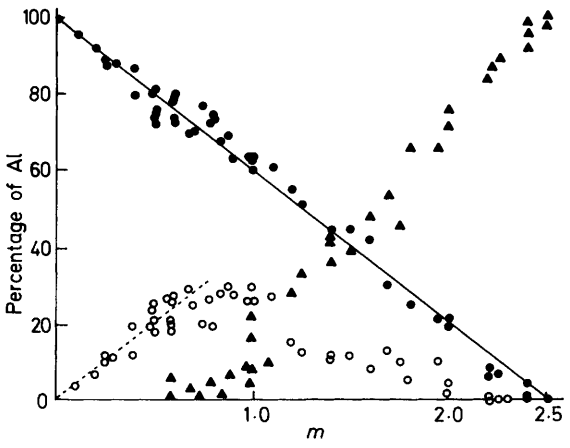

Figure 1. Hydrolysis profile of the hydrolysis of Al^{III} forced by added base determined by quantitative ^{27}Al n.m.r. spectroscopy at 104.2 MHz for total aluminium concentrations in the range 0.5—0.8 mol dm^{-3}. (●) $[Al(H_2O)_6]^{3+}$, (○) the small oligomer, and (▲) the tridecamer (Al_{13})

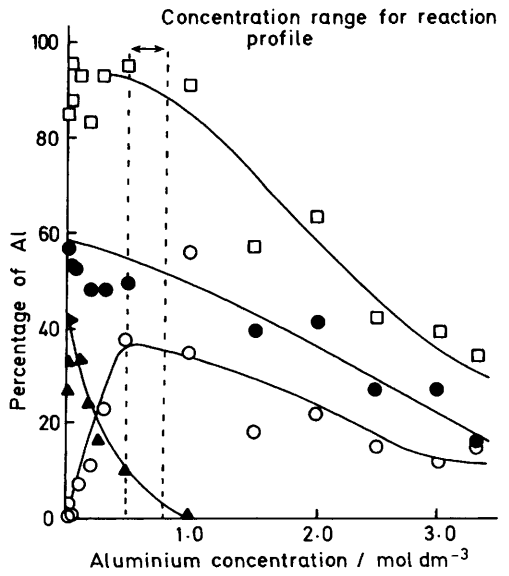

Figure 2. Variation in the proportion of aluminium present in the various cations in base-hydrolysed aluminium salt solutions with m = 1.0 as a function of the total aluminium concentration; Al_o is the proportion of oligomer. The lines are drawn through the points for guidance only. (□) Al_{TOTAL}, (●) Al^{3+}, (○) Al_o, and (▲) Al_{13}

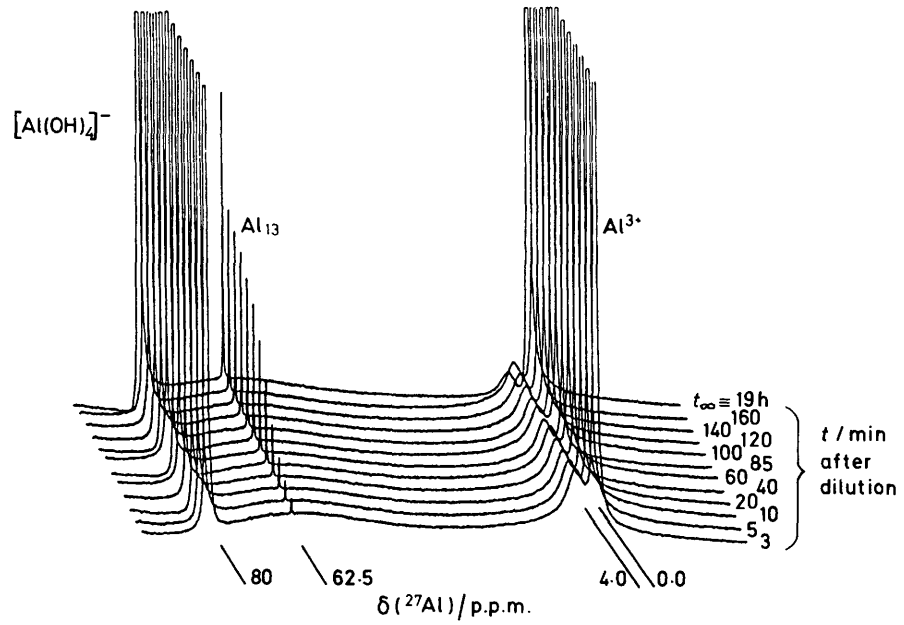

Figure 3. The evolution with time of the 104.2-MHz ^{27}Al n.m.r. spectra of a solution prepared by rapid ten-fold dilution of a 1.0 mol dm^{-3} $AlCl_3$ solution previously base hydrolysed to $m = 1.0$. The low-field resonance of $[Al(OH)_4]^-$ was used as a quantitative standard and the high-field resonance of the monomer did not change in intensity, thus permitting us to truncate these peaks

in concentration, essentially to zero at 0.02 mol dm^{-3} Al. At the lowest concentrations then almost the sole species present are the monomer, a small concentration of its hydrolysed form (inevitably), and the tridecamer. The hydrolysis profile described above is thus not unique and depends markedly upon the total concentration of aluminium present. This result provides unequivocal spectroscopic evidence that the earlier conclusions that the oligomer concentration is low in dilute solution were indeed correct.[7-10]

