N.m.r. Evidence of Solvation by Dioxan in Aqueous Dioxan Solutions of Aluminium Perchlorate

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THERE has been some question raised in the literature as to whether or not ions in aqueous dioxan solutions can be solvated by dioxan.[1–5] An n.m.r. study of certain electrolytes in 1 : 1 dioxan–water solutions indicated that the ions were not solvated by dioxan.[6]

We report evidence obtained by n.m.r. of dioxan solvation in aqueous dioxan solutions of $Al(ClO_4)_3$. A plot of proton chemical shift, corrected for bulk susceptibility, against mole fraction of dioxan at 0·85M-$Al(ClO_4)_3$ is shown in Figure 1 for water and dioxan. In each case a down-field shift, relative to the water and dioxan resonance in a comparable nonelectrolyte solution, was observed. The down-field shifts obtained for dioxan, although much less than that of water, are far beyond experimental error and therefore must be considered as representative of a real association process involving ions or ion-pairs and dioxan. As further evidence for this, a significant broadening was observed in the dioxan resonance peak in the electrolyte solutions as compared with the nonelectrolyte solutions (Figure 2).

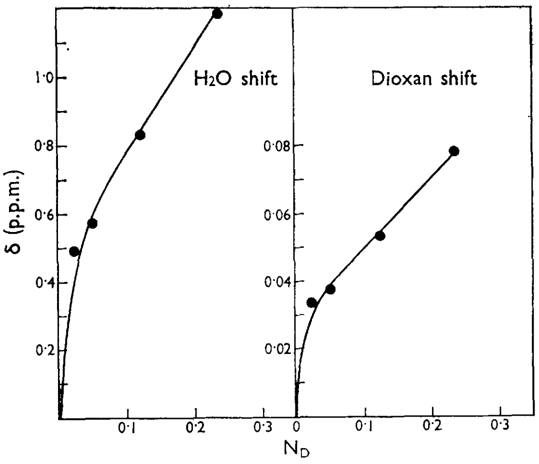

FIGURE 1. *Plots of down-field chemical shifts (p.p.m.) of water and dioxan against mole fraction of dioxan. The concentration of* $Al(ClO_4)_3$ *was constant at* 0·85 M.

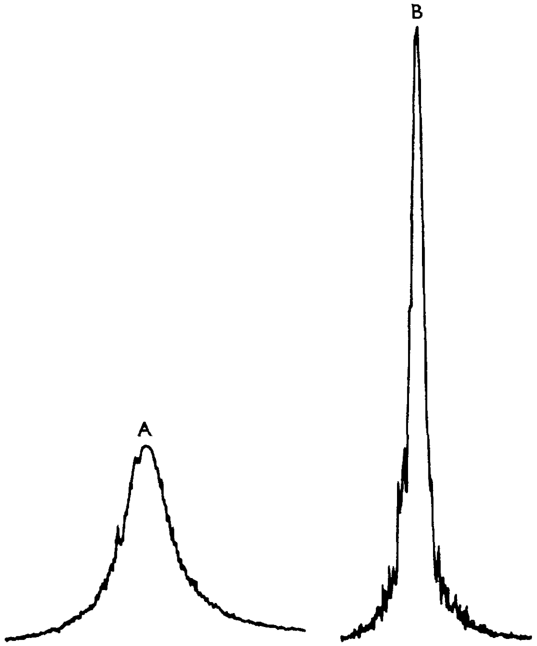

FIGURE 2. *Broadening of dioxan resonance peak in* $Al(ClO_4)_3$ *solution* (A). *Resonance peak of dioxan in nonelectrolyte solution* (B). *The solution composition was* 3 : 2 *w/w dioxan : water respectively and* 0·85 M-$Al(ClO_4)_3$. *Each resonance peak was recorded at the same instrument settings.*

Preliminary n.m.r. chemical-shift investigations on aqueous dioxan solutions of $Al(NO_3)_3$ and $Mg(ClO_4)_2$ indicated solvation by dioxan in the

$Mg(ClO_4)_2$ solutions but not in the $Al(NO_3)_3$ solutions. Down-field shifts of dioxan in the $Mg(ClO_4)_2$ solutions were somewhat less than that observed for the $Al(ClO_4)_3$ solutions and no significant broadening of either the water or dioxan resonance peaks occurred. A large down-field shift of the water resonance was observed in the $Al(NO_3)_3$ solutions while the dioxan resonance was shifted up-field. In the $Al(NO_3)_3$ solutions only the water resonance peak was broadened.

A comparison of the results in the $Al(NO_3)_3$ and $Al(ClO_4)_3$ solutions would seem to indicate solvation of the ClO_4^- ion by dioxan. Polarographic studies[5] and thermodynamic studies[3] on electrolytes in aqueous dioxan solutions have indicated that the ClO_4^- ion may be solvated to a certain extent by dioxan while ions such as Br^-, Cl^-, and NO_3^- are hydrated. The possibility of selective solvation of ion-pairs by dioxan cannot be completely disregarded since ion-pairing would be greatly enhanced in solutions of high dioxan concentration. However no experimental evidence has been obtained as yet to support this.

We feel that the evidence presented here strongly indicates dioxan solvation of ions or ