Aluminium-27 Nuclear Magnetic Resonance Studies of the Hydrolysis of Aluminium(III). Part 6.[1] Hydrolysis with Sodium Acetate

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If acetate anions are added to aluminium salt solutions, they are protonated by the strong acid $[Al(H_2O)_6]^{3+}$ which itself polymerises to form the dimer cation $[(H_2O)_4Al(\mu\text{-}OH)_2Al(H_2O)_4]^{4+}$ which loses two further protons. This is the only hydrolysis product detected and no evidence was obtained for the presence of the tridecameric polymeric cation in such solutions. If acetate is added to the extent that the ratio $[MeCO_2^-]/[Al^{3+}]$ is greater than 1.5, then acetate groups become attached to the dimer cation to form a complex which is presumably the precursor of the dialuminium dihydroxo tetra-acetate which is known to precipitate from aluminium acetate solutions. Changes in the ^{27}Al linewidths of the species observed provide a useful measure of the rates of the exchange processes present.

The significant step in the hydrolysis of aluminium salt solutions is probably the loss of a proton from $[Al(H_2O)_6]^{3+}$ to form the monomer hydrolysate, usually written $Al(OH)^{2+}$, which, however, seems never to be a major constituent of the solutions since it polymerises to form the dihydroxy-bridged dimeric cation.[2] The degree of hydrolysis may be forced by adding base, additions of up to 2.5 mol of base per mol Al being possible and the initially formed dimer is then converted into a tridecameric cation which may be formulated as $[Al_{13}(OH)_{32}]^{7+}$. Any means of removing protons from the system is of course equally effective in causing hydrolysis and even simple boiling of an aqueous $AlCl_3$ solution leads to loss of protons as HCl vapour.[3,4] This example suffices to show that the hexa-aqua-aluminium cation is effectively a strong acid, and indeed aluminium salt solutions will dissolve metals.[1,5] The dissociation to monomer seems insufficiently strong to account for this behaviour (K_d *ca.* 10^{-5})[6] and the driving force must be the displacement of the equilibrium caused by the subsequent dimerisation step. It has already been shown that addition of sodium acetate to $AlCl_3$ solutions results in the observation of possibly two new ^{27}Al n.m.r. resonances, which have been ascribed to the dimer cation, formed because the acetate anion is protonated by dissociation of the cation, and its acetate complex.[7] The present paper is an extension of this work and studies the dimerisation quantitatively over a wide range of acetate addition into the region in which the tridecameric cation would be expected to form.

Experimental

Solutions were made up by weight using AR sodium acetate and fresh AR hydrated $AlCl_3$. Spectra were obtained on a Bruker HFX3 instrument at 23.45 MHz and 25 °C using a ^2H lock with D_2O at a level of 10% in each solution. Data were collected in the Fourier-transform mode using two sets of accumulation conditions, the free induction decays (FID) being collected in 1K and expanded to 4K by zero filling for Fourier transformation in each case. Slow accumulation with a 500-Hz spectrometer window allowed only the monomer resonance to be observed, whose width could be measured to an accuracy of *ca.* 0.2 Hz. Fast accumulation with a window of 10 000 Hz gave a response from both monomer and dimer, though the scale was then too extended to allow accurate measurement of the width of the monomer signal. Quantitative estimates of the proportions of the two species were obtained, though uncertainties in the location of the baseline and overlap of the two resonances meant that a specialised technique based on manipulation in the time domain had to be developed. The FID from these samples consists of two components, one decaying rapidly and one slowly, and this difference can be used to separate them. The computer was programmed to print out the first 60 or so data points of each FID, representing the first 3 ms of the decay. This was plotted and the slowly decaying monomer signal (T_2 typically 30 ms) produced linearly back to zero time. The rapidly decaying dimer signal ($T_2 \approx 0.4$ ms) was then reproduced to zero time using an exponential extrapolation on this baseline. This procedure should give relative initial intensities to better than 12%, the main difficulty being to know the delay time for the signal to traverse the Butterworth noise filter.[8] The broad line of the acetate complexed dimer is not detectable under these conditions due to its short T_2 of *ca.* 50 μs, or one dwell time (sampling interval).

