Proton Chemical Shifts of Aqueous Aluminium Salt Solutions

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Proton chemical shifts have been measured in 1 M-aqueous solutions of aluminium nitrate, perchlorate, and sulphate over a range of temperature. The effects of hydrolysis and of acid addition have been studied in detail and have a marked influence on the shifts which arise as the exchange average between bulk water and three ionic environments: the cationic hydration complex $Al(H_2O)_6^{3+}$, which has a temperature-independent low-field shift, its second hydration sphere which has a small electric-field-induced shift, and broken water structure around the anion which thus introduces an upfield temperature-independent shift. Exchange averaging is not complete in the region in which measurements were made and this has introduced errors into previous determinations of hydration numbers. The measurements are shown to be consistent with a primary cationic hydration number of six.

THE proton resonance of 1M-aluminium salt solutions at room temperature is a broadened singlet lying some 0·6 p.p.m. to low field of the pure water resonance.[1-3] The shift increases with increasing temperature and Malinowski and Knapp used this data to estimate an effective hydration number of *ca.* 13.[2] It is, however, commonly accepted that the cationic hydration number of aluminium is only six [4-8] and it has been pointed out that this is sufficient to account approximately for the total measured shifts.[9]

A recent study of the shifts of protons in the hydration complexes of highly charged cations [10] has enabled a quantitative measure to be obtained of the influence of the anions on solution shifts.[11] The results confirm the previous assumption that anions make a marked upfield contribution, which opposes the cationic shift. When this anionic contribution is introduced into calculations involving aluminium salt solutions, it is found that the measured shifts can no longer be accounted for and that a further source of shift remains, giving a pronounced downfield contribution (Table 1). The electric field in the second hydration sphere of Al^{3+} is similar in magnitude to that in the first hydration sphere of K^+, and one might attribute the effect to the Al^{3+} second hydration sphere.[2] However, the chemistry of these solutions is

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[8] A. Takahashi, *J. Phys. Soc. Japan*, 1970, **28**, 207.

[9] J. W. Akitt, *J. Chem. Soc.* (*A*), 1971, 2865.

[10] J. W. Akitt, *J.C.S. Dalton*, 1973, 42.

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particularly complex;[12,13] hydrolysis renders them highly acidic and one must also consider the contributions due to H_3O^+, complexed OH^-, and the few percent of the dimeric ion $Al_2(OH)_2(H_2O)_8{}^{4+}$ which seems invariably to be present.[13,14] The fact that the proton linewidth varies by nearly an order of magnitude with small acid additions also suggests unsuspected complexity.[14] The purpose of this paper is to examine these possibilities in detail and determine the primary source of the excess of shift.

TABLE 1

Contributions to the shift (p.p.m.) of 1M-aluminium nitrate solutions with reference to water at 28 °C

Measured shift	−0·57
Contribution of $Al(H_2O)_6{}^{3+}$	−0·50
Contribution of $NO_3{}^-$	+0·16
Contribution not accounted for	−0·23

EXPERIMENTAL

Chemical shifts were measured usually at 90 mHz using a Bruker HFX3 instrument fitted with a variable-temperature device which was calibrated between 30 and 100 °C using ethylene glycol and at 0 °C with melting ice; ^{27}Al spectra were obtained at 23·45 mHz. A few proton results were also obtained at 60 mHz using a Perkin-Elmer R10 instrument. A capillary of distilled water served as a standard, except in solutions cooled below 0 °C when internal Me_4NCl was used. Measurements using the Me_4NCl standard at 28 °C were identical with those made using external water, confirming that Me_4N^+ is a good standard.[3] The measurements were made to 0·1 Hz using a counter and with the spectrometer locked to the standard signal. The accuracy of the results was limited by the linewidths, by the proximity of some signals to the standard, and by temperature variations and is probably not better than ±0·01 p.p.m.

