Multinuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 9.[1] Prolonged Hydrolysis with Aluminium Metal monitored at Very High Magnetic Field

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Aluminium(III) salt solutions hydrolysed by boiling with aluminium metal over extended periods of time have been examined by ^{27}Al n.m.r. spectroscopy and, after drying and redissolution in acetone, by ^{1}H n.m.r. spectroscopy, both at very high magnetic field. At low hydrolysis ratios, $m \leqslant 1.4$(where m is defined by the stoicheiometric formula $AlX_{3-m}(OH)_m$, X being the coanion), the solutions contain the oligomer species observed in base hydrolysis. There are three minor components and one major one whose spectroscopic properties suggest it is the 3,8 trimeric species $[Al_3O_2(OH)_4(H_2O)_8]^+$. The fully hydrolysed solutions ($m = 2.5$) have complex proton spectra which differ between preparations and it is concluded that they contain a hierarchy of species whose structures are related to that of the tridecameric cation but many of which lack the tetrahedrally co-ordinated metal atom. It is not possible to suggest a structure for any individual species but it is made clear for the first time that a wide range of products are formed in these solutions.

The previous paper in this series[1] described the forced hydrolysis of aluminium salt solutions produced by rapid addition of base which causes the $[Al(H_2O)_6]^{3+}$ to polymerise and form initially, at high concentration, a mixture of small oligomers followed by the tridecameric cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, which is the sole species detected at the lowest concentrations. Ageing, or heating, solutions containing this cation produce spectral changes[2] and it is clear that while we have defined what species are formed initially during hydrolysis of Al^{III}, these are not the only polymeric cations which can form in these solutions. Hydrolysis with aluminium metal is achieved by dissolving the metal in a salt solution, usually in the presence of mercury as a catalyst, but requires some 48 h of heating near 100 °C and so we observe new spectral features which are similar to those obtained on ageing the base solutions. We have already reported some results for the system in Part 5 of this series[3] and have shown that the highest magnetic fields are required if we are to see any real details.[3,4] When a solution is prepared to give a formulation Al_2X, where X is the anion of the salt used, we have effectively achieved a hydrolysis ratio, m, of 2.5, m being defined in Part 8[1] as the ratio $[OH^-]$ added/total [Al]. The ^{27}Al n.m.r. spectra of such solutions show that they contain a trace of the tridecameric cation (sharp line at 62.5 p.p.m.) and also of the non-hydrolysed cation $[Al(H_2O)_6]^{3+}$, which suggests that some species is present which is hydrolysed to an m value greater than 2.5. The major species are represented by two broad resonances at *ca.* 70 and 12 p.p.m. and it was inferred that they contained octahedrally co-ordinated Al and some or all contained a small proportion of tetrahedrally co-ordinated metal. Increasing the concentration, up to as much as 6 mol dm^{-3} in Al, reduced both the total aluminium intensity detected and the proportion of tetrahedrally co-ordinated metal. It was not possible to determine the nature of any of the new species formed, indeed many were not observable, and the present work was undertaken in an attempt to obtain further details about the composition of these solutions. Such knowledge is of importance since the commercially produced chlorohydrates which are used widely as antiperspirants, for sealing strata in oil well drilling, and for the manufacture by ICI of the refractory fibre SAFFIL, have spectra which indicate they have many features in common with those of our laboratory produced solutions.

Experimental

AR aluminium wire was dissolved in aqueous $AlCl_3$ or $Al(ClO_4)_3$ solutions by boiling under reflux with a small amount of mercury as catalyst. The wire was added in portions over 48 h when dissolution was generally complete. Two types of solutions were prepared for investigation: dilute solutions for which an initial salt concentration of 0.2 mol dm^{-3} Al was used and which when fully hydrolysed to $m = 2.5$ had a final concentration of 1.2 mol dm^{-3} Al; and concentrated solutions for which the starting concentration was 1.0 mol dm^{-3} Al, increasing to 6.0 mol dm^{-3} at $m = 2.5$. In both cases a series of solutions was prepared with values of m lying between 0 and 2.5. There is a slight overlap in concentration between the two sets but the spectra indicate that they are to be regarded as producing quite different types of data. GPR quality hydrated salts, $AlCl_3{\cdot}6H_2O$ or $Al(ClO_4)_3{\cdot}9H_2O$, were used without further purification.

The ^{27}Al n.m.r. spectra were obtained from the solutions as prepared and over a range of temperatures. Quantitative data were extracted using a capillary containing a known amount of $[Al(OH)_4]^-$. Proton n.m.r. spectra were also obtained as described previously, by drying perchlorate solutions over P_2O_5 and redissolving the solid obtained in [$^2H_6$]acetone and then examining the samples at reduced temperature. The ^{27}Al n.m.r. spectra of some such samples were monitored to estimate the influence of the drying–redissolution process on the species initially present.