The complex resonance is, however, visible on a very high-field instrument (such as the 400-MHz Bruker at Sheffield)[7] which has a much wider band-width and also a greatly superior chemical shift dispersion. A set of measurements were thus made at 104.2 MHz and analysed using conventional curve analysis techniques.[9,10] In principle, this gives unequivocal data on the resonance of the complex though the underlying aluminium probe resonance of this spectrometer[7] means that a rather uncertain correction has to be made to the values. However, results agree with the low-field results, within the rather large experimental error.

Results

Some typical high-field spectra are shown in Figure 1 and one of the low-field FID plots is in Figure 2. The variation in species concentration derived from these data is shown in Figure 3 and the linewidth changes observed are in Figure 4. The data reported here are based on samples with constant Al concentration of 0.5 mol dm^{-3}, though we did examine a range of concentrations but found the n.m.r. technique to be too insensitive to detect any changes with metal concentration. The signal intensity of course falls in proportion to reductions in concentration and the accumulation time increases with the inverse square of concentration, so that the broad component becomes very difficult to observe and almost impossible to measure quantitatively in dilute solution. We also studied the effect of adding HCl to $AlCl_3$ or $AlCl_3$–NaO_2CMe solutions. The first, small additions of acid cause a reduction in the

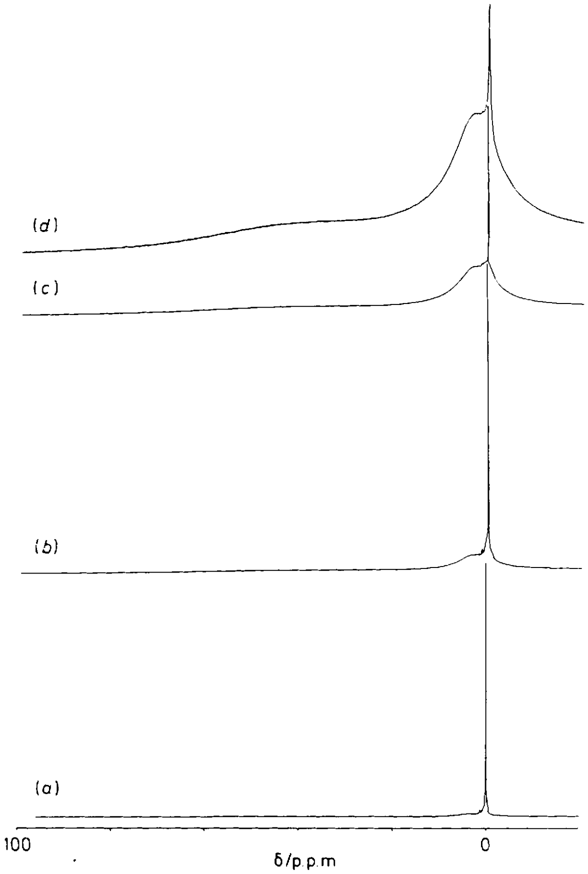

Figure 1. Aluminium-27 n.m.r. spectra at 104.2 MHz of solutions in H_2O-D_2O, 0.5 mol dm^{-3} in $AlCl_3$, and with various additions of sodium acetate. The concentration ratios [acetate]/[$AlCl_3$] are (*a*) 1.00, (*b*) 1.52, (*c*) 2.00, and (*d*) 2.58. The small, sharp peak to low field of the $[Al(H_2O)_6]^{3+}$ ion resonance is a spinning side-band