Three methods were tried for measuring the susceptibility corrections: (*a*) t-butyl alcohol (2%) was added to each solution and the methyl resonance position compared with that in pure water; (*b*) calculation using tabulated ion susceptibilities;[15] and (*c*) by using calibrated static coaxial cells with different substances in the central compartment. The methods gave different results; t-butyl alcohol seems to be anion sensitive while (*c*) appeared to be the most reliable. Corrections for added perchloric acid were negligible,[16] and none were made for hydrolysed solutions since one is effectively adding only Na^+; this ion has low polarisability[15] and its molality varies only slightly over the full range of hydrolysis. Fortunately the corrections were also small for nitrate and perchlorate salt solutions and the error introduced by inaccuracies in the susceptibility determinations probably does not exceed ±0·01 p.p.m. A larger correction was needed for sulphate salt solutions and here the error may be ±0·02 p.p.m. The correction with respect to water probably does not vary significantly with temperature.[2]

Solutions were made up by weight using AnalaR [$Al_2(SO_4)_3$ and $Al(NO_3)_3$] or G.P.R. [$Al(ClO_4)_3$] reagents. Concentrations were checked by a back-titration method using EDTA. Hydrolysed solutions were prepared by dissolving weighed amounts of solid anhydrous sodium carbonate in aluminium salt solutions at 90 °C in covered beakers, followed by heating on a water-bath (1 h) and then making up to the correct volume. Acid additions were made using standardised perchloric acid solutions.

RESULTS

N.m.r. Measurements.—The corrected shifts are plotted in Figure 1(*a*) as a function of the ratios $[Na^+]:[Al^{3+}]$ or $[H^+]:[Al^{3+}]$, as appropriate, $[Na^+]$ and $[H^+]$ being the quantities of Na_2CO_3 and $HClO_4$, respectively, added to the so-called neutral salt solution. Proton linewidths at half height are shown in Figure 1(*b*). The variation of chemical shift with temperature for several solutions is illustrated in Figure 2, which also includes some linewidth data.

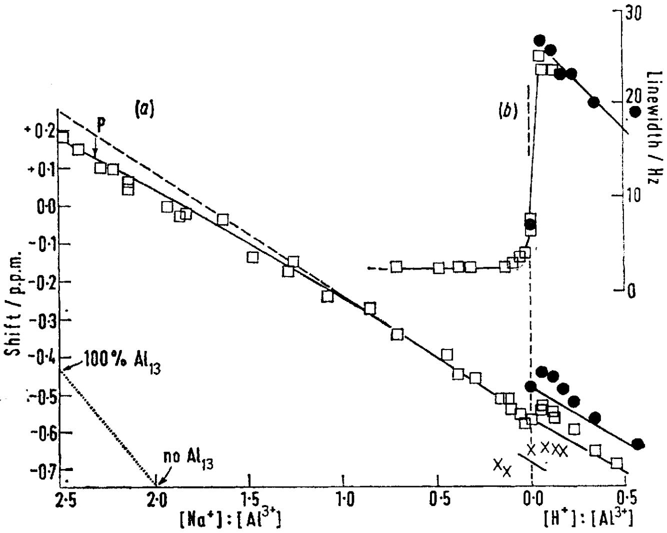

FIGURE 1 (*a*) Water proton chemical shifts as a function of acid or sodium carbonate addition: (●), $Al(ClO_4)_3$; (□), $Al(NO_3)_3$; (×), $Al(SO_4)_{1\cdot5}$ (all *ca.* 1M); (——) calculated shifts including probable effects of sphere-like $Al_{13}{}^{7+}$ and $Al_8{}^{4+}$ polymeric ions; (– – – –) calculated shifts ignoring hydrolysis products; (· · ·) proportion of $Al_{13}{}^{7+}$ polymeric ion; P is the increment due to polymeric ions. (*b*) Linewidths observed in perchlorate and nitrate salt solutions; sulphate salt solutions showed smaller changes. The linewidth changes by less than 1 Hz if hydrolysis is increased past the point shown

