Hydrolysis and Dimerisation of Aqueous Aluminium Salt Solutions

By J. W. AKITT, N. N. GREENWOOD,* and G. D. LESTER

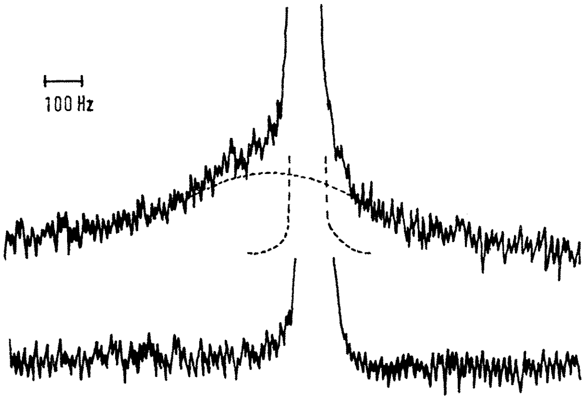
(*Department of Inorganic Chemistry, The University, Newcastle upon Tyne* NE1 7RU)

Summary Direct evidence for a dimeric cationic aluminium species in acidic aqueous solutions of aluminium salts has been obtained by means of ^{27}Al n.m.r.; the species undergoes rapid proton exchange with bulk water at $-50°$ but not with the hexa-aquoaluminium ion.

BY using ^{27}Al n.m.r. at 23·45 MHz and a temperature of about 25°, we have detected the presence of a dimeric aluminium ion in acidic solutions of the chloride and nitrate salts. Such species have often been postulated, particularly in the least acid solutions, but this is the first direct experimental evidence for their existence. We have observed that the area of the ^{27}Al resonance in these solutions is markedly pH-dependent, the signal obtained from a 2M-solution of pH 2·5 having only one third the area of the signal obtained at pH 0. The changes in peak area with pH are consistent with the formation of a dimeric hydrolysed species $[(H_2O)_nAlOH]_2^{4+}$, a slope of 1·8 being obtained from a graph of log x against pH + log y, where x = aluminium concentration deduced from the ^{27}Al measurement and y = the difference between the total aluminium concentration and x.

Experimental confirmation of this interpretation has been obtained by direct observation of the normally obscured dimer resonance. Such resonances are so broad[1] as to be unobservable under the conditions used to record the very narrow line of $[Al[H_2O)_6]^{3+}$. However, by using conditions under which this latter line is considerably saturated it is possible to obtain the dimer signal as a broad line 500 Hz wide and some 3·4 p.p.m. to low-field of the $[Al(H_2O)_6]^{3+}$ line. The spectra of solutions at pH 0 and pH 2·0 are compared in the Figure. The linewidth is consistent with a dimer; a higher polymer would be expected to give a much broader line. The observation of a separate dimer peak indicates that the lifetime of the dimer is considerably in excess of 3 msec. Our results thus confirm the interpretation of recent pH titration experiments in dilute solutions which suggested that significant dimerisation of the hydrolysed ion $[Al(H_2O)_5OH]^{2+}$ occurs.[2]

We have also re-investigated the low-temperature ^{1}H n.m.r. of these solutions at 90 MHz and have confirmed that at about −50° proton exchange is slowed sufficiently for separate resonances to be observed for bulk and complexed water.[3] When these resonances are studied in more detail it becomes clear that the area of the complexed water resonance decreases as the pH is raised, while the bulk water resonance area increases by the same amount. The resonance assigned to complexed water thus arises solely from the $[Al(H_2O)_6]^{3+}$ ion whereas the bulk water resonance arises both from solvent and from dimer when this is present, the two undergoing rapid proton exchange, even at these low temperatures. This observation may well be of significance in interpreting the values of hydration numbers found by n.m.r. for these systems particularly where they vary slightly from the expected integral number of six. In addition we have found that the temperature at which bound and bulk water signals coalesce depends on pH, the solutions of highest pH exhibiting fastest exchange so that careful control of pH should be maintained during kinetic experiments involving these systems.



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