Hydrogen–Deuterium Isotope Effects in the Proton N.M.R. Spectra of Hydrated Al^{III} Species

J. W. Akitt, Julie M. Elders, and Xavier L. R. Fontaine

Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT, U.K.

Proton n.m.r. spectra have been obtained for a number of hydrolysed Al^{III} perchlorate salt solutions dissolved in deuterioacetone, with which they exchange deuterium and become partially deuteriated: bound H_2O and OH entities can be distinguished since the former appear as HOD/H_2O doublets, though the isotope shift is negative, in contrast to the normal positive effect seen with free water; the resonances also contain a fine isotope shift structure which appears to permit the number of protons around a given Al to be counted and so potentially to provide structural information about the polymeric species present.

We have recently found it possible to advance our studies of the hydrolysis of Al^{III} salts using a technique which allows us to obtain the proton spectra of the various OH and OH_2 moieties present in the species formed. This is achieved by hydrolysing an aqueous perchlorate salt, drying over P_2O_5, and then dissolving the remaining solid in deuterioacetone. The proton exchange rate is then sufficiently slow that the chemically individual sites can be distinguished, water protons to low field and hydroxide protons a little to high field of these. It has recently been shown that fine structure can be observed in partly deuteriated carbohydrates and that this sheds light on the hydrogen bonding network present in solution. This has been designated as SIMPLE n.m.r. (Secondary Isotope Multiplet n.m.r. spectra of Partially Labelled Entities).[1—3] We decided to investigate whether this technique would allow us to probe the intimate environments of the protons in the polymeric cations which are formed upon hydrolysis of Al^{III} and whose structures are even today unknown, the only well

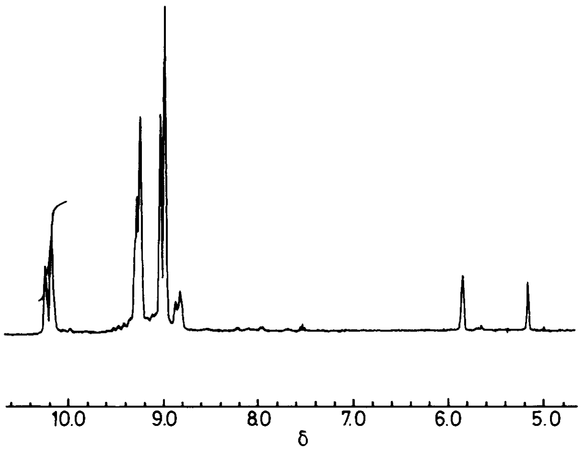

Figure 1. The 400 MHz n.m.r. spectrum taken at −30 °C, of a solution containing $Al(ClO_4)_3$ and sodium butyrate in the ratio of 1 : 1.5, dried and redissolved in [$^2H_6$]acetone. The resonances of solvent, alkyl protons, and remnant free water are not shown. The bound water molecules appear as doublets after deuterium exchange with the solvent, whereas the two OH resonances remain as singlets. The signals at *ca.* δ 10.2 are due to $[Al(H_2O)_6]^{3+}$ and the remainder to polymeric, hydrolysed cations. The integral trace was used to determine the fraction deuteriated.

characterised species being the tridecameric cation, $[Al_{13}O_{40}H_{48}]^{7+}$.[4] Partial deuteration is carried out by performing hydrolyses in H_2O/D_2O mixtures, or by giving a solution in deuterioacetone sufficient time for deuterium exchange with the solvent to take place. The resulting spectra are highly complex and contain a wealth of information, whose preliminary interpretation we report here and indicate some unusual features which have emerged.