The chemical shift and linewidth varied markedly as the solution composition was changed. Addition of acid caused particularly abrupt changes, since the proton exchange rate is decreased when the dimeric ion is decomposed.[12,14] Thus the bound and bulk water resonances began to separate so that the latter moved upfield to produce a marked discontinuity in the shift plot and an increase in linewidth. Heating to 60 °C, however, increased the exchange rate, and the resonance moved to the position expected, downfield of the pure salt solution (Figure 2, dotted line). The sulphate salt behaves differently to the nitrate and perchlorate, as might be expected from its more complex chemistry.[13] Cooling an acidified solution slowed the exchange further and separate bound and bulk water

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[15] P. W. Selwood, 'Magnetochemistry,' 2nd edn., Interscience, 1956.

[16] R. W. Duerst, *J. Chem. Phys.*, 1968, **48**, 2275.

peaks could be observed at much higher temperatures than in normal pure solutions (Figure 3). Cooling, of course, caused the major, bulk resonance to move upfield[9] in the opposite direction to that expected.

At a high degree of hydrolysis the polymeric ion $Al_{13}O_4(OH)_{24}(H_2O)^{7+}$ is formed and can be detected by ^{27}Al n.m.r. spectroscopy.[12] Its concentration is also indicated in Figure 1(*a*).

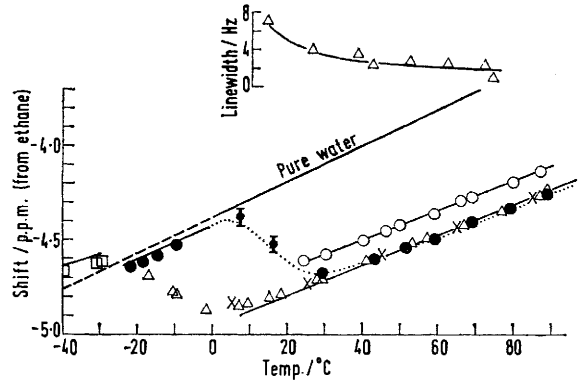

FIGURE 2 Water proton chemical shifts as a function of temperature: (●), $[H^+]:[Al^{3+}] = 0{\cdot}06:1$; (△), pure solution; (○), $[Na^+]:[Al^{3+}] = 0{\cdot}39:1$ (all in 1·06 mol kg^{-1} aluminium nitrate); (□), bulk water resonance in 3M-$AlCl_3$ (ref. 9). External water was reference above 0 °C and internal Me_4N^+ below 0 °C. (×), Results from ref. 6 in 1·47 mol kg^{-1} $Al(NO_3)_3$ adjusted to 1·06 mol kg^{-1}; (——) calculated shifts for $h_1 = 6$. A plot of the linewidth variation is also included in the upper part of the Figure

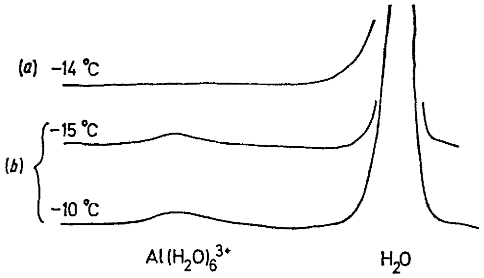

FIGURE 3 Water proton resonances in cooled 1M-aluminium nitrate solutions: (*a*), pure; (*b*), with added acid, $[H^+]:[Al^{3+}] = 0{\cdot}06:1$

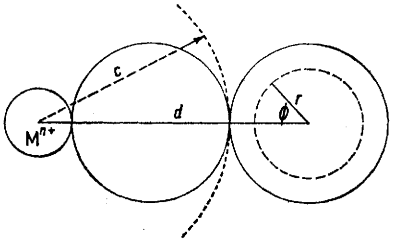

FIGURE 4 Model used to calculate the electric-field effect for a water molecule rotating near an ionic hydration complex; *r* is the H–O distance