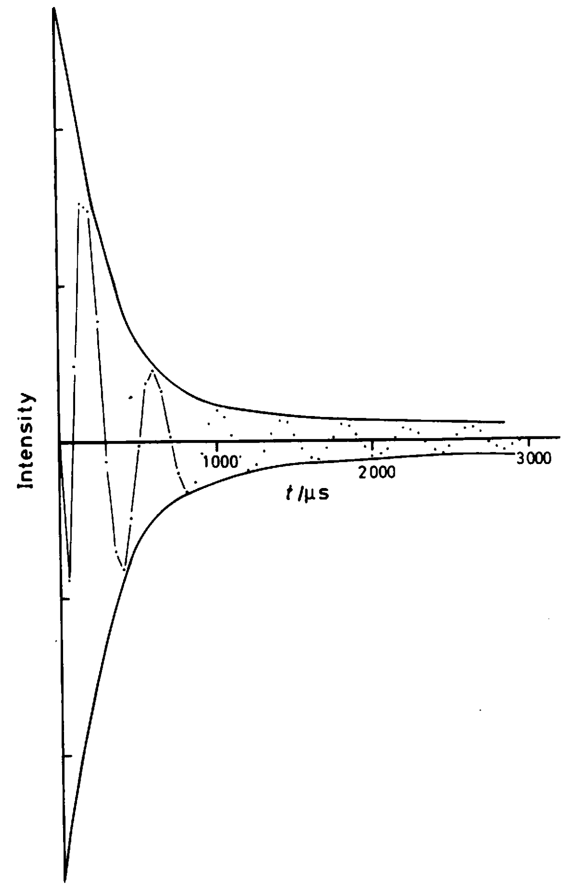

Figure 2. A typical FID plot of ^{27}Al data obtained at 23.45 MHz showing the slowly decaying monomer signal and the rapidly decaying dimer signal. The envelope is the calculated extrapolation to zero time. The points refer to actual data

monomer linewidth, from 5.6 to 3.2 Hz with an acid concentration of 0.015 mol dm^{-3}. The behaviour parallels that reported for more concentrated solutions.[11] Further addition of acid causes an increase in linewidth due to increased viscosity. The acetate-containing solution chosen for acid addition had an acetate : Al ratio of 2.74 : 1 and a broadened monomer linewidth of 46.4 Hz. Addition of acid reduced the linewidth and the changes observed were exactly the same as would have been expected if the acetate content of the solution had been reduced stoicheiometrically by the added acid (Figure 4, open circles). This is good supporting evidence that protonation of the acetate by hexa-aqua-aluminium is the essential step in the process. Some spectra were obtained at high temperatures also on the high-field machine. A sample with acetate : Al ratio of 2.58 : 1 was chosen for this experiment; its room-temperature spectrum is illustrated in Figure 1. Increasing temperature favoured the presence of the dimer over the other species and we observed clearly that the monomer resonance broadened but remained separate even at 353 K. We will argue below that the broadening occurs partially because the dimer : monomer ratio increases. Exchange between dimer and monomer then remains slow on our time-scale, a conclusion which modifies our earlier beliefs based on a more complex, less well understood system.[5]

Finally, since the solutions must contain both free and complexed acetate undergoing exchange, a ^{13}C spectrum was obtained at high field on a sample with an acetate : Al ratio of 2.58 : 1. Both carbonyl and CH_3 carbons appeared as broad

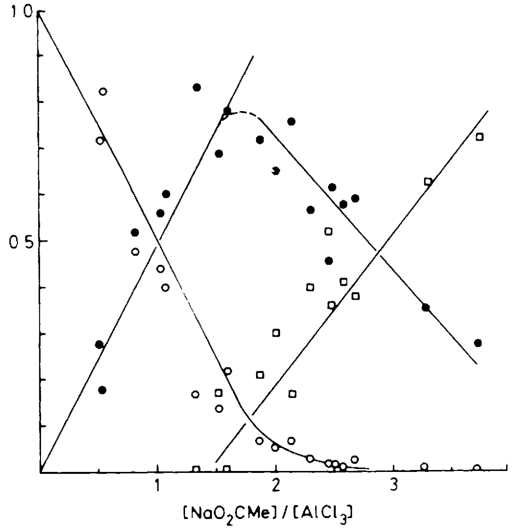

Figure 3. The variation in concentration of $[Al(H_2O)_6]^{3+}$ (○), dimeric $[Al_2(\mu\text{-}OH)_2(H_2O)_{8-n}(OH)_n]^{(4-n)+}$ (●), and dimer complexed by acetate (□), as a function of the concentration ratio [acetate]/[$AlCl_3$]. The lines covering the range of ratios 0—1.5 were calculated on the basis that all the acetate was protonated by hydrolysis of the Al and that the value of *n* in the dimer was 2. The lines drawn at higher ratios have no significance other than to act as a guide through the rather scattered data