Solutions were also prepared at room temperature by the dissolution of aluminium foil in aluminium salt solutions containing a little $HgCl_2$ solution. A preparation with $m = 2.5$ could thus be obtained in 24 h which contains essentially only the tridecameric cation without the NaCl which necessarily accompanies the standard base hydrolysis. Such solutions are

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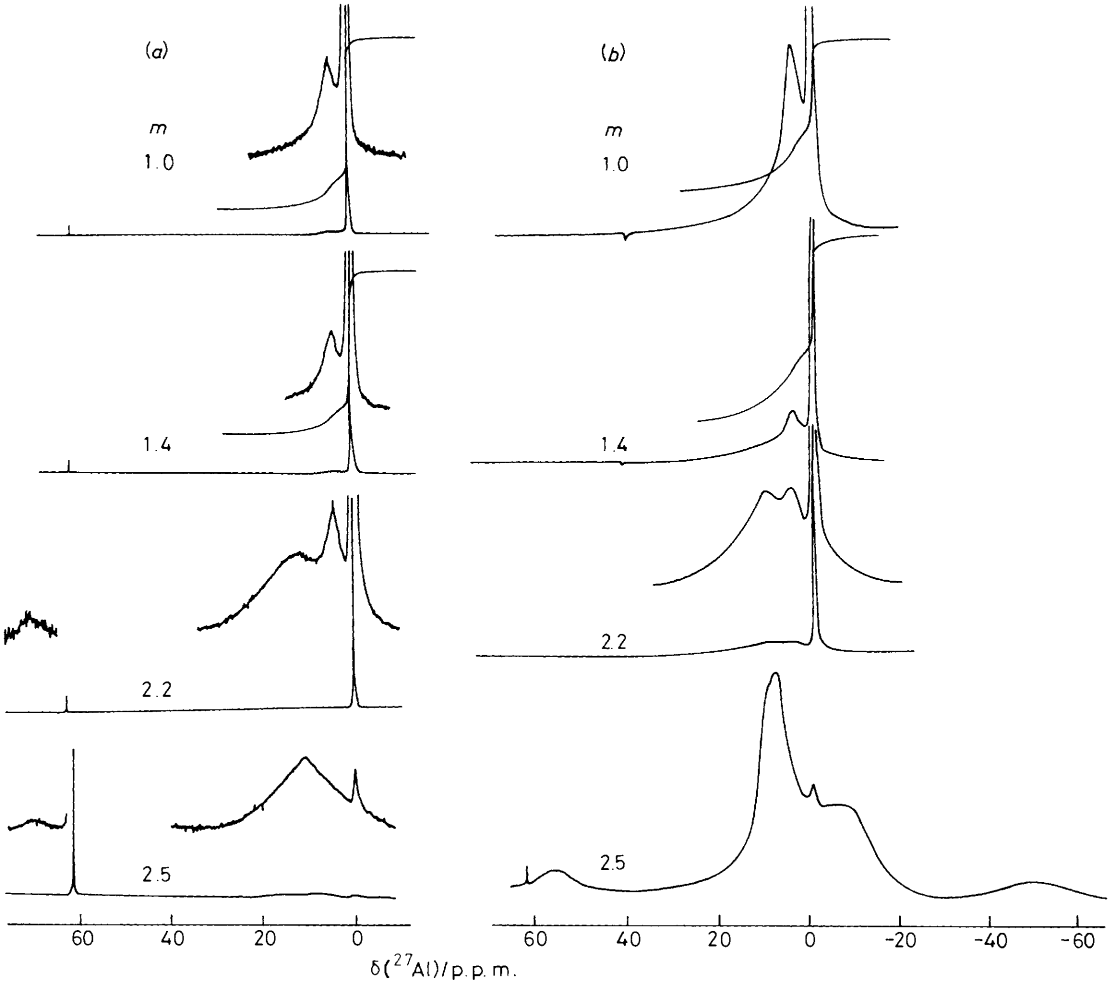


Figure 1. (*a*) Aluminium-27 n.m.r. spectra at 104.2 MHz of metal hydrolysed aluminium salt solutions at 25 °C and a starting concentration of 0.2 mol dm^{-3} (dilute series). The tridecamer shows as a spike at 62.5 p.p.m. and the monomer a peak at 0 p.p.m. The oligomer appears as the broad line at 4 p.p.m. and the new species at 12 and 70 p.p.m. The broader lines are also displayed at high gain. (*b*) Similar spectra for a starting concentration of 1.0 mol dm^{-3} (concentrated series). The oligomer concentration is higher at low *m*, the new species appear earlier during hydrolysis and the trace for the fully hydrolysed solution is quite different

remarkably stable with time and were used to study the effects of added salts on ageing processes over a period of about 8 months.

N.m.r. spectra were obtained using a Bruker HX400 cryo instrument at frequencies of 400 MHz for ^1H and 104.2 MHz for ^{27}Al. The solvent was used as lock in the first case and D_2O in the standard capillary in the second. Variable-temperature ^1H n.m.r. spectra were obtained at 360 MHz also using a Bruker SP 360 instrument.