Solutions which have been subjected to only moderate, forced hydrolysis contain a significant proportion of unchanged $[Al(H_2O)_6]^{3+}$ and the behaviour of this species forms a basis upon which the other species may be judged. The ^1H spectrum of the all proton form of this cation is a singlet resonating well to low field, at about 8 p.p.m. from the solvent resonance (CD_2HCOCD_3) which has a shift of δ 2.06. The shift is temperature dependent and a small doubtlet splitting has been reported previously,[5] which we will show is an isotope effect due to the then unsuspected exchange of deuterium with the solvent. The doublet splitting is clear when partially deuteriated samples are examined at high field (400 MHz using a Bruker WH 400) and arises from the H_2O and HOD molecules bonded to the aluminium. The isotope shift is −0.07 p.p.m. between HOH and HOD (the latter to low field) in complexes with the remaining five ligands in the all proton form. The negative shift is unusual and substantial and is to be contrasted with that in water in organic solvents where it is 0.03 p.p.m. with HOD to high field.[6]

The isotope shift is believed to arise because there is a slight shortening of the bond to H upon substitution of the other H by D.[7,8] The water in the complex is subject to the strong electric field of $[Al]^{3+}$ and we observe in the spectrum illustrated in Figure 1 that the isotope effect is less in the hydrolysed species, which carry a lower net charge. This suggests that the electric field may cause the reversal of sign of the isotope shift. The bond shortening would increase the downfield influence of the field[9] but is insufficient to explain the actual magnitude observed and we suggest that a change in polarisability of the water may play some part.

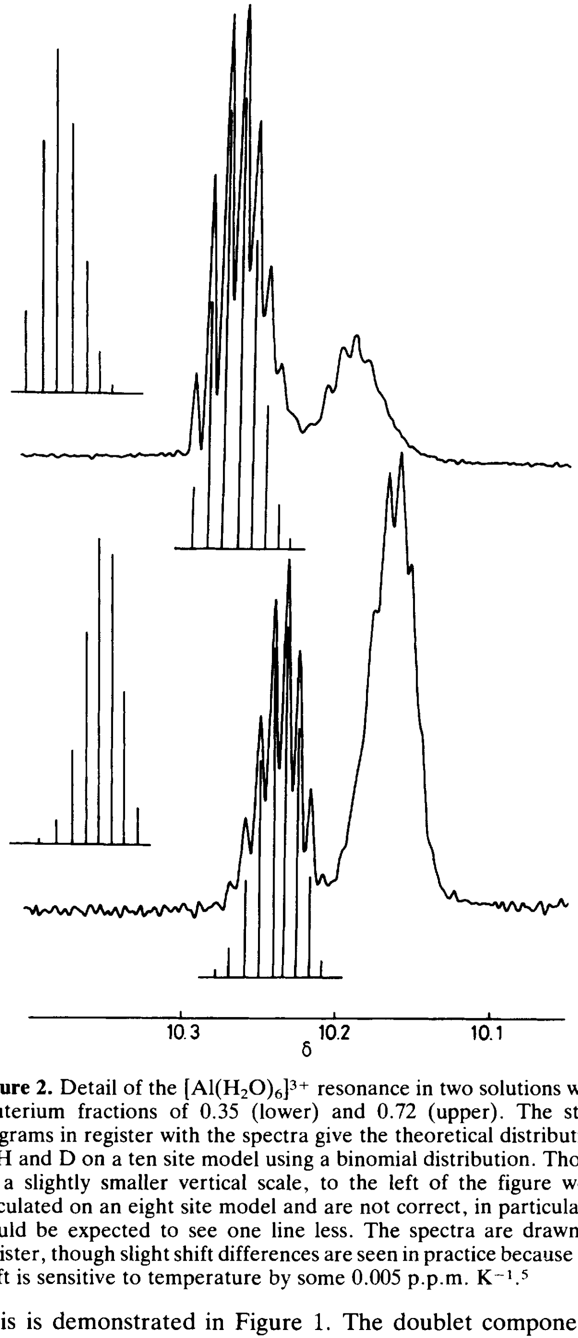

Figure 2. Detail of the $[Al(H_2O)_6]^{3+}$ resonance in two solutions with deuterium fractions of 0.35 (lower) and 0.72 (upper). The stick diagrams in register with the spectra give the theoretical distribution of H and D on a ten site model using a binomial distribution. Those, on a slightly smaller vertical scale, to the left of the figure were calculated on an eight site model and are not correct, in particular it would be expected to see one line less. The spectra are drawn in register, though slight shift differences are seen in practice because the shift is sensitive to temperature by some 0.005 p.p.m. K^{-1}.[5]

