

A Nuclear Magnetic Resonance Study of the Solvation of Aluminium Perchlorate by Water and Acetonitrile; Separate Resonances from Differently Hydrated Aluminium Ions

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IN a number of cases¹⁻⁹ separate ^1H n.m.r. resonances have been obtained from 'bound' and 'free' solvent molecules in metal-ion/solvent systems.

Here we describe a series of proton resonances obtained from differently hydrated aluminium ions in solution in a mixed water-acetonitrile solvent

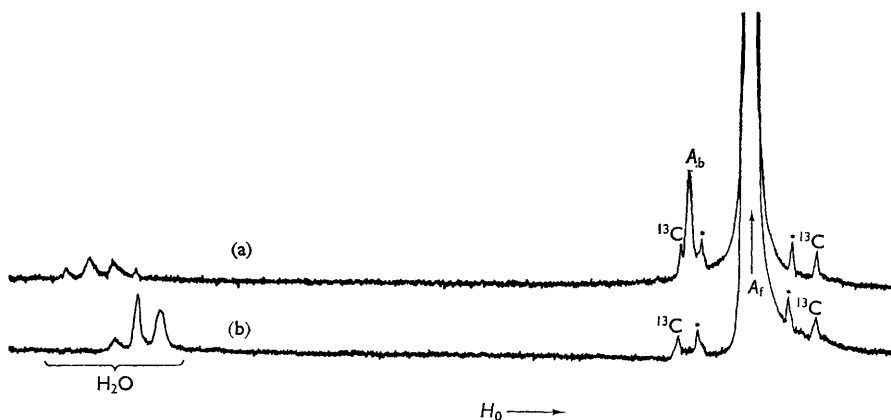


FIGURE 1. Survey ^1H n.m.r. spectra of $\text{CH}_3\text{CN}:\text{Al}(\text{ClO}_4)_3:\text{H}_2\text{O}$ solutions of molecular composition 57.8:1:2.3 (spectrum a) and 4.4 (spectrum b). (^{13}C denotes ^{13}CH satellites; * spinning sidebands; A_t , resonance from free acetonitrile; A_b , resonance from bound acetonitrile molecules; H_2O , resonances from differently aquated Al^{3+} ions.)

system. The use of acetonitrile as the predominant medium slows down the transfer of water protons between free and bound sites and thereby assists the observation of separate resonances. It also enables studies to be made of solutions in which virtually all the water molecules are bound to ions.

Figure 1 shows survey ^1H n.m.r. spectra of solutions of molecular composition $\text{CH}_3\text{CN}:\text{Al}(\text{ClO}_4)_3:\text{H}_2\text{O}$ of 57.8:1:2.3 and 4.4, respectively. The very large resonances, A_f , are those of free acetonitrile (^{13}C H and spinning side-bands are indicated); the resonance A_b is from acetonitrile bound to the aluminium ions in the solution of smaller water content. The series of small resonances, H_2O , to low field are from various solvated ions containing water.

In an anhydrous solution of aluminium perchlorate in MeCN the strength of the A_b resonance indicates an approximate solvation number of 2.8 at 27° for MeCN; bound MeCN resonances disappear when a value of ~ 4 is reached for the $\text{H}_2\text{O}/\text{Al}^{3+}$ ratio, R . A resonance from 'free' water occurs for $R \approx 5.3$ at $\tau \sim 6$ p.p.m. As R is increased the free water resonance broadens rapidly and finally merges with that from 'bound' water molecules. It is clear that at this temperature (27°) exchange processes would make it impossible to obtain separate proton resonances from free and bound water molecules in solutions of aluminium perchlorate in water alone.