Results

Figure 1 shows how the ^{27}Al n.m.r. spectra evolve with increasing *m* for the dilute and concentrated solutions. In interpreting these traces it has to be borne in mind that the time of preparation is not linear with the *m* value. The reaction can be written as in equation (1) so that in terms of the amount of metal

$$AlCl_3 + XAl \longrightarrow (1 + X)\,AlCl_{3/(1+X)}(OH)_{3X/(1+X)} \qquad (1)$$

dissolved *m* has the value $3X/(1 + X)$. The rate of dissolution of metal is such that although this occurs rather more slowly as the reaction proceeds one can regard the value of X as a measure of the time elapsed from the start of reaction. This means that $m = 2.2$ is achieved after about 24 h and that the remaining three points increase in *m* requires another 24 h. It is thus not surprising to find that the new species of cation start to become evident in the spectra of solutions with $m > 2.2$. At values of $m < 1.5$ the dilute samples have spectra very reminiscent of those obtained by base hydrolysis and both the oligomer and tridecamer are present, in addition to monomer. Increase in concentration, as would be anticipated from the results for base hydrolysis,[1] causes the tridecamer signal to be lost and the concentration of oligomer to increase. These features persist as hydrolysis proceeds to $m = 2.2$, but a fourth resonance appears also near 12 p.p.m. which is particularly intense for the concentrated solution and a weak one is observed near 70 p.p.m. for the dilute solution. What is not immediately evident from the traces though is the fact that by $m = 2.2$ the total aluminium visible has decreased significantly, the loss in intensity being particularly marked for the concentrated solution. This is shown in Figure 2 where it will be seen that by the completion of hydrolysis at $m = 2.5$ only some 20% of the Al can be accounted for in the spectrum of the concentrated solution and 32% in that of the dilute solution. By this point the oligomer resonance has disappeared and that at 12 p.p.m. has assumed an unusual triangular shape for the dilute sample. Tridecamer is evident in the concentrated solution but the shape of this spectrum has changed quite dramatically with a new resonance at 50 p.p.m.

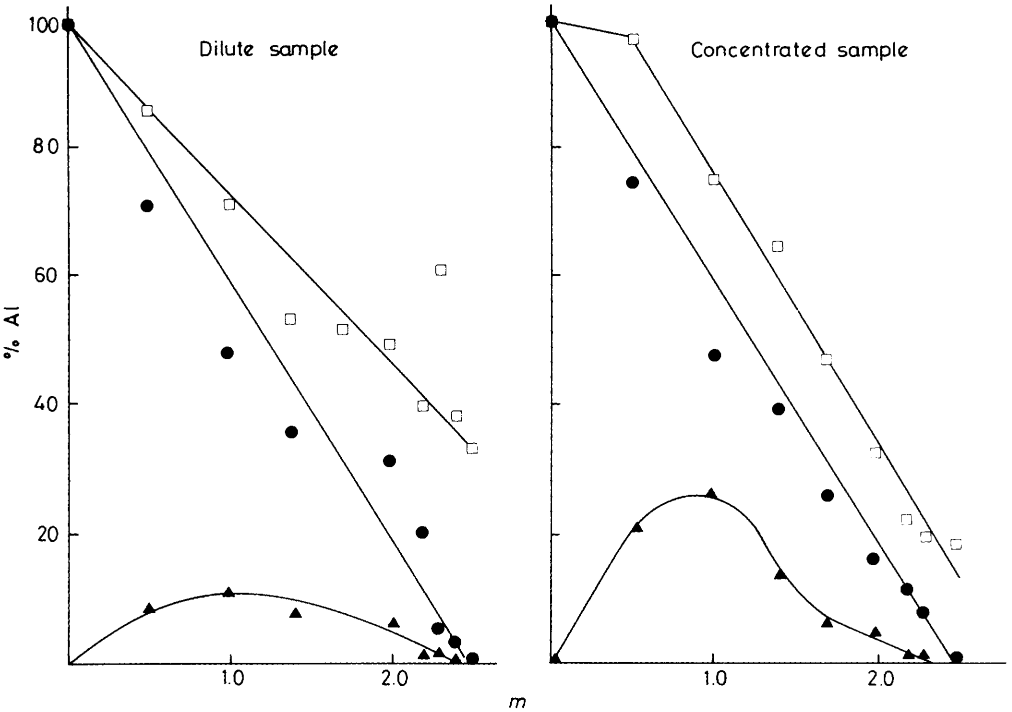


Figure 2. Plots of aluminium concentrations estimated from Figure 1 as a function of *m*. ●, Monomer; ▲, oligomer; and □, total concentration. Note how the latter falls off rapidly as *m* increases

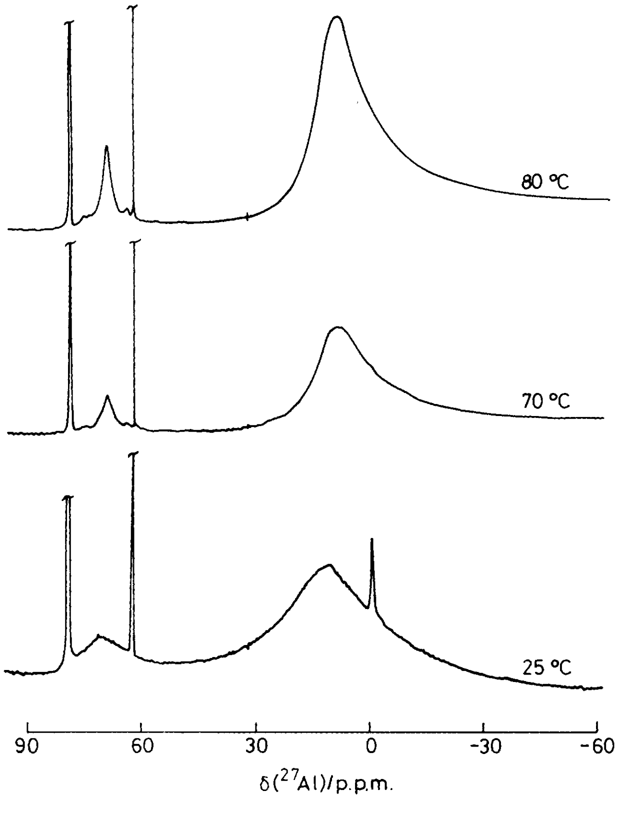


Figure 3. Aluminium-27 n.m.r. spectra at 104.2 MHz of a dilute sample with *m* = 2.5 as a function of temperature. The line at 80 p.p.m. is due to the standard capillary. The very small blip at 71 p.p.m. is real. The amounts of aluminium visible in the spectra are 32% at 25 °C, 54% at 70 °C, and 85% at 80 °C