The fact that the solution composition for a given m value might depend upon concentration suggests a simple dynamic experiment,[11] as described in the Experimental section. The evolution of the ^{27}Al n.m.r. spectra following dilution of a partially hydrolysed solution with water is shown in Figure 3 and the spectra obtained after sufficient time for equilibration at two dilutions are shown in Figure 4. Dilution produces a system which is not in equilibrium and so is followed by changes, some of which are slow enough to monitor spectroscopically and some of which are not. Measurement of the total aluminium concentrations before and after dilution, *i.e.* at 3 min, indicates that a rapid process occurs in which the proportion of oligomer is decreased. Reference to Figure 3 will show that this is followed by the much slower formation of the tridecamer at a rate which follows a pseudo-first-order law with a rate constant of the order of 1.4×10^{-4} s^{-1}, this being the average of determinations at ten- and 100-fold dilutions. It is evident from the figure that the oligomer proportion changes little in the first 160 min. It was not possible to measure a rate constant accurately for this slow change but it was clear that the continuing loss of oligomer occurred at least 2.3 times more slowly than the tridecamer appeared. The monomer concentration was constant throughout. The total aluminium visible (multiplying the 62.5 p.p.m. resonance by 13) increased at the same rate as the tridecamer. The evolution of the proportion of species is plotted on Figure 5. The changes in pH which occur on dilution were also monitored in separate experiments. These are shown in Figure 6 and exhibit some curious features. The pH of the initial 1.0 mol dm^{-3} solution at $m = 1.0$ was 2.99. Ten-fold dilution should in principle increase this to 3.99 and 100-fold dilution to 4.99.

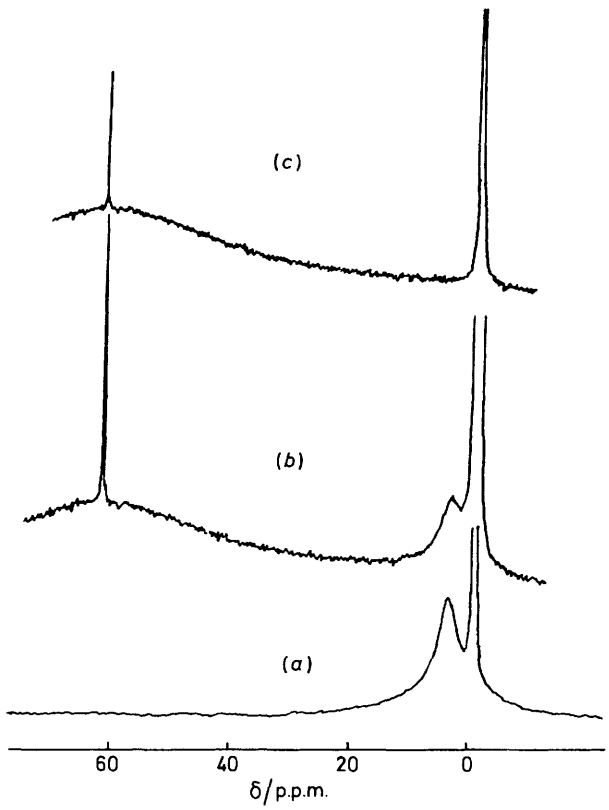

Figure 4. 104.2-MHz ^{27}Al N.m.r. spectra for base-hydrolysed solutions with $m = 0.5$ and total aluminium concentrations of (*a*) 1.0, (*b*) 0.1, and (*c*) 0.01 mol dm^{-3}. No oligomer was detected in the latter. The low-field hump is a probe resonance

There is, however, a very rapid re-equilibration in the first few minutes which corresponds to the loss of oligomer signal and during which the pH falls as hydrogen ions are liberated to the

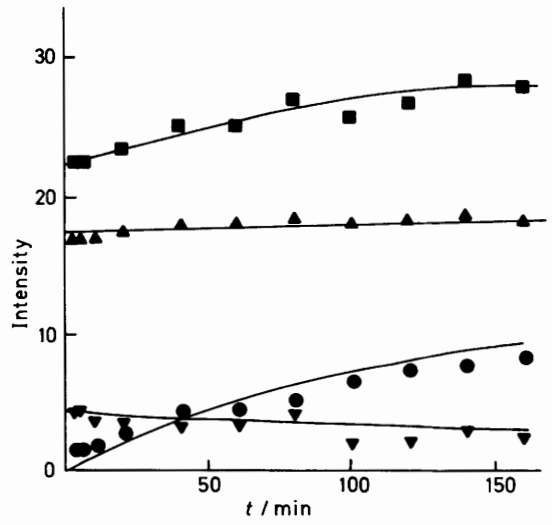

Figure 5. Plots extracted from the spectra of Figure 3 showing the evolution with time after dilution of the various species. The two lower curves are drawn with appropriate time constants of 119 and 278 min respectively. (■) Total Al, (▲) monomer, (●) tridecamer, and (▼) oligomer