Chemical Shifts in the Second Hydration Sphere.—The model used for calculation is shown in Figure 4. The second hydration sphere exists outside the sphere radius *c* defined by the ion $Al(H_2O)_6^{3+}$ and will differ considerably from the primary sphere, particularly in that it will undergo rapid reorientation at a rate comparable with that of the bulk solvent. The electric-field effect must therefore be calculated as an average over some range of orientation. Thus the Buckingham equation[17]* was used to calculate $\Delta\sigma_E$[10] as a function of the angle of rotation ϕ defined in Figure 4. The average $\Delta\sigma_E$ was then found by integrating over that part of a spherical surface defined by some range of ϕ. Two models were examined. For isotropic rotation the limits are $0 < \phi < \pi$ and equation (1) is obtained where

$$(\Delta\sigma_E)_i = -Bn^2e^2/(d^2 - r^2)^2 \qquad (1)$$

e is the charge on the proton. This result is of interest in that it shows that the linear $AE\cos\theta$ term of the Buckingham equation is averaged to zero by isotropic rotation in the non-uniform field of a point charge. This term will thus always be averaged to zero in any field conformation. Only the term in E^2 remains and the shift is always paramagnetic and independent of the sign of the charge. $(\Delta\sigma_E)_i$ is, however, too small to explain the shifts of the aluminium salt solutions and it has to be assumed that the electric field of the ion M^{n+} orients the water to some extent so including a contribution from the linear term. If the assumption is made that the water protons move isotropically about the hemisphere remote from the M^{n+} ion, then the second model has the limits $\pi/2 < \phi < \pi$, and, for limited rotation, equation (2) is obtained. Values of

$$(\Delta\sigma_E)_l = -Ane\{1 - [d/(d^2 + r^2)^{\frac{1}{2}}]\}/r^2 - [Bn^2e^2/(d + r)^2(d^2 + r^2)] \qquad (2)$$

$\Delta\sigma_E$, calculated for several ions from (1) and (2), are in Table 2. These shifts will of course be direct increments to the water shift, since there should only be small structural effects in the second hydration sphere.

DISCUSSION

Shifts at Ambient Temperature.—It can immediately be discounted that either hydrolysis or the natural acidity make significant contribution to the excess of downfield solution shift. Hydrolysis produces a shift in the wrong direction[18] [Figure 1(*a*)] indicating, as discussed below, that the products have small proton shifts. The natural acidity will of course produce a small downfield shift, calculated as only —0·004 p.p.m.,[11] which can be neglected here. That there are no unexpected effects of acidity[10] is confirmed by the observation that small acid additions increased the shift by the expected amount at 60 °C (Figure 2).

It thus appears that the second hydration sphere must account for the whole of the excess of shift. The previous model may be modified to obtain equation (3), where δ_{obs} is the solution shift, h_1 the number of water

$$55{\cdot}5\,\delta_{obs} = h_1m\delta_1 + h_2m\delta_2 + \delta_N[55{\cdot}5 - m(h_1 + h_2 + Fz/2)] \qquad (3)$$

molecules in the hydration complex and δ_1 their shift (δ_s in previous notation[2,10]), h_2 the number of water

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* $\Delta\sigma_E = -AE\cos\theta - BE^2$, where *A* and *B* are constants characteristic of the O–H bond of water,[10] *E* is the electric field at the hydrogen atom, $E\cos\theta$ is the component of the field along the O–H bond, and $\Delta\sigma_E$ is the resulting shift increment.

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molecules closely surrounding the hydration complex and δ_2 their shift, δ_N the shift of bulk water whose *concentration* is reduced by the hydration sphere and by an anionic structural factor F, z the charge on the cation, and m the solution molality. The shifts all refer to gaseous ethane in order to simplify the equation.[10] Only two quantities in equation (3) are unknown, h_2 and δ_2. The latter can be taken simply as the electric-field increment to δ_N, given in Table 2 for limited rotation of the water, namely —0·90 p.p.m.. The value of h_2 is however difficult to define, there being sufficient space for *ca.* 18 water molecules in the second hydration sphere, though not all will be equally close to the metal ion and those furthest away probably undergo full isotropic rotation and suffer relatively small shifts. For example, rotating molecules separated from the hydration complex by only 33 pm would have their shift reduced by a factor of 3·4 [*cf.* $(\Delta\sigma_E)_i$ for In^{3+}].