and two to high field at −9 and −50 p.p.m. This latter trace is similar to those obtained from many samples of commercial chlorohydrate. It must be emphasised that these traces are not unique and that, in particular, the tridecamer is observed in some concentrated samples at low *m*. There is evidently some sort of equilibrium between the visible and non-visible species.

These spectra demonstrate that the metal hydrolysed solutions differ markedly from the base hydrolysed solutions although oligomer and tridecamer are common to both and, as has already been deduced,[1] are the primary products of hydrolysis. They do not however, allow us to make much advance in understanding the nature of the new species formed, not least because of the loss in spectral intensity. Since the aluminium nuclei are situated in rigid structures it is not likely that this loss in intensity is due to exchange effects but arises because there are significant electric field gradients at the nuclei which lead to efficient quadrupole relaxation and so broadened lines. It has already been demonstrated that the octahedral resonance of the tridecamer is not visible at room temperature due to this cause.[1] It will be argued elsewhere that if the linewidth is comparable with the width of the spectrometer computer window then its intensity is lost, effectively because it cannot be distinguished from the baseline position, which becomes indeterminate.[5] The limiting factor is not the electronic bandwidth of the instrument. Spectra were obtained in the present work using a sweepwidth of 21.7 kHz and line intensities will be perturbed if they are wider than *ca.* 3.6 kHz (34.5 p.p.m. of the figure scales). It is well known that if solutions containing quadrupolar nuclei are heated then the rate of quadrupole relaxation is decreased and we decided to investigate the effect of increased temperature on the spectra of these solutions. We hoped to see line narrowing and better resolution of the visible resonances and to bring the broad resonances to the point at which they contribute significantly to the total intensity.

Spectra obtained at several temperatures for fully hydrolysed solutions with *m* = 2.5 are shown in Figures 3 and 4. While it is true that exchange is unlikely to be sufficiently fast to affect the

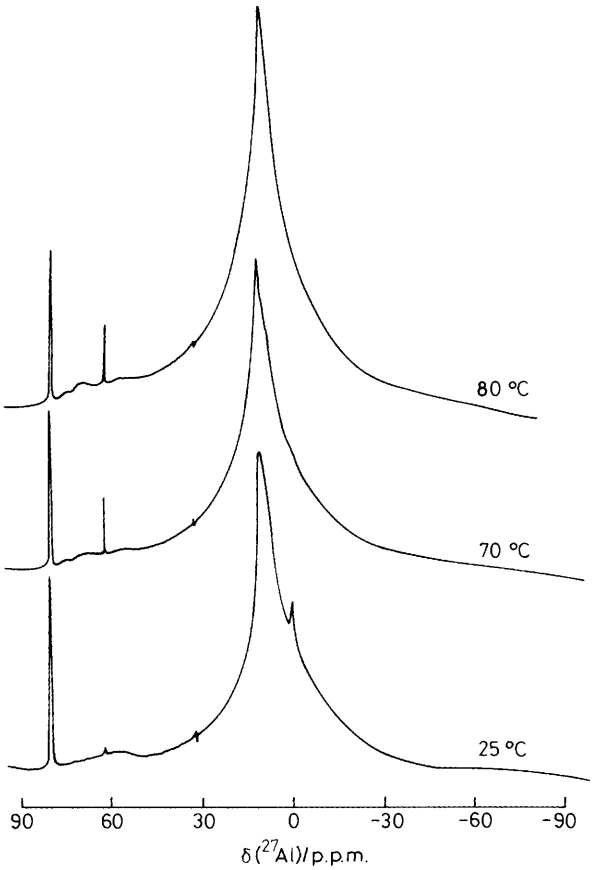


Figure 4. Aluminium-27 n.m.r. spectra at 104.2 MHz of a concentrated sample with $m = 2.5$ as a function of temperature. The line at 80 p.p.m. is due to the standard capillary. Note the increase in tridecamer concentration. The amounts of aluminium visible in the spectra are 14% at 25 °C, 30% at 70 °C, and 39% at 80 °C. The spectrum at 25 °C differs from that given in Figure 1(*b*) in detail though some intensity is still evident to high field. This illustrates the inherent variability of the system