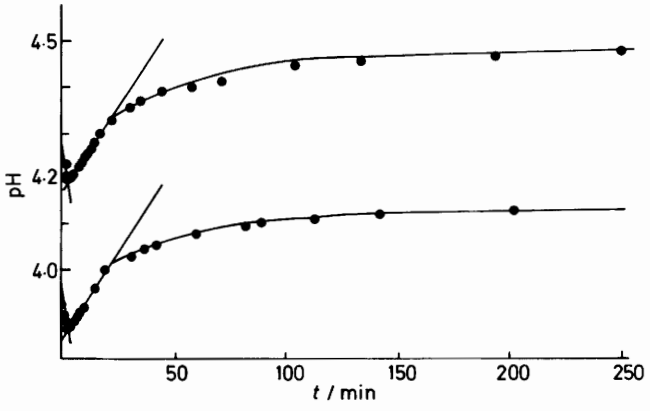

Figure 6. Variation of solution pH as a function of time after rapid dilution of a base-hydrolysed $AlCl_3$ solution (1.0 mol dm^{-3}) with m = 1.0. The lower curve follows a ten-fold dilution and the upper a 100-fold dilution

solution. There are two sources of these ions. First an increase in the degree of hydrolysis of the monomer which will be an almost instaneous process on our time-scale (*ca.* 10^{-5} s[14]) and which will lower the pH base from which the plots of Figure 6 originate though by an amount which it is not possible to estimate accurately. This process is then followed by a slower one in which protons are released by oligomer and whose rate indicates a chemical rearrangement or perhaps an increase in the degree of polymerisation. In any event, the species formed does not give a detectable ^{27}Al resonance. It must be more highly hydrolysed with an [OH]/[Al] ratio surpassing 2.5:1. the pH quickly reaches a minimum and then rises slowly and linearly with time over about 25 min as the invisible component again takes up protons and is transformed into the tridecamer. After this time the rate of change of pH decreases and becomes non-linear, indicating a change in mechanism though the products are unchanged. This complex behaviour is perhaps not surprising since a small molecule has to associate and rearrange to give the particular tridecamer structure and this is most likely to proceed by successive steps.

The realisation that the hydrolysis ratio of the crystalline dimer sulphate was much less than that of the oligomer in solution suggested that if the crystals could be dissolved in water then we should observe spectroscopic changes in the solution. The dimer sulphate is crystallised from sulphuric acid solution and we found that the crystals are quite easily dissolved in pure water to the extent of *ca.* 300 mg cm^{-3}. The ^{27}Al n.m.r. spectrum of such solutions contains three resonances, narrow ones at 0.0 and −3.1 p.p.m. due to the monomer cation and its sulphate complex respectively,[15] and a broader one at 3.5 p.p.m. attributable to the oligomeric cation. The fact that non-hydrolysed cations had formed on dissolution indicates an increase in the degree of hydrolysis of the other components. The dihydroxo dimer thus disproportionates in solution to give species of lower and higher hydrolysis ratio. In principle the relative intensities of the resonances could be used to calculate the hydrolysis ratio in the oligomeric cation. This did not agree with the hydrolysis profile given above and we believe that other species are present whose signal is not observed. Certainly, solid material precipitates from these solutions on standing and they are not stable. Assay of the precipitate for Al, H, and S suggested that it had the formula $Al_3(OH)_5(SO_4)_2 \cdot 8H_2O$.

The ^{27}Al n.m.r. spectra of solutions 0.5—1.0 mol dm^{-3} in Al with $m \not> 1$ show the monomer and oligomer resonances to be well resolved and so exhibiting no aluminium exchange. We investigated the effect of increased temperature to see whether exchange occurred at the higher temperatures. The chemical shift and linewidth of the oligomer are somewhat variable, the former being 3.3—4.7 p.p.m. at room temperature. Some of this range will be due to the difficulty of measuring the position of a broad line overlapping a narrow one but it may indicate some unsuspected influence also. This could perhaps be variation of the number of OH ligands present, or there could be several closely related species present with broad, overlapping unresolved resonances. Heating the sample caused random changes in chemical shift, an indication of a small increase in the proportion of oligomer present and significant changes in the linewidths of both resonances. The latter are summarised in Figure 7. The linewidths of both resonances decrease with temperature at first in the manner typical for a quadrupolar nucleus. Both reach a minimum value though not at the same temperature and thereafter increase again. In the case of the oligomer resonance the behaviour suggests the onset of slow exchange above 50 °C. The data are too scattered to measure the rates but it is possible to estimate a lifetime to exchange of some 2.7 ms at 100 °C. The monomer resonance behaves similarly and it is tempting to suggest straightforward slow exchange between the two observed species. However, this cannot be assumed since the monomer resonance behaves in this way even in solutions which undergo only self hydrolysis,[16] and we have ascribed this behaviour to an increase in the proportion of $[Al(OH)]^{2+}$ with increasing temperature.[1] This change may well influence the oligomer parameters also and it seems that it would be hazardous to attempt to analyse these data at the present time. We were however, able to confirm that the exchange processes involving the oligomer are relatively slow by observing the pH changes which occur after a small addition of acid is made and this indicates a process with a rate constant of the order of 1 s^{-1}.[17]