It is thus proposed that only those molecules in contact with the hydration complex should be regarded as forming the second hydration sphere, and that the hydrogen-bonding possibilities for a hexa-aquo-ion will limit their number to *ca.* 12. Substitution of the above values of h_2 and δ_2 in equation (3) gives the calculated figures in Table 3. The model proposed above gives a remarkably good fit to the observed chemical shift values. This result should, however, be treated with some caution since the value of A used in the Buckingham equation was chosen somewhat arbitrarily,[10] as was that of h_2, and the errors introduced may have conveniently cancelled. We can nevertheless state with certainty that the absolute shifts of these solutions are sensitive to the presence of water molecules close to the hydration complex, which interact with the electric field of the ion.

Temperature-dependent Effects.—Changes in shift with temperature for several samples are given in Figure 2. The shifts were measured relative to water, but are presented as if ethane gas were the standard. The pure water line is shown linearly. This is probably not strictly correct [19] and the Figure should be read as depicting the relative behaviour of solution and solvent where water is the standard, while the results using Me_4N^+ may be displaced to low field below 10 °C.

TABLE 2

Calculated chemical-shift increments for a water molecule rotating in the electric field of a metal ion *

	Radius of hydration complex [a]	10^9 Electric field at H_2O centre		Calculated chemical shifts	
		V m^{-1}		p.p.m.	
Ion	pm	1st Sphere [b]	2nd Sphere [b]	Isotropic rotation	Limited [c] rotation
Sn^{4+}	351	129	23·8	−0·514	−1·15
Al^{3+}	328	122	↗ 19·7	−0·352	−0·90
Ga^{3+}	335	113	19·0	−0·332	−0·86
In^{3+}	361	88·3	↗ 17·2	−0·265	−0·73
Be^{2+}	303	108	↗ 14·6	−0·203	−0·87
Mg^{2+}	345	67·8	↗ 12·2	−0·135	−0·52
Ca^{2+}	380	49·8	10·6	−0·101	−0·44
Li^+	331 [d]	39·4 ↙	6·5	−0·038	−0·24
Na^+	375	26·0 ↙	5·4	−0·026	−0·20
K^+	413	19·3 ↙	4·7		
Rb^+	428	17·3 ↙			
Cs^+	449	15·0			

[a] The radius which contains the first hydration sphere. [b] Arrows indicate which pairs of ions have comparable electric fields in the different hydration spheres. [c] $\pi/2 < \phi < \pi$. [d] Tetrahedral radius.

* The Table suggests that second-hydration-sphere effects should also be found for Sn^{4+}, Group III ions, and Be^{2+}. Certainly shifts of solutions of the latter ion are similar to those of Al^{3+}.[1] No significant effect would be expected for the larger Group II cations since the electric field of the second hydration sphere is smaller than that in the first hydration sphere of Cs^+, a finding supported by previous calculations.[10]

TABLE 3

Comparison of the calculated and measured chemical shifts of aluminium salt solutions at 28 °C

	Concn.	Chemical shifts/p.p.m.[a]			
Salt	mol kg^{-1}	Calc.	Measured		
$Al(NO_3)_3$	1·057	−0·568	−0·570 [b]	−0·571 [c]	−0·574 [c]
$Al(ClO_4)_3$	1·108	−0·483	−0·480 [b]		
$Al(SO_4)_{1\cdot5}$	0·982	−0·683	−0·650 [b]		
$AlCl_3$	1·00	−0·540		−0·519 [d]	

[a] With reference to water. [b] This work. [c] Ref. 2 (see footnote *d*). [d] Ref. 3, adjusted to 28 °C and the molality quoted in the second column.

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[19] J. C. Hindman, *J. Chem. Phys.*, 1966, **44**, 4582.