shape of the traces, it is possible that the equilibria between the different species present may change with temperature. For this reason the samples were heated for 1 h at the temperature of measurement prior to taking the spectra and the sample taken to the highest temperature (80 °C) was cooled to room temperature and remeasured to ensure that the changes observed were reversible. The traces in Figure 3 in fact seem to show little change with temperature. The monomer peak broadens and disappears about 70 °C due to exchange with the monomer self hydrolysate,[6] and there are changes in the main resonance at 12 p.p.m. which indicate that it is a composite line, but there is no dramatic line narrowing. The spectrum obtained from the concentrated sample (Figure 4) differs from that shown in Figure 1 though the general features are the same and the main difference is the reduced intensity of the high-field lines. Heating brings out two resonances at 75 and 56 p.p.m. which suggests that three types of tetrahedral Al exist. The proportion of tridecamer is also irreversibly increased (on a short time-scale). The most dramatic change is however not evident from the spectra shown and is that the total aluminium visible increases with temperature from 14% at 25 °C to 39% at 80 °C, almost all the change arising in the resonance at 12 p.p.m. It thus appears that as the components of this resonance visible at 25 °C become narrower with increasing temperature, this is obscured by the emergence of new intensity underneath which gives the appearance of maintaining the width. There are clearly a large number of octahedral aluminium environments in this solution. The resonance at 12 p.p.m. in the dilute sample (Figure 3) behaves similarly in that it increases markedly in intensity with increase in temperature, the total aluminium visible increasing from 32% at 25 °C to 85% at 80 °C. There is no accompanying change in shape of the resonance which is obviously multicomponent but with even less differentiation than seen in the concentrated solution. The peak at 70 p.p.m. narrows satisfactorily with increased temperature and this shows up two narrow flanking peaks due to minor components. We note that as the broad tridecamer resonance becomes visible also at high temperatures,[1] this contributes to the increased signal intensity. The effect is nevertheless small since the tridecamer is always a minor constituent of the solutions and the major change is due to the emergence of the resonances of unknown species.

These spectra tell us that we have molecular species present which contain aluminium in octahedral environments with a variety of structural differences, and that some of them are associated with tetrahedrally co-ordinated metal and so may have a structure related to that of the tridecamer. Certainly the tridecamer is easily generated in the concentrated solutions on heating, a rather strange observation when it is remembered that these solutions were prepared at 100 °C. It is, however, obvious that the amount of information obtainable in this way is limited, and that a technique which may see as little as 14% of the contents of a solution has limited application. For this reason we turned to the examination of the proton n.m.r. spectra on the basis that at least all the spins should give observable signals. Again, the development of the spectra was followed with increasing *m* and the complexity of the resulting traces forms a useful indication of the real complexity of the solutions. The changes observed in the dilute sample are shown in Figure 5. Up to $m = 1.4$ the spectra closely resemble those obtained from base hydrolysis and represent the oligomer together with a small amount of tridecamer, which is hardly visible. The fact that the resonance of free water moves around allows us to identify five hydroxide resonances though their relative intensities are variable. By comparing how these vary relative to the water resonances to low field we can obtain some idea of the number of species present and this will be analysed below.

The uppermost spectrum of Figure 5 is from a solution with $m = 2.5$. We have obtained spectra of this type from many different preparations and they are invariably complex but differ one from the other. This confirms the conclusion based on the ^{27}Al n.m.r. spectra that there are several species present but shows further that the composition is variable. Unfortunately, the closeness of the hydroxide resonances makes it difficult to monitor changes in relative intensity with change in composition and we have not been able to separate the spectra of different species. The integrals show that overall there are equal numbers of H_2O and OH protons.

We have already shown that if these hydrolysed solutions are made up to be partially deuteriated, then the HOH and HOD ligands attached to aluminium have different isotope shifts, and on $[Al(H_2O)_6]^{3+}$ show fine structure which permits the number of water ligands to be counted.[7-9] The primary HOH/HOD isotope splitting also allows water and hydroxide ligands to be differentiated. We therefore decided to apply this technique to the solutions described here and chose two in the concentrated series with $m = 1.2$ and 2.5. We also investigated the effect of temperature on the form of the spectra. The results for $m = 1.2$ are shown in Figure 6 where the water ligand resonances are split into unequal doublets while the signals ascribed to OH protons show no signs of such structure. Unfortunately, it has not so far proved possible to observe any fine structure of the water resonances though this is probably a physical limitation of the system due to the rate of motion of the polymeric species