It will be immediately obvious that this isotope splitting is of practical use in that it distinguishes bound water and OH resonances in these spectra, the latter always being singlets. This is demonstrated in Figure 1. The doublet components also exhibit a small secondary splitting which is particularly well resolved in the HOD resonances. The multiplet structure of all the resonances can be revealed by judicious line narrowing and two examples with different degrees of deuteriation are shown in Figure 2. The lines in the HOD multiplets should each be triplets due to H–D spin–spin coupling,[6] but this fine structure is hidden by the linewidth. The lines are separated by 0.0088 p.p.m. in the HOD multiplet and by 0.0082 p.p.m. in the H_2O multiplet. This is the wrong relative order if isotope shifts depend upon relative mass changes but could result from a change in polarisability in the electric field. The lines in the H_2O multiplet are also broader than in that due to HOD even though there is no H–D coupling hidden in the former. It seems possible that this may be because the two protons of H_2O have slightly different orientations relative to the remainder of the complex and so experience slightly different isotope effects. This long range isotope effect is also negative. The intensity patterns in both the HOD and HOH multiplets are identical and have the correct binomial distribution for partition over ten sites. Isotopic substitution anywhere in the remainder of the complex then has the same effect, the implication being that the effects are transmitted *via* the aluminium cation rather than over the surface *via* a hydrogen bonding network. In the latter case only the eight positions *cis* to the ligand giving the main isotopic shift would be expected to have an influence. The involvement of the aluminium is supported by there being an isotope shift also in the ^{27}Al resonance of the complex, with the fully deuteriated form 0.22 p.p.m. downfield of the fully protonated form.

These conclusions presumably also will apply to the fine structure observed on the ligand resonances of hydrolysed species. It is not our purpose in this note to address fully the much more complex problem of their structure, though we can observe that the multiplicity of the bound water resonances to high field of the aquaion resonances is only four or five. These species then have relatively few protons per aluminium ion and must contain many bridging OH ligands. The most likely species thought to be present in solutions containing carboxylate anions or in partly hydrolysed solutions was a form of a dihydroxo bridged dimer with up to eight protons per aluminium[10] but the present results indicate that this view will have to be reassessed. A more highly condensed trimeric[11] or tetrameric structure may be appropriate and the exciting possibility now exists that these structures may be solvable.

We thank the department of Inorganic and Structural Chemistry at Leeds for time on the very high field n.m.r. spectrometer.

Received, 3rd March 1986; Com. 290

References

1 J. C. Cristofides and D. B. Davies, *J. Chem. Soc., Chem. Commun.*, 1982, 560; 1985, 1533.
2 J. C. Cristofides and D. B. Davies, *J. Am. Chem. Soc.*, 1983, **105**, 5099.
3 J. C. Cristofides and D. B. Davies, *Magn. Reson. Chem.*, 1985, **23**, 582.
4 J. W. Akitt and A. Farthing, *J. Chem. Soc., Dalton Trans.*, 1981, 1617.
5 J. W. Akitt, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 289.
6 J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Chem. Phys.*, 1962, **37**, 150.
7 C. Jameson, *J. Chem. Phys.*, 1977, **66**, 4983.
8 L. J. Altman, D. Laungari, G. Gunnarsson, H. Wennerstrom, and S. Forsen, *J. Am. Chem. Soc.*, 1978, **100**, 8264.
9 A. D. Buckingham, *Can. J. Chem.*, 1960, **38**, 300.
10 J. W. Akitt and J. M. Elders, *Bull. Soc. Chim. Fr.*, 1986, 10.
11 P. L. Brown, R. N. Sylva, G. E. Batley, and J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1985, 1967.