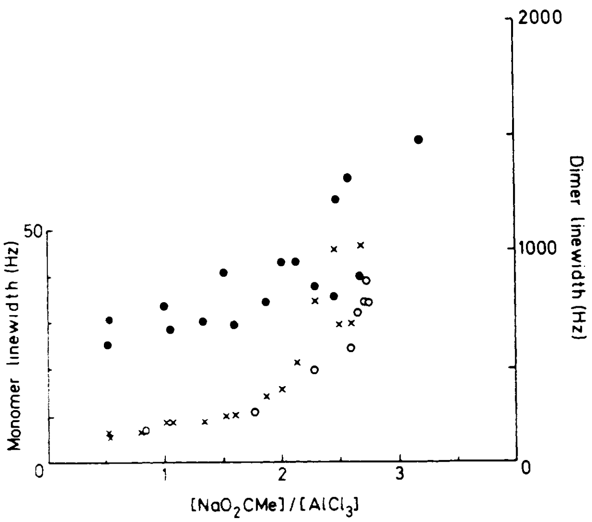

Figure 4. The linewidths of the monomer (×, ○) and dimer (●) ^{27}Al resonances as a function of [NaO_2CMe]/[$AlCl_3$]. The points (×) in the monomer plot arise from NaO_2CMe–$AlCl_3$ mixtures and the points (○) from a solution with an acetate : Al ratio of 2.74 : 1 to which HCl was added. The effective acetate : Al ratio in this solution was calculated on the assumption that the added acid fully protonated a proportion of the acetate present

doublets with the classical two-site exchange shape. Since about half the aluminium is complexed by acetate in this sample, then the dihydroxo-complexes contain *ca.* 2.6 acetate ligands per two Al atoms on average. Clearly this is not a simple two-site exchange system, though we nevertheless calculate a lifetime for bound acetate on this basis of 3.0 ± 0.2 ms.

The pH values of a few solutions were recorded and are given below, in brackets, for acetate : Al ratios of 0.00 (2.34), 0.52 (2.53), 1.00 (2.67), 1.52 (2.84), 2.00 (3.16), and 2.48 (3.39).

Discussion

The changes in species concentration depicted in Figure 3 are typical of a series of equilibria of the type $A \rightleftharpoons B \rightleftharpoons C$ being forced to the right as more acetate is added. The accuracy with which it is possible to make these measurements using n.m.r. in this way is unfortunately too low to make any computational analysis of the results worthwhile so that although the existence of the species is shown unequivocally, details of the equilibria cannot be extracted. The pH measurements do allow us to give a firm estimate of the degree of hydrolysis of the dimer, since we may assume that virtually all the acetate anion is protonated, $K_a = 1.6 \times 10^{-5}$.[12] It is thus clear that while only dimer and monomer are the principal species present, the hexa-aqua-aluminium cation loses two hydrogen ions per aluminium, its concentration being halved when the acetate : Al ratio is unity. The dimer in this system should thus be formulated $[Al_2(OH)_4(H_2O)_6]^{2+}$ and is presumably the dihydroxo-bridged ion in a state of further hydrolysis, as has been proposed earlier on the basis of several different techniques.[13] The replacement of water or hydroxide ligands by acetate appears to proceed stepwise since the average acetate content of the complex ions is only about half that of the material which eventually precipitates. This process may be aided by the increasing availability of ionised acetate as the pH rises.

No evidence is ever obtained that the tridecamer cation may be formed, *i.e.* no sharp resonances were observed near 62.5 p.p.m., and this is probably prevented by the involvement of the acetate with the dimer. It has been suggested that the formation of this cation proceeds through interaction of dimer and local concentrations of $[Al(OH)_4]^-$,[2] but addition of NaOH to $AlCl_3$–NaO_2CMe solutions did not cause any to form, though such negative evidence does not disprove the earlier hypothesis.