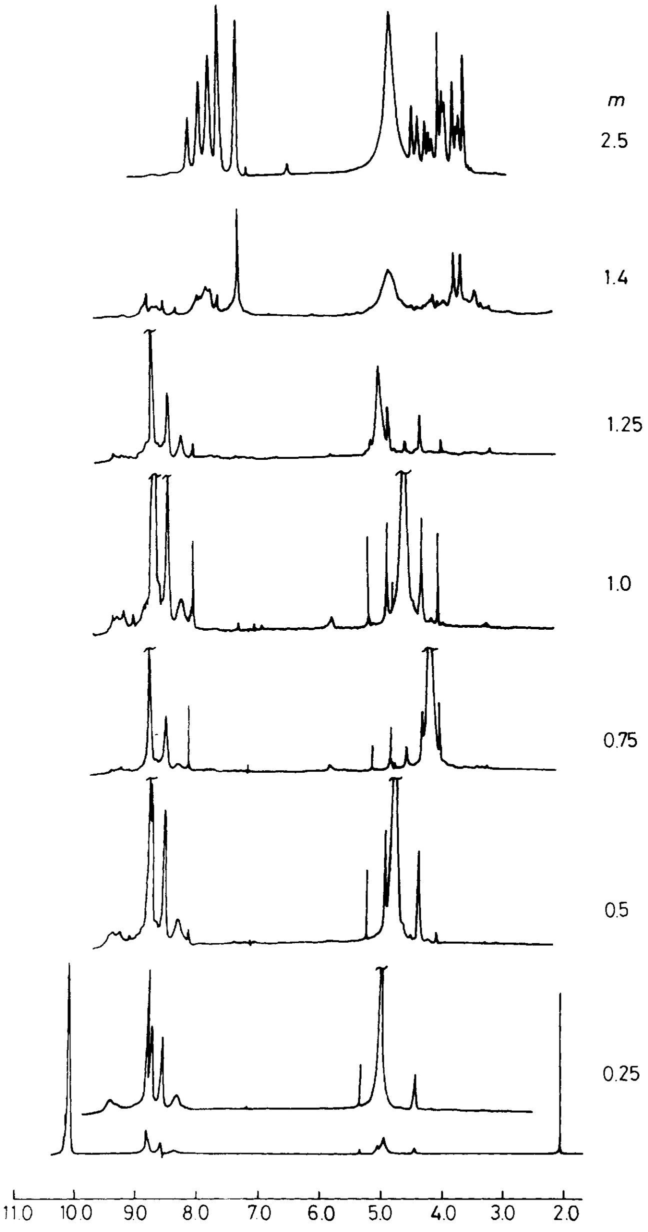


Figure 5. Proton n.m.r. spectra at 400 MHz of dilute metal hydrolysed solutions at different values of *m* following drying and dissolution in [$^2H_6$]acetone. The bottom spectrum is complete and shows the resonances of the aqua cation at 10.2 p.p.m. and of the solvent at 2.05 p.p.m. These are omitted from the remaining spectra. The resonance of variable position and high intensity near 5 p.p.m. is due to free water and the remaining signals arise either from co-ordinated water (7—10 p.p.m.) or from co-ordinated OH (3—6 p.p.m.)

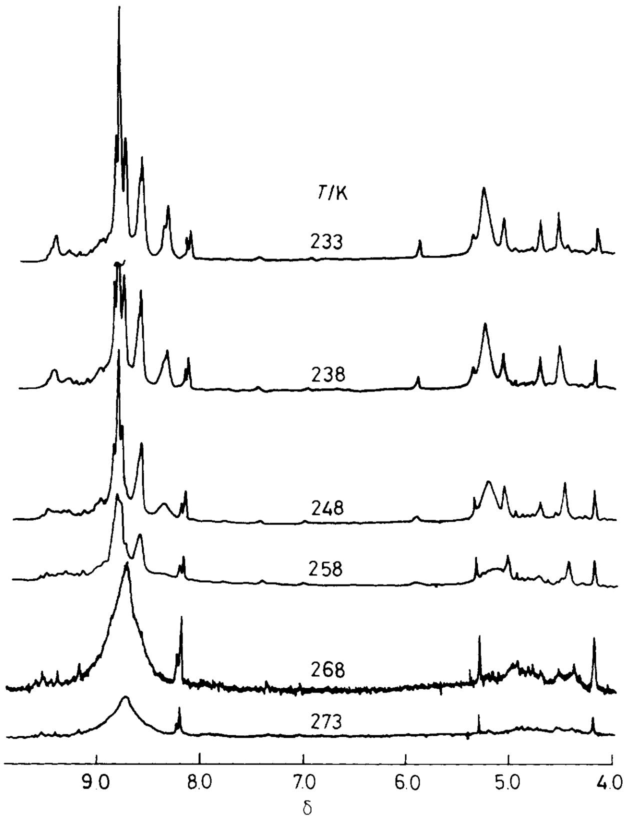


Figure 6. Proton n.m.r. spectra at 360 MHz of a concentrated metal hydrolysed solution with *m* = 1.2 as a function of temperature. The hydrolysis was carried out in 25% D_2O

being past the T_1 minimum at these high magnetic fields (where T_1 is the proton dipole–dipole relaxation time).[9] The different species behave differently with change in temperature, the major species showing intramolecular exchange and line broadening as the temperature increases while a minor species represented by resonances at 8.2 and 4.2 p.p.m. actually becomes better resolved and shows no tendency to exchange. Figure 7 shows the spectra for $m = 2.5$ and the difference with Figure 5 will immediately be evident. The water resonances show the expected isotope splitting and this is lost in some of the resonances as the temperature is increased. It is clear, however, that these spectra are not so sensitive to temperature as are the oligomer spectra. There are more hydroxide resonances at the lowest temperature but this is not due to the onset of coalescence at high temperature but to changes in chemical shift which cause lines to merge. Neither does the free water appear to be involved significantly in any exchange process, even at 273 K. The hydroxide region is rather sensitive to temperature and no doubt to small changes in species make-up, and this perhaps explains some of the variability in the spectra.