Proton exchange is fast in these solutions and one would not expect to be able to observe separate resonances for solvent or bound water even at reduced temperature.[14] It was nevertheless clear that we required supplementary data for these systems and that the proton might be the most informative nucleus. The reason that the rate of exchange is rapid in water is essentially that there is a large excess of solvent present. The rate constants

k(H) are related to the proportions of protons P in the complex cation (com) and solvent (so) by $k(H)_{com}/k(H)_{so} = P_{so}/P_{com}$. Thus $k(H)_{com}$ can be much reduced by decreasing the water content of the medium and so P_{so}. This can be achieved by working in a non-aqueous solvent such as acetone or acetonitrile, as described in the Experimental section. The ^{27}Al n.m.r. spectra are not apparently affected significantly by the drying and redissolution process so that it appears that the hydrolysed species may be transferred to non-aqueous solvent in this way and suffer little change, at least within the limits of resolution of our spectroscopic methods. We have thus obtained spectra of the tridecameric cation and of a partially hydrolysed solution containing the oligomer and monomer in acetone and acetonitrile. The spectra are shown in Figures 8 and 10, taken at 400 MHz. That of the tridecamer is the easiest to assign (Figure 8) and apart from the solvent contains just four major resonances. The broad one near 5 p.p.m. is due to the remnant free water and varies in intensity according to how well the initial drying process has been carried out. The other narrow resonances at 7.5, 3.8, and 3.9 p.p.m. have the intensity ratio 2:1:1. The structure of this cation is shown in Figure 9 where it will be observed that there are 24 equivalent water protons and two sets comprising 12 each of distinguishable hydroxide-bridge

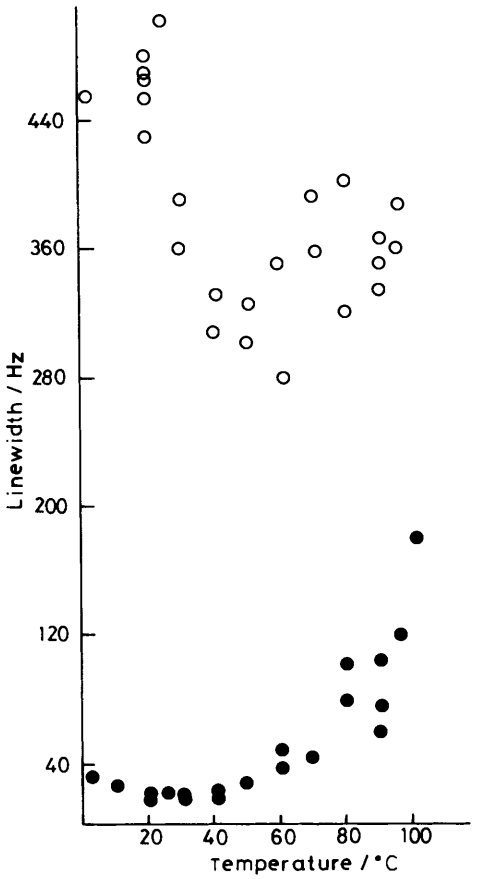

Figure 7. The variation with temperature of the linewidths of the ^{27}Al n.m.r. resonances of the monomer (●) and oligomer (○) observed at 104.2 MHz for a base-hydrolysed solution of $AlCl_3$ with $m = 0.6$

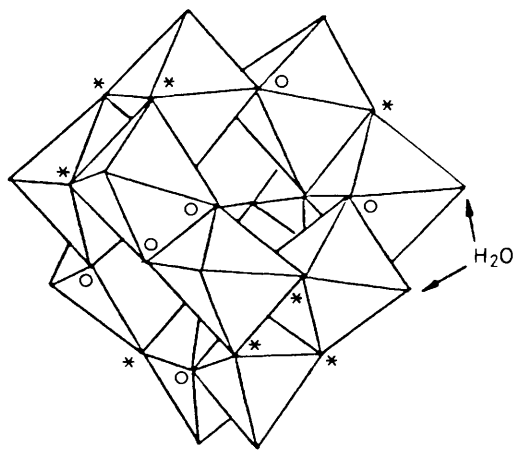

Figure 9. The arrangement of the twelve octahedra of the tridecameric cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. There are twelve apical water ligands (24 H), four triplets of bridging OH (*), and six pairs of double OH bridges (○). The central AlO_4 unit is not shown. The structure is one of the Keggin isomers

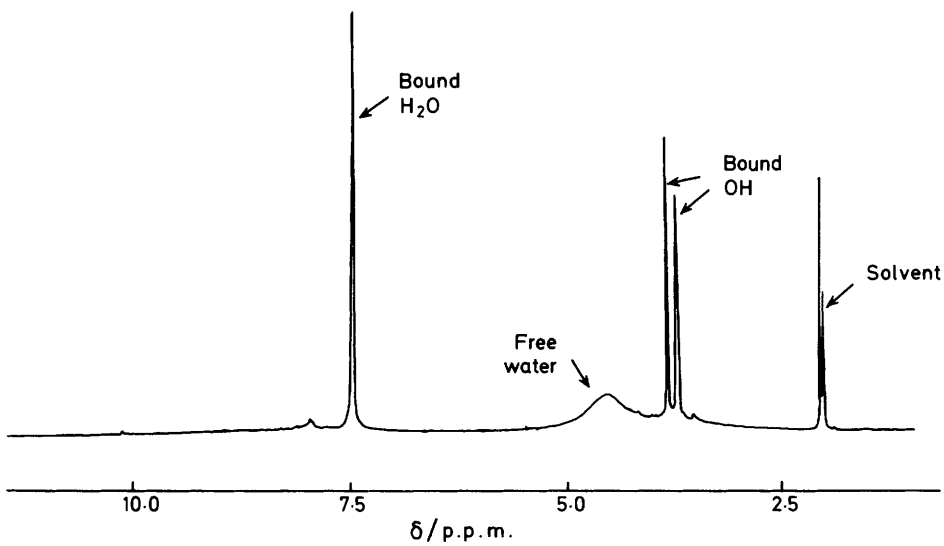

Figure 8. 400-MHz Proton n.m.r. spectrum of the tridecamer perchlorate dissolved in $(CD_3)_2CO$ taken at −30 °C. The assignment of the resonances is given. The two solvent peaks are deuteriated and non-deuteriated forms. Note the lack of contamination by other species

