Individual Ion Shifts from Nuclear Magnetic Resonance Spectra of Aqueous Solutions of Electrolytes

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Summary Two methods for assigning separate cation and anion shifts in aqueous electrolytes are suggested, the results being similar to those obtained for methanolic solutions; the trend for alkylammonium ions below room temperature indicates a structure enhancement.

WHEN discussing the n.m.r. spectra of aqueous electrolytes it is customary to assign one ion an arbitrary shift, typical values being δ ClO_4^- = 0·085 and δ NH_4^+ = 0·00 p.p.m.[1,2] No serious justification for these values has been put forward. A method for determining absolute ion shifts in methanol has recently been outlined,[3] but the low temperatures required to allow the detection of separate cation solvation shells makes this method difficult to apply to aqueous solutions. To prevent freezing it is necessary to use high salt concentrations or to add co-solvents. We have recently shown[4] in the case of methanol that the cation solvation shell and residual hydroxyl signals shift with concentration by approximately equal increments, and hence the cation shift can be estimated even for fairly concentrated solutions. We have therefore been able to determine an approximate ion shift for Al^{3+} at low temperatures from published spectra for aluminium salts, and from our own low-temperature results. This method does not require the use of an arbitrarily chosen standard. Extrapolation of the data to higher temperatures utilising Hindman's results leads to −0·53 p.p.m. at 273K and −0·56 pp..m. at 298K for the Al^{3+} molal shifts. Positive shifts are taken as upfield. Hence, using our measured salt shifts

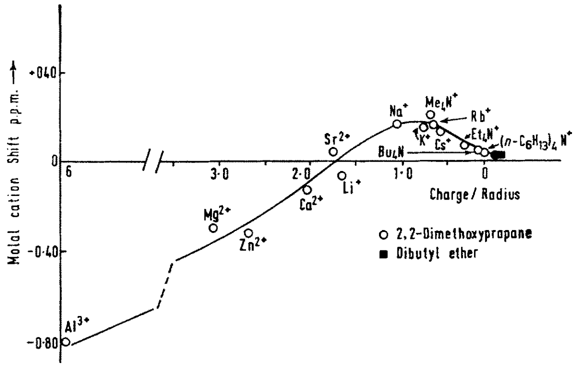

FIGURE 1. *Individual cation shifts (p.p.m.) as a function of the charge ÷ radius (Pauling scale) derived from the n.m.r. spectra of methanolic salt solutions at* 204K.

for $AlCl_3$ at these temperatures we obtain +0·03 p.p.m. at 273K and +0·02 p.p.m. at 298K for the molal Cl^- shifts.

For methanolic solutions a plot of the cation shift for mono and bivalent ions of the alkali and alkaline-earth metals against charge/radius ratio gives a continuous curve (Figure 1). For aqueous solutions a comparable plot, using δ $Cl^- = O$, gives a curve of similar form but containing a discontinuity [Figure 2 (i)]. The magnitude of this discontinuity can be directly related to the arbitrarily chosen anion shift, and by elimination of this discontinuity a unique value for the chloride shift can be derived. Hence, we have calculated the value for the chloride ion given below.

$$273K: \delta\,Cl^- = +\,0{\cdot}08\text{ p.p.m.} \pm 0{\cdot}03$$
$$298K: \delta\,Cl^- = +\,0{\cdot}03\text{ p.p.m.} \pm 0{\cdot}03$$

Considering the assumptions involved in these two approximate methods the agreement between the δ Cl^- values is surprisingly good. Using mean values, we have calculated individual ion shifts at 273 and 298K. The results closely resemble those previously reported for methanol[5] and in particular, there is a good correlation between the anion shifts and the pK_a values of their conjugate acids.

We also report our results for a series of quaternary ammonium ions in water. Hertz and Spalthoff[6] have reported that at 298K increasing the length of the alkyl chains causes the water proton resonance to shift upfield. This would normally be interpreted in terms of "structure-breaking," but since other data for such alkylammonium ions suggest that they are predominately "structure-makers," alternative theories have had to be devised.[7,8] We have confirmed this trend at 303K, but as the temperature is lowered the trend is reversed, and at 273K the trend shown in Figure 2(ii) was obtained. This is now in good accord with expectation, being similar in sign and form to that obtained from aqueous solutions of t-butyl alcohol.[9]

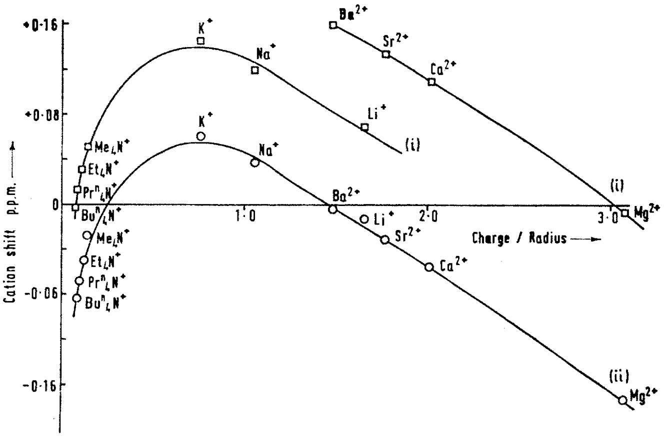

FIGURE 2. *Individual cation shifts as a function the charge ÷ radius for the n.m.r. spectra of aqueous salt solutions at* 273K, (i) *using* δ $Cl^- = 0{\cdot}00$ *p.p.m., and* (ii) *using* δ $Cl^- = 0{\cdot}08$ *p.p.m.*

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