The room-temperature metal hydrolysis produces a solution which contains entirely the tridecamer and which is capable of giving sulphate crystals of this cation some weeks after preparation, in contrast to base hydrolysed solutions which quickly become useless for this purpose. The tridecamer thus appears to be extremely stable in the absence of dissolved foreign salts and we decided to investigate the effect of ageing in the presence of such dissolved materials in comparison with the stable, room-temperature hydrolysed solution. Solutions were made up to 0.2 mol dm^{-3} in Al and 1.0 mol dm^{-3} in salt and examined after standing at ambient temperature. In almost all cases the addition of salt caused the solution to go cloudy. The alkali-metal salts were left for 3 d and while $KClO_4$ had almost no effect, the cloudiness increased along the series CsCl < KCl < NaCl < LiCl. However, in the latter case we found that all the aluminium had been precipitated with the Li and this probably means that some lithium aluminate phase has been precipitated. With the alkaline-earth metal salts, clouding was found to occur more rapidly and it was possible to provide a ranking after only 21 h, which includes some alkali-metal salts for comparison with the previous experiment. Thus cloudiness increases in the order [$Ba(ClO_4)_2 \approx Sr(ClO_4)_2 \approx NEt_4Cl$] < NaBr < [$NaCl \approx Mg(ClO_4)_2 \approx BaBr_2 \approx NaNO_3$] < [$BaCl_2 \approx$

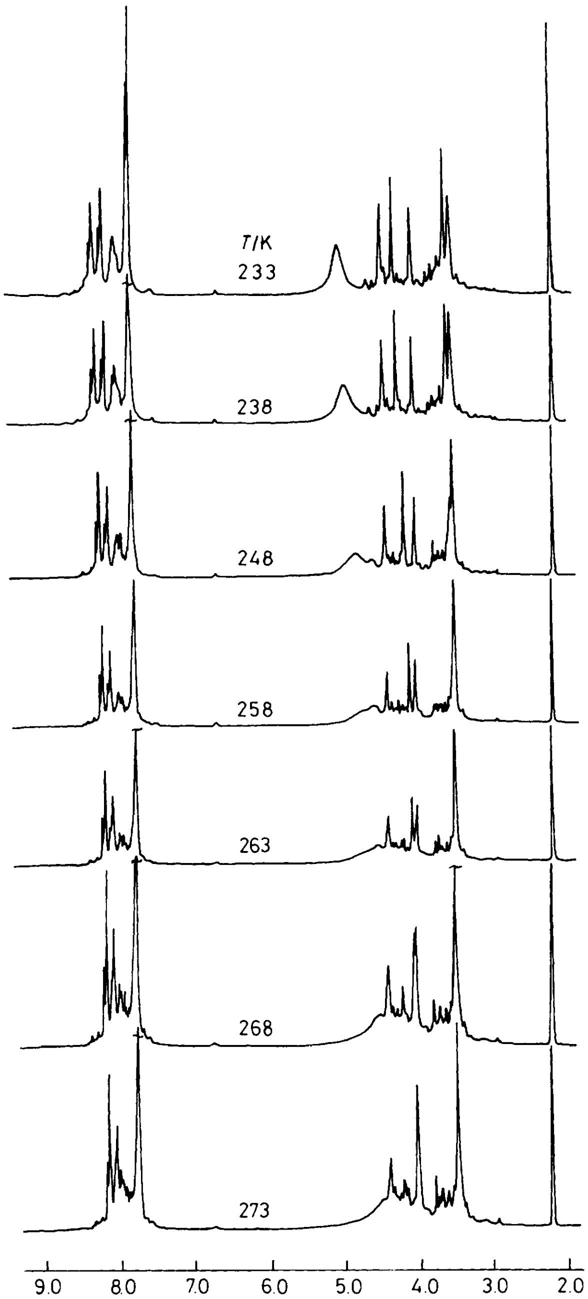


Figure 7. Proton n.m.r. spectra at 360 MHz of a concentrated metal hydrolysed solution with $m = 2.5$ as a function of temperature. The hydrolysis was carried out in 25% D_2O

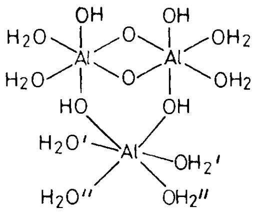
$Sr(NO_3)_2 \approx CaCl_2] < MgCl_2$. The salts $Mg(NO_3)_2$ and $CaBr_2$ produced heavy cloudiness also but accompanied by some gel formation. Ageing in these solutions, as we have already pointed out,[3] is a complex reaction which may or may not produce precipitates, the two extreme terminal conditions being full precipitation of a solid phase from a fluid supernatant or the solidification of the whole to a transparent glass, and the cloudiness and gel formation observed here are presumably precursors of these two types of behaviour. The effect does not appear to be simply a manifestation of the influence of the ionic strength of the medium since the type of anion and cation present so obviously influence the rate. The influence of the anions increases in the order $ClO_4^- < Br^- < Cl^-$ and of the cations in the order $Cs^+ < K^+ < Na^+$ and $Ba^{2+} < Sr^{2+} < Mg^{2+}$. Clearly from these rankings, the size of the ion is important, the smaller the ion the stronger is the effect.