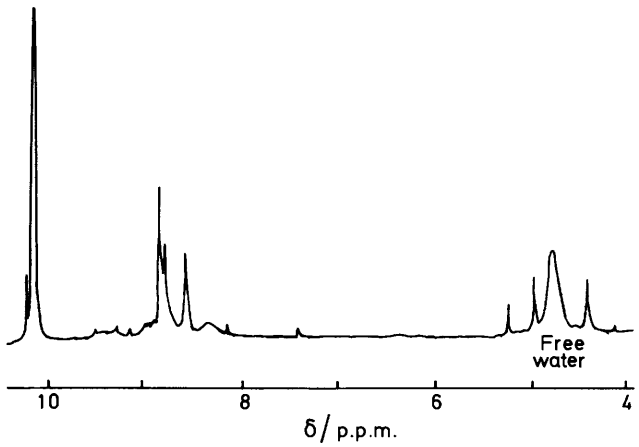

Figure 10. 400-MHz Proton n.m.r. spectrum of a $(CD_3)_2CO$ solution prepared from $Al(ClO_4)_3$ base hydrolysed to $m = 1.0$. The water protons bound to monomer appear below 10 p.p.m. and those bound to oligomeric species lie between 9.5 and 8 p.p.m. The three sharp signals near the broad free-water resonances at 4.8 p.p.m. are believed to represent hydroxide bridges

protons. The spectrum is clearly consistent with this structure and we should also note the low level of contamination by other species. The terminal water resonance has a chemical shift which is some 2.5 p.p.m. upfield of the resonance of the water bound to Al^{3+}.[12] The electric field at the tridecamer water molecules is similar to that calculated for water hydrating K^+,[18,19] though the measured shift is more to low field than that estimated for K^+.[19] However it is now clear that the chemical shifts of hydration water in acetone solution are not determined solely by the electric field,[20] and one would expect that the fact of the formation of a co-ordinate bond would also have some influence. The displacement upfield is however, completely consistent with water co-ordinated to an ion of reduced charge/radius ratio, Z_i/r_i^2. Little is known about the appropriate position of co-ordinated OH, though one of us has already suggested that a resonance at 1.3 p.p.m. in aqueous, hydrolysed beryllium salt solutions is due to a bridge hydroxide proton.[21] The OH protons in other inorganic species are also observed surprisingly to high field though they are often involved in exchange processes.[22] The hydroxide bridge in $[\{Rh(C_5Me_5)\}_2H(OH)(O_2CR)][PF_6]$ is observed at 3.0 p.p.m. in acetone solution and the OH in $[R_2Al(\mu\text{-}OH)_2AlR_2]$ are at 5.9 to 6.5 p.p.m.[23] The chemical shift of the tridecamer bridge hydroxide protons is within this range. These bridge-hydroxide resonances are markedly to high field of that of the free hydroxide anion,[24] and appear to behave much more like those of substituted water molecules. The spectrum was also obtained in acetonitrile solution and was similar except that the resonances all moved to high field at 6.3 (H_2O on Al), 3.0 and 2.8 (OH), and 3.9 (free H_2O) p.p.m. We also attempted to differentiate between the two types of OH by means of a nuclear Overhauser effect (n.O.e.) experiment, since the distances between the two types of bridge and the terminal water molecules are probably significantly different. However, slow exchange processes dominate the resulting difference spectra even at −30 °C and only magnetisation transfer due to this cause could be observed. Proton exchange occurs between bound water and OH but does not involve the free water and so is probably an intramolecular process. Increasing the temperature to 20 °C causes the resonances of the bound and free water to broaden so that there is an increase in the rate of intermolecular exchange, though the OH resonances are unaffected, except that the high-field one moved further upfield.

The ^1H n.m.r. spectrum of a solution hydrolysed to $m = 1$ at an aluminium concentration of 0.8 mol dm^{-3} is shown in Figure 10. The water bound to monomer appears at 10.1 p.p.m. with a small spike to low field due to deuterium exchange with the solvent.[12] The remainder of the spectrum can be assigned to the oligomer with the bound water occurring between 9.5 and 8.0 p.p.m. and three sharp OH resonances and a broad one probably due to free water between 5.5 and 4.0 p.p.m. The assignments are based on chemical shift arguments and will be supported by isotopic substitution. The spectrum always has the general form shown however the sample is prepared, but the relative intensities of the lines is variable though measurement is made difficult by the underlying weaker resonances of bound water on minor components, and by the free water in the OH region. It will immediately be clear that this spectrum is far too complex to originate from a dihydroxo dimer, and indeed that more than one species is present. The amount of OH observed is also rather small, between 20 and 25% of the bound water. The amount in the tridecamer is 50% and in a hypothetical dimer $[Al_2(OH)_5(H_2O)_5]^+$ it would be 33%, these values representing the probable limits in the variation of composition. We are thus not observing sufficient OH and suggest that any terminal OH is exchanging with the 'free' water and only bridge OH is observed. N.O.e. difference spectra show that some resonances do not undergo exchange, *e.g.* those at 8.4 and 8.62 p.p.m., though both these exchange with the doublet at 8.85 p.p.m. All exchange with free water and this may be a result of the terminal OH exchange suggested above.