The chemical shifts of the two dimeric species are for the complex, 38 ± 2 p.p.m., and for the dimer, 3.27 p.p.m. The latter is of course difficult to obtain precisely because of the width of the line, though its shift does appear to vary between 3.3 and 4.2 p.p.m.,[7] and this may also be caused by a variation in its state of hydrolysis. The low-field shift of the complex to 38 p.p.m. is also of interest, since it is unusually low field for aluminium octahedrally co-ordinated by oxygen ligands [14] and there is now evidence that this may be symptomatic of co-ordination by small-ring-forming bidentate ligands.[15] This conclusion is in accord with the composition of the complex which eventually precipitates from these solutions [16] and with the relative linewidths of the species, monomer : dimer : complex = *ca.* 10 : 700 : 6 000 Hz which correlates with increased distortion at Al down the series.

The changes in linewidth are also of interest in that the acid addition experiment shows that the monomer linewidth is determined by chemical factors. In fact, interpretation of linewidth changes in the spectra of quadrupolar nuclei is not straightforward since they depend among other things upon changes in viscosity, both macro and micro, in a way which is still not understood. In particular, the linewidths do not in general extrapolate to zero width at zero viscosity; there is likely to be a constant addition to be made in calculating any viscosity correction, and this cannot be separated when other line-broadening processes intervene.[11,17] Limited viscosity data are available for sodium acetate solutions [18,19] which is sufficient to suggest that the dimer linewidth is viscosity controlled. If then we normalise the monomer linewidths using the dimer linewidths we find a distinct though scattered trend for this to increase with the ratio [dimer]/[monomer]. This would be expected if the increase were caused by a reduction in monomer lifetime due to slow exchange between monomer and dimer. The monomer lifetime varies between 0.2 s at acetate : Al = 1.0 : 1 and 0.03 s at the values of *ca.* 2.5 : 1. These estimates carry a probable error of 25% and make very drastic assumptions about the equivalence in viscosity terms of sodium acetate and the present solutions which are effectively ($NaCl + MeCO_2H + Al$) species. Ignoring any viscosity correction, however, gives much higher exchange rates at the larger acetate : Al ratios.

It is instructive to consider the role played by the species $Al(OH)^{2+}$ which is considered to be the principal, initial product of hydrolysis. Clearly the interpretation given here is that the initial product is the dimer and this can be justified using the measured pH and the given formation constant of *ca.* 10^{-5} for $Al(OH)^{2+}$.[6] Thus at an acetate : Al ratio of 0.5 : 1, the concentration of $Al(OH)^{2+}$ is *ca.* 10^{-3} mol dm^{-3}, two orders of magnitude less than that of the dimer. The formation constant of the latter according to the reaction scheme given below is about unity. These values presumably can be extrapolated to the much lower concentrations used for earlier work, and suggest that the dimer will always be the dominant species. Such a suggestion is of course contentious in view of the mass of work whose interpretation has assumed otherwise, but it remains a fact that the dimer has now been characterised spectroscopically and crystallographically [20] whereas $Al(OH)^{2+}$ has not. These conclusions are of particular

$$[Al(H_2O)_6]^{3+} + Al(OH)^{2+} \rightleftharpoons [Al_2(OH)_2]^{4+} + H^+$$

importance to the current studies being undertaken into the complexation of both Al^{3+} or Ga^{3+} by bio-organic ligands in an attempt to discover how these ions are transported in the body, to produce respectively aluminium dementia in kidney dialysis or to concentrate in cancerous tissue.[21,22] A broad resonance in the octahedral region of the ^{27}Al spectrum in the presence of a ' proton sink ' (*i.e.* a substance likely to be protonated by Al^{3+} dissociation) may simply indicate the presence of the dimer rather than a complex and a means of distinguishing these possibilities will have to be found. Such complications are also likely in the gallium system, though their resolution will be much more difficult since the resonances of the complexes and hydrolysis products are too broad to observe. It is also difficult now to regard the acetate buffer used in many spectrophotometric studies as completely inert and perhaps this body of data should be re-assessed.[23,24]

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