The results for the acidified sample emphasise the fact that, in the region examined, the spectrum changes with temperature from a singlet to a doublet and that these changes influence the observed gradients of the shift temperature dependencies. Above 50 °C, the gradient is similar to that of the pure solution, whereas if the points at 29 and 43 °C are included the average gradient is smaller. The same effect can be seen below 20 °C for the pure solution, so that an estimation of the gradient using the low-temperature exchange-perturbed points leads to an overestimation of the hydration number.[2,20] Under these circumstances it is not correct to regard as significant the deviations from the line drawn with a gradient appropriate to $h_1 = 6$. Thus while the absolute solution shift can only be accounted for if the second hydration sphere is included, the variation of shift with temperature detects only the first hydration sphere. Such a conclusion means that the temperature dependence of the shift of the water in the second hydration sphere is the same as that of pure water, and that the calculated shift for the second hydration sphere is indeed to be used as a simple increment to that of pure water. Small deviations of the gradient from the $h_1 = 6$ value will of course occur if the temperature dependence does differ slightly from that of water, but the deviations observed hardly exceed the experimental error. The gradient (and absolute shifts) calculated for the partially hydrolysed solution, allowing for the presence of Na^+, $Al(H_2O)_6^{3+}$, and NO_3^- ions, also agrees remarkably well with that determined experimentally. Here proton exchange is faster and we can regard all the results as being adequately exchange averaged.

If the acidified solution is cooled sufficiently, the bulk and bound water resonances separate and the shift of the bulk water can be measured relative to Me_4N^+ (Figures 2 and 3). The resonances separate almost completely and this provides the opportunity of studying the shift of water containing effectively only anions and second-hydration-sphere interactions. The shifts calculated on this basis agree closely with those observed. Results for 3·27 mol kg^{-1} solutions have been reported previously [9] and some obtained at the lowest temperatures are also plotted in Figure 2. In this case the bulk water resonance is upfield of the projected pure water shift, suggesting that some of the second hydration sphere has been destroyed. At this concentration only nine molecules of bulk water remain per aluminium ion. Shifts calculated for $h_2 = 9$ fall close to the observed resonances, and on the correct side of the water line.

Effects of Hydrolysis.—Hydrolysis leads to a high-field shift at all temperatures. The hydrolysis products catalyse exchange and so the linewidth is smaller, though still temperature dependent. The concentration of $Al(H_2O)_6^{3+}$ falls regularly to zero when $[Na^+] : [Al^{3+}] = 2{\cdot}5 : 1$ and several polymeric, hydroxo-bridged products are formed.[12] The results of Figure 1 can be reproduced over a large range by calculating the shifts as resulting from only $Al(H_2O)_6^{3+}$, its second hydration sphere, Na^+ and its first hydration sphere, and NO_3^-. Hydrolysis products thus have a negligible effect on the water and this indicates that there is considerable charge delocalisation from OH^- on to Al^{3+} particularly in the planar dimeric ion. Only at a high degree of hydrolysis, where the polymeric complexes have spherical symmetry, is any effect detected but it is small due to the large dimensions of the ions (P in Figure 1 is the calculated effect) and so not easily substantiated.

Comparison of First and Second Hydration Spheres.—The present results strongly reinforce the conclusion that aluminium salt solutions contain the hydrated cation $Al(H_2O)_6^{3+}$ surrounded by a so-called second hydration sphere of about twelve water molecules. The chemical shift of the latter is given a downfield increment by the electric field of the ion, though in other respects it behaves very like solvent water. The value of the electric-field increment, however, is such that the motion of the molecules in the second hydration sphere must be constrained by the electric field, which indeed is similar in magnitude to that in the first hydration sphere of alkali-metal cations. There is a marked contrast here, however, in that, whereas the water shift is temperature independent for the first hydration sphere, the usual temperature dependence is exhibited by water in the second hydration sphere. This implies that an electric field alone is not sufficient to account for all the properties of hydration water in contact with an ion and that, even for the alkali-metal cations, some chemical interaction must occur between an ion and its first hydration sphere.

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