The ^{7}Li N.m.r. Spectra of Aqueous Lithium Halide Solutions

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IN the course of an extensive survey of ^{7}Li n.m.r. spectra of solutions of lithium salts at 20 Mc./sec., measurements on a series of aqueous lithium halide solutions have revealed that, contrary to previous reports,[1,2] increase in concentration is accompanied by a small yet significant downfield chemical shift. We have found that the true ^{7}Li shift in these solutions is partly masked by changes in the volume diamagnetic susceptibility, for which corrections have been applied to obtain the results shown in Figure 1, where the chemical shifts, δ, are plotted as a function of the mole fraction, m, of lithium halide in solution. By using elevated temperatures it was possible to examine very concentrated solutions with values of m up to 0·5; these results are also included in Figures 1 and 2.

The relaxation time for the ^{7}Li nucleus in chloride solutions is surprisingly long for a quadrupolar nucleus.[1] In this study line-widths for all the halides were limited to a minimum of 0·3 c./sec. by the field inhomogeneity, and slight line-broadening was observed only for the most concentrated solutions ($m > 0{\cdot}2$), implying that in all cases the relaxation time remains abnormally long. The product $(\eta T_1)^{-1}$ was estimated for chloride solutions giving slightly broadened lines to be 0·05 sec.$^{-1}$, a value comparable with that previously obtained by the more accurate pulse method.[1] This behaviour is diagnostic of extremely rapid exchange of ligands around the Li^+ ion, with a correlation time shorter than a single Larmor period of the ^7Li nucleus (5×10^{-8} sec.); association of the Li^+ ions with either water molecules or anions appears therefore to be very short-lived.

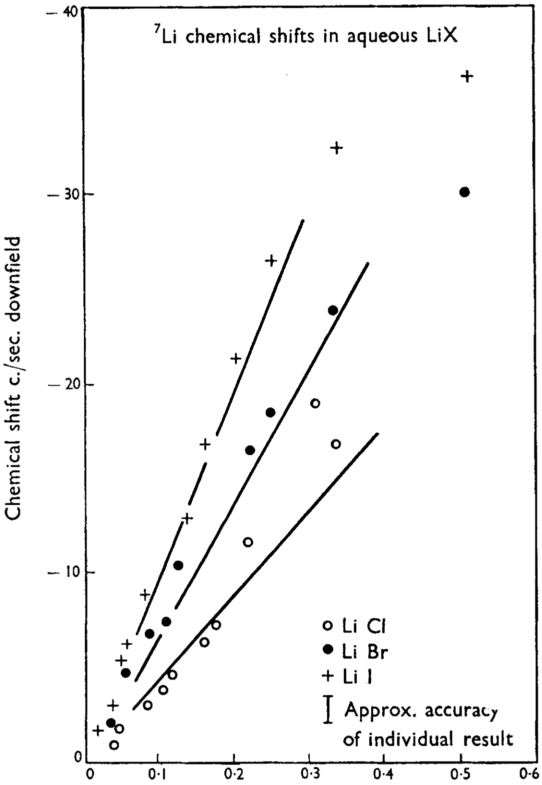

FIGURE 1

By regarding an aqueous lithium halide solution as an assemblage of ions and water molecules in which the anions and water molecules spend similar short times near a particular cation, we can explain the variation in ^7Li chemical shift in terms of progressive polarisation of the cations by the close approach of an increasing proportion of anions. Such a model is consistent with the observed downfield chemical shift, the magnitude of which is also determined by the nature of the anion; possibly the larger, more easily polarised anions enter into some measure of covalent association with the cations, giving rise to an enhanced shift to low field.

Two other features of the results are especially notable:

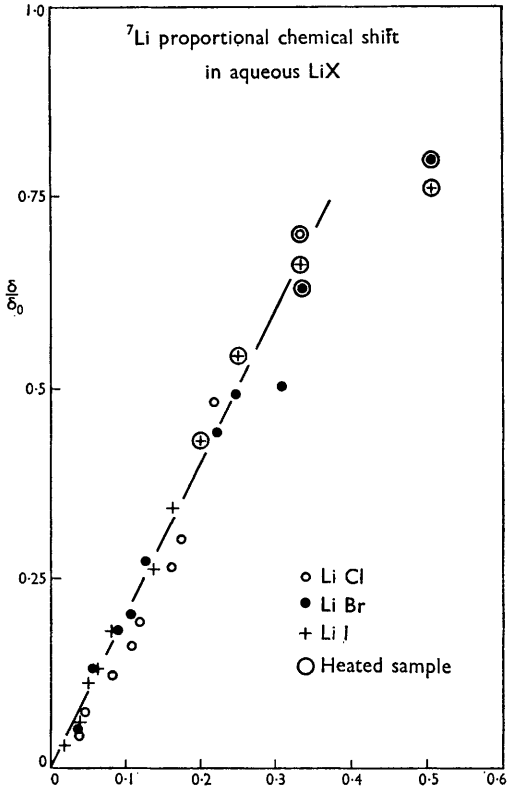

FIGURE 2

(1) The plot of δ against m is virtually linear for all but the most concentrated solutions ($m > 0·3$).

(2) The measurements made at elevated temperatures fit into the pattern of those made at room temperature; thus, δ is apparently temperature-independent.

These observations are less compatible with an equilibrium between, say, simple aquated Li^+ ions and ion-pairs, Li^+X^-, than with an almost statistical competition between water and halide ions for a position near the cation. The picture of the solutions that emerges is of a relatively random mixture of ions and molecules with no lasting interaction between any of them;[3] in this sense, our data are incompatible with the concepts of a complete hydration shell[4] of tightly bound water molecules, or of a discrete, tightly bound ion-pair, Li^+X^-. In reaching a similar conclusion, Hindman[2] has proposed that the Li^+ ion has a complete first hydration shell of four H_2O molecules; our data, which apply to conditions where the ratio $[H_2O]/[Li^+]$ is less than 4, indicate that any such shell is subject to rapid and reversible substitution of water by halide ions.

If there are, on average, x sites available for competition around the Li^+ ion, our simplified model leads to the relationship,

$$\delta = \delta_0 x m.$$

δ_0 is a (hypothetical) limiting chemical shift appropriate to the pure liquid halide; approximate values estimated by extrapolation are: LiCl, 24; LiBr, 37·6; LiI, 48·9 c./sec. In a plot of δ/δ_0 as a function of m (Figure 2) the experimental points for all three halides fall around a single straight line (as long as $m < 0{\cdot}3$) for which $x = 2$. At the highest concentrations attainable the points lie on a curve of slope < 2; under such extreme conditions ion–ion distances cannot be large, and it is necessary to envisage a highly mobile polymeric system wherein, for example, halide ions are capable of being simultaneously near to two lithium ions. The surprisingly low value of $x = 2$, which apparently applies to a wide concentration range (~1—~28 molal), represents not so much the classical hydration number[4] of the cation as the average number of sites accessible to halide substitution, or it may be regarded merely as a measure of the effectiveness of water molecules in excluding anions from the cation.

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[1] R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, 1963, **59**, 1972.

[2] J. C. Hindman, *J. Chem. Phys.*, 1962, **36**, 1000.

[3] *cf.* O. Y. Samoilov, *Discuss. Faraday Soc.*, 1957, **24**, 141.

[4] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955.