It is evident from Figure 10 that a small amount of deuterium exchange produces an isotope-shifted peak beside the monomer water resonance. An expanded spectrum of a solution in which the deuterium exchange had been allowed to proceed further is shown in Figure 11, and line narrowing has been applied to improve the resolution. The fine structure in the HOD (to low field) and HOH peaks of the monomer is easily seen and has allowed us to show that the monomer is precisely hexahydrated.[12] This type of spectroscopy is analogous to the so called 'simple n.m.r.' which has proved so informative in carbohydrate chemistry.[25–27] In addition all the sharp lines in the bound-water region of the oligomer spectrum are split into doublets in the same intensity ratio as that of the monomer. This of course confirms that they arise from water molecules and not OH. These latter resonances remain singlets and are not shown. Comparison of Figures 10 and 11 demonstrates some of the variability exhibited by these spectra. In addition the intense doublet is not resolved in Figure 11, presumably because the lines are broadened by the fine structure caused by hydrogen–deuterium substitution on different oxygen atoms co-ordinated to the same aluminium atom. Only one of the oligomer water resonances shows such fine structure and this quite clearly does not have the same form as that of the monomer signals. The other resonances are also significantly narrower than the monomer signals and presumably contain similar, unresolved structure. We have not been able to display this in acetone solution though recent initial measurements in acetonitrile confirm this supposition.[28] The pattern follows the binomial distribution expected for a four- or five-site system and suggests that there is a water molecule and four of five other co-ordinated hydrogen atoms either in H_2O or OH attached to the relevant aluminium cations. We should also note in Figure 11 that the primary isotope splitting is not constant but decreases for the water resonances appearing to higher field. This tendency is continued for the tridecamer and its 'simple' spectrum consists of a doublet for the co-ordinated water with isotope splitting of only 0.018 p.p.m. The OH resonances are again singlets. No secondary structure could be detected.

Since these hydrolysed cations also contain oxygen, then it should be possible to obtain information using ^{17}O n.m.r.

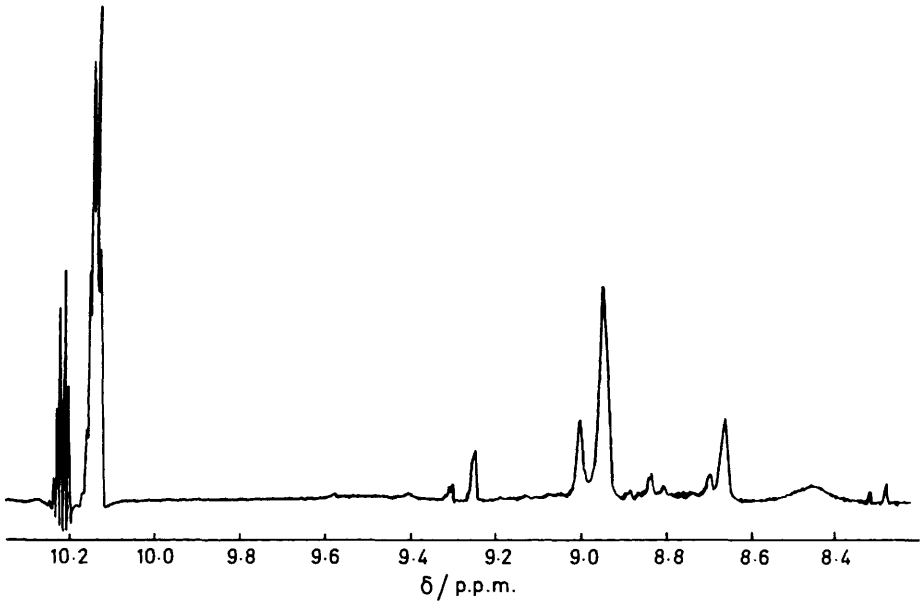

Figure 11. 400-MHz 'Simple' proton n.m.r. spectrum of a base-hydrolysed solution with $m = 1.0$, dried and dissolved in $(CD_3)_2CO$. The resonances are all due to water bound to Al^{3+} and are doublets with HOD to low field of HOH

spectroscopy, especially with ^{17}O-enriched samples. We have thus obtained spectra of some base-hydrolysed solutions containing either oligomer or tridecamer and of some metal-hydrolysed solutions which contain different species of unknown structure.[29] A report of similar work has also appeared during the preparation of this paper,[30] and it is useful to compare the two sets of results. The ^{17}O chemical shifts are small, in contrast to those seen for the heteropolyanions where metal–oxygen multiple bonding is possible,[31] and as a result the resonance of the water solvent interferes. Thompson *et al.*[30] removed this by a gated solvent-saturation pulse technique whereas we resorted to shift or relaxation reagents. We tried using Co^{2+} which moves the bulk water signal well to low field,[32] but found it also broadened the other resonances. Europium(III) moves the water a little to high field,[33] away from the region of spectral interest and gives much less perturbation of the spectra and was used routinely. We also tried Mn^{2+} which broadens the solvent beyond detection,[34] and obtained comparable results. The ^{17}O n.m.r. spectrum of a pure aluminium salt solution consists of the solvent resonance with a shoulder to low field due to the cation solvation water, at 23 p.p.m. This differs from a previous estimate made in the presence of Mn^{2+}.[34] Addition of Eu^{3+} improves the resolution of this spectrum. Base hydrolysis to $m = 0.6$ produces no change in this spectrum and the oligomer oxygen does not give a differentiable signal. Thompson *et al.*[30] reported this signal to be at 22 p.p.m. though their tentative assignment that it represents only OH oxygen seems to be incorrect since we see the same resonance in a non-hydrolysed solution. We believe that this peak arises from both co-ordinated water and OH, whose oxygen chemical shifts are essentially the same for the monomer and oligomer. Such an assignment is in accord with the well known slow rate of oxygen exchange in solutions of the monomer.[32,34] The rate of exchange is increased on heating and the peak at 23 p.p.m. then coalesces with the solvent resonance, in accord with the variable temperature ^{27}Al n.m.r. spectra of the oligomer. Solutions containing only the tridecamer give two sharp resonances at 20 °C with shifts of 55 (540 Hz wide) and 17 p.p.m. (900 Hz wide) with a possible broad component between and underlying these two. Increasing the temperature to 75 °C reduces the linewidths and a sharp peak is still seen at 56 p.p.m. (210 Hz wide), a new peak occurs at 30 p.p.m. (760 Hz wide), and the high-field peak moves to 20 p.p.m. but is very much reduced in intensity. Thompson *et al.*[30] obtained similar results and were able to give definite assignments based upon oxygen isotope-exchange studies and a ^{17}O-$\{^1H\}$ cross-polarisation study in the solid state which shows that the peak at 55 p.p.m. is due to the AlO_4 oxygens and the high-field peaks to OH oxygen.

The results for our metal-hydrolysed solutions were disappointing in that the oxygen spectra were identical with those of the tridecamer. This is a useful observation since it confirms earlier proposals that the species present in such solutions are structurally related to the tridecamer,[29] but otherwise means that we were unlikely to obtain any new structural insights from the ^{17}O n.m.r. studies. In view of the high cost of ^{17}O enrichment we therefore decided to abandon this part of the work.

Discussion

The hydrolysis of Al^{III} has been investigated by potentiometric methods for some 50 years and different laboratories have suggested at various times hydrolysis profiles based on a very wide range of poly(hydroxo) species. If we represent these generally as $[Al_p(OH)_q]^{(3p-q)+}$ then values of p and q have been suggested in the ranges $1 \leqslant p \leqslant 24$ and $1 \leqslant q \leqslant 60$,[35–54] and some even larger species have been proposed.[53,54] It is usual to represent individual species by their p,q values and we shall follow this convention here. The internal hydrolysis ratio of each species is given by q/p. The most recent report of work in this field surveys and criticises the currently favoured schemes and concludes that there is general agreement on the formation of the 1,1 cation, that a small 2,2 or 3,4 polymeric species may be formed, and that significant quantities of a larger polymer is formed, the 13,32 cation being often quoted since the tridecameric cation known in the solid state is clearly related to such a species. It has the same formal q/p but somewhat different structure to the general formulation above.[10] The new results presented by these workers show that as hydrolysis is forced by added base the principal species present are the 1,0 and 1,1

cations, a small quantity of the 3,4 species whose concentration is reduced at lower total aluminium concentrations, and a big polymer with q/p in the range 2.4—2.5 and p having a value within the range $5 \leqslant p \leqslant 14$, though they are unable to distinguish which and chose the 13,32 cation simply because it is a known species.[3] They are of course unable to distinguish between the OH and O ligands in the tridecamer structure and it is important to emphasise that the p,q formalism can give no structural details about the species formed. It is pointed out that the structure of a solid precipiated from solution does not necessarily reflect the nature of the main species present,[10,55] and, for instance, the 2,2 species exists in the crystalline state,[6] but the weight of the potentiometric evidence seems to be that it is not formed in dilute solution at all,[10,56] and this conclusion is in accord with the quantitative ^{27}Al n.m.r. data presented here. Indeed, our results at low concentrations and the dynamic dilution experiment indicate that the two sets of data obtained using two very different techniques are in substantive agreement. We can, however, provide in addition some detailed structural information and also quantitative data which allow us to estimate q/p ratios for the species formed. This will allow us to provide a much more detailed model of the solutions, and will give further insights into the system. We will also be able to extend this detailed knowledge to much higher concentrations than are possible with potentiometric methods,[10] and will be able to make a number of definitive statements about the hydrolysis behaviour of Al^{III}.

We should first note an important difference between the n.m.r. work described here and elsewhere,[2] and the potentiometric work. At high concentrations it is necessary to carry out hydrolyses at about 100 °C in order to ensure rapid dissolution of the precipitates which form even after small additions of base. The tridecamer which is formed is unstable at high temperatures and so the solutions have to be cooled immediately after the completion of hydrolysis if the formation of new, unknown species is to be avoided. It is clear from our results that such decomposition is negligible below aluminium concentrations of 0.8 mol dm^{-3}. The potentiometric work was carried out at room temperature and at low concentrations the dissolution of precipitates is apparently quite rapid and sufficient time seems to have been given between base additions to ensure equilibrium. The tridecamer is particularly stable at these lower temperatures.[29]