Discussion

The Oligomer System at m $\leqslant$ 1.4.—These solutions differ from the base hydrolysed solutions in that they contain much less dissolved inorganic salt. The spectral data obtained at these relatively high concentrations and low m are closely similar to those presented in Part 8[1] but the absence of excess of sodium perchlorate seems to give better resolved spectra and the resonance of free water moves with m in a different manner which permits us to know with certainty that the system has five bound hydroxide resonances. Sufficient data are presented in Figures 5 and 6 to show that the solutions contain principally a major component and three minor components. The first is represented by the unequal doublet at 8.8 p.p.m. and the singlet at 8.6 p.p.m. in the bound water region and two hydroxide resonances at about 4.4 and 5.0 p.p.m. with intensity ratio 4:2:2:1:1. The minor components are a species (a) with water resonance of intensity 2 at 8.2 p.p.m. and hydroxide resonance at 4.2 p.p.m. of intensity 1, both resonances showing no tendency to exchange on heating, a species (b) with two broader resonances at 8.4 and 4.7 p.p.m. which exchange much more readily but whose intensity is difficult to define, and a species (c) with resonances at around 9.5 and 5.4 p.p.m. which sharpen appreciably on heating but whose relative intensities are also difficult to define. We believe that we can assign structures with reasonable certainty to the major component and to species (a).

The minor component (a) has a very simple spectrum which shows it contains one water ligand per hydroxide. Further, the fine structure in the deuteriated sample is not resolved even though the lines are quite narrow. This is consistent with there being relatively few water ligands on a given aluminium and with there being no contribution from the bound hydroxide to this fine structure.[8] All water or hydroxide ligands are identical. These data can be explained in terms of a structure of $Al(OH)_2(H_2O)_2$ units linked together by double hydroxide bridges and which most likely would be hexameric rings in the form of the gibbsite structure. This has a hydrolysis ratio, m, of only 2, whereas that of the overall mixture is 2.5. There is, however, no reason why a minor constituent should not have m different from 2.5.

The major component is much more difficult to assign. Since it contains the bulk of the aluminium then it must have a hydrolysis ratio near 2.5 or slightly higher.[1] The ease with which it is converted into the tridecamer on dilution suggests that the structure should be that of a tridecamer fragment but its ^{27}Al n.m.r. chemical shift of only 4 p.p.m., when compared with that of 12 p.p.m. for the tridecamer, indicates that there must be important differences between the two structures. The proton n.m.r. spectrum shows that there are three types of water ligand in the ratio 2:1:1 and two types of hydroxide and that there are two water ligands per hydroxide. Thus, if the oligomer contains n aluminium atoms and $m = 2.5$ its formula has to be $[Al_n(OH)_{2.5n}(H_2O)_{5n}]^{\frac{1}{2}n+}$. This clearly contains too many ligands and we are forced to accept that the oligomer also contains oxide bridges. The formula is then $[Al_nO_x(OH)_{2.5n-2x}(H_2O)_{5n-4x}]^{\frac{1}{2}n+}$ which contains $7.5n-5x$ oxygen ligands and which can be accommodated by n aluminium atoms if x is sufficiently large. This formulation implies either that n is even, or if n is odd then m differs from 2.5. We cannot solve the structure from this information alone since the number of ligands needed for a given n is not unique, for instance a pentamer could have 19, 21, or 23 oxygen ligands in various states of protonation. The problem reduces to finding a ligand number which also satisfies the symmetry requirements to



reproduce the intensities in the proton spectrum. We have looked at the possibilities for $2 \leqslant n \leqslant 5$ and have only found one structure which has the necessary properties. This is the 3,8 cation with two oxide bridges shown above.

It is to be emphasised that this is the form most likely to exist in acetone solution, though the OH and O bridges could be interchanged without altering the symmetry. In the acidic aqueous solution in which the oligomer is normally encountered its structure is probably similar according to the ^{27}Al n.m.r. chemical shift, but there may be a dynamic interchange of protonated sites. There are two aluminium environments with, in principle, two ^{27}Al n.m.r. chemical shifts. The lines are no doubt broad and overlapping and this, coupled with a dynamic effect, could account for the small range of chemical shifts that we have recorded for this resonance.[1] The structure can also be easily converted into that of an Al_3O_{13} fragment of the tridecamer simply by the loss of a water ligand from the unique aluminium atom and the formation of a bridge to one of the oxide bridges. The slow growth of the tridecamer from such units would not seem to be unreasonable. It may also be significant that as the temperature is increased the hydroxide resonances show signs of splitting into higher multiplicity as would be required by a change in structure.

The Polymer System at m ≈ 2.5.—Both the ^{27}Al and ^{1}H n.m.r. spectra indicate that there is a hierarchy of different species formed in these solutions and the proton results show that, even at a given concentration, no composition is unique. We cannot suggest any detailed structures for the species formed but can make some general comments. The proton integrals are similar overall to those of the tridecamer and the ^{17}O n.m.r. spectra are identical with those of solutions of the tridecamer.[1,10] The inference is that the structures must be related to that of the tridecamer though many appear to lack the tetrahedrally co-ordinated aluminium. The proton chemical shifts cover the range between those of tridecamer and oligomeric species. We do not know the significance of this but it seems reasonable to suggest that it may indicate some reduction in the number of multiply bonding oxygen atoms and so less restrained structures with lower electric field gradients at aluminium and narrower lines than for the tridecamer. The change is, however, insufficient to affect the ^{27}Al n.m.r. chemical shift which is always well to low field of the oligomer resonance. Despite this lack of detail, we have been able to show clearly that these commercial hydrolysed solutions have a very complex chemistry, that their compositions are not fixed, and that determining any actual structures is not a trivial problem.

Acknowledgements

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