Figure 2 shows the various resonances from bound water molecules for different values of the $\text{H}_2\text{O}/\text{Al}^{3+}$ ratio, R . It is seen that six resonance regions can be distinguished and these are considered probably to correspond to solvated Al^{3+} ions containing one to six water molecules respectively on going from low to high field. Sub-structure within these regions corresponds to different sub-species (see below). The broader resonance to highest field is found to sharpen on double irradiation of the ^{27}Al nucleus showing that it is caused by unresolved, partially collapsed, Al-H couplings. This broad resonance of the 6-aquo-species, and the sharp one found for 5-aquo-, are as expected when taking into account the interaction of the quadrupole moment of the ^{27}Al nucleus with field gradients—the latter should be particularly small for the, presumably octahedral, 6-aquo-solvated ion, and greater (leading to quadrupole relaxation and collapse of Al-H fine structure) for the 5-aquo-ion.

Multiple ^{27}Al resonances, with broad and sharp components, have also been obtained from a similar series of solutions. Infrared spectra show that for the lower R values the perchlorate ions also participate in the primary 'solvation' shell as

bidentate and as unidentate ligands. This explains the low solvation number of acetonitrile in the anhydrous solution and, together with geometrical isomerism involving solvated water molecules,

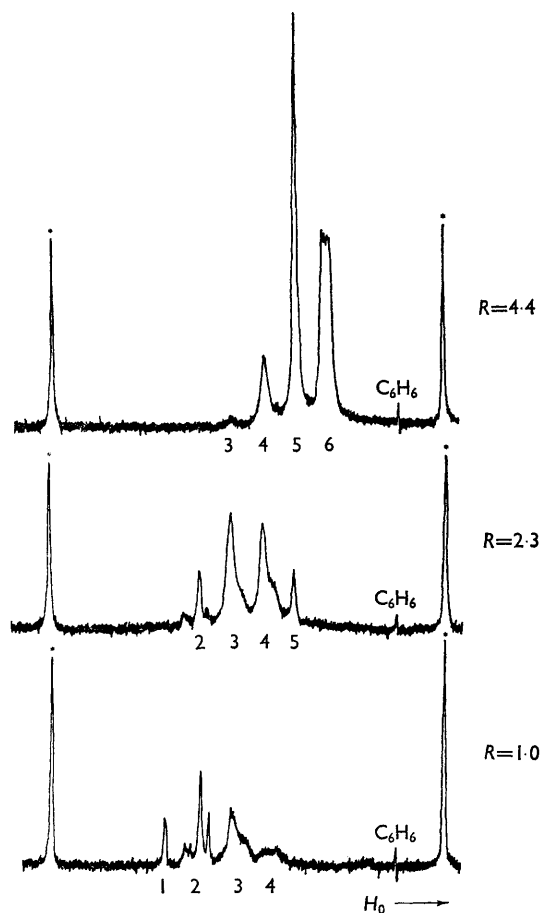


FIGURE 2. ^1H resonances of the n.m.r. spectra from dilute solutions of $\text{Al}(\text{ClO}_4)_3$ and water in acetonitrile. (R denotes the $\text{H}_2\text{O}:\text{Al}^{3+}$ molecular ratio in these solutions. The numerals show our tentative assignment of the H_2O resonances in terms of the number of water molecules in each aquated Al^{3+} species. * denotes reference frequency markers; C_6H_6 the resonance from a small amount of benzene in the CH_3CN solvent.)

probably contributes to the sub-structure observed in some of the water resonances.

Further work is being carried out on these and

similar solutions at various temperatures in order to elucidate the details of the solvation equilibria.

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- ¹ J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 1962, **37**, 1579.
- ² Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 1058, 1066.
- ³ S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, 1966, **44**, 3148.
- ⁴ N. A. Matwiyoff, *Inorg. Chem.*, 1966, **5**, 788.
- ⁵ A. Fratiello, R. Schuster, and D. P. Miller, *Mol. Phys.*, 1966, **11**, 597.
- ⁶ A. Fratiello and D. P. Miller, *Mol. Phys.*, 1966, **11**, 37.
- ⁷ J. F. Hinton and E. S. Amis, *Chem. Comm.*, 1967, 100.
- ⁸ J. F. Hinton, L. S. McDowell, and E. S. Amis, *Chem. Comm.*, 1966, 776.
- ⁹ A. Fratiello, D. P. Miller, and R. Schuster, *Mol. Phys.*, 1967, **12**, 111.