The Tridecameric Cation.—We are able to state quite unequivocally that the large polymeric species formed at the greatest base additions is the tridecameric cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ which formally is the 13,32 species with $q/p = 2.46$. The only detail that we are unable to provide is the precise state of protonation of the cation in solution. The formulation given is in close accord with the m value needed to produce a solution containing only the tridecamer. If the charge were 6+, q/p is 2.53 and if it were 8+ then q/p is 2.38. The conclusion is then that the charge is most likely 7+ or 6+ and solid salts of both species are known.[3] The evidence that the tridecameric cation is present in solution is now quite overwhelming. The ^{27}Al n.m.r. resonance of the AlO_4 unit is observed at 62.5 p.p.m. in solution and also at an almost identical position for the sulphate crystals.[57,58] Metathesis of these with $BaCl_2$ solution gives a solution for which the same resonance is evident.[59] If the broad resonance of the six-co-ordinate aluminium atoms is observed then the intensities are consistent with a tetrahedral-Al/octahedral-Al ratio of 1:12,[4,29,58] and the fact that, in our quantitative estimates, multiplying the intensity of the resonance at 62.5 p.p.m. by 13 gives a near 100% aluminium balance is further evidence in support of this. The relatively small width of this resonance also means that it can be detected at very low concentrations and so shown to exist even for millimolar solutions. The proton spectra are also correct for the 7+ formulation and the new ^{17}O n.m.r. data show that non-protonated oxygen atoms are present in a fairly symmetric environment consistent with that of the AlO_4 oxygen atoms of the tridecamer.[30] In this case we note that the crystal and solution structures are identical.

The Oligomer and its Dependence upon Aluminium Concentration.—Our quantitative data eliminate the 2,2 cation from consideration and further evidence in support of this conclusion is obtained from the way the dimer sulphate crystals disproportionate when dissolved in water. Like others, we were previously misled by the evident solid-state structure to accept this as a likely solution constituent but we are now certain this is wrong. Further evidence of this can be obtained if we extrapolate the solid-state ^{27}Al n.m.r. chemical shifts obtained for the dimer sulphate by Thompson *et al.*[30] to infinitely high magnetic field. This gives a value of *ca.* 2 p.p.m. and is significantly to high field of the chemical shift of the solution species, even allowing for the likely inaccuracy of the solid-state chemical shifts.[60] It follows, incidentally, that the correlation time of the oligomer in solution cannot be determined from the quadrupole coupling constant of the solid dimer. Solid- and solution-state structures are here different.

The recent potentiometric data are used to support the presence of a 3,4 oligomeric cation at low base additions and low aluminium concentrations.[10] This attains perhaps 8% of the total aluminium concentration in the 1 mmol dm^{-3} region. We have attempted previously to observe the oligomer resonance in this concentration region,[1] but did not obtain reproducible results and must conclude that this species does not give a detectable signal, as is also evident from the dilution experiment. This, coupled with the measured q/p ratio of 2.5, means that the oligomer signal at *ca.* 4 p.p.m. cannot be due to a 3,4 species. We also note that the oligomer q/p of 2.5 is obtained at high concentrations and that this is unlikely to decrease as the concentration, and acidity, are decreased. We intend to investigate this point further but note for the moment that our data do not support the actual existence of 3,4 species.

It remains to ask what is the structure of this oligomeric species or mixture of species. If we could measure its q/p value exactly we could make a reasonably good estimate of its average stoicheiometry. The hydrolysis profile in Figure 1 is insufficient to allow us to do this but does show a distinct tendency in the region where $m = 1$ that suggests that q/p has a value greater than 2.5, perhaps 2.6. This is an indication that the species involved are the 3,8 or 5,13 cations though we cannot reject the 2,5 or 4,10 species. We also note that the measured ^{27}Al n.m.r. chemical shifts of the oligomer resonance are rather variable, all values lying in the range 3.3—4.7 p.p.m. The line is broad, *ca.* 4 p.p.m. at 104.2 MHz, and we initially ascribed the variation to the difficulty of measuring the position of a broad line. However it should be possible to measure to within 1/20th of a linewidth, or 0.2 p.p.m., and we now believe that the variation in position is real. The linewidth is also rather variable (see Figure 7) and the implication is that this is a composite resonance with two or more broad, overlapping components. Such a conclusion is entirely consistent with the variability observed in the proton spectra of the oligomer. It is clear that in order to proceed further with an analysis of the nature of these species we need to find means of developing their 'simple' spectra, and one in which the exchanging OH groups do not blur the fine structure. The dilution experiment indicates that the oligomer system can be converted with relative facility into the tridecamer and this we believe is a structural clue. Marty and co-workers[61,62] have examined the hydrolysis products obtained with Cr^{3+}. These are very stable and can be separated by chromatography and examined individually (our dilution

experiment shows that the aluminium system is too labile to separate in this way) and it has been shown that a tetrameric species exists in two forms, all OH-bridged $[Cr_4(OH)_7(H_2O)_{11}]^{5+}$ and the species $[Cr_4O(OH)_5(H_2O)_{10}]^{5+}$, with an O bridge. Both species can be further protonated. The rate of interconversion of the forms is comparable with the rate of immediate loss of oligomer upon dilution in our system and it is very tempting to suggest that a similar interconversion occurs on diluting the oligomer. The necessary O-bridge feature is formed and would be expected to give a species with an undetectably broad ^{27}Al n.m.r. resonance because of the distortion around the bridge. The aluminium species are more highly hydrolysed than the chromium species and would then have to have terminal hydroxide ligands. Certainly it seems that in order to account for the complexity of the proton spectra we need to postulate a species with chemically different bound water ligands and so an asymmetric structure, with a small bridge OH to H_2O ratio, with reduced numbers of protons around each aluminium and capable of easy conversion to the tridecamer. We will not give such a structure here since the possibilities are almost limitless and await some more accurate proton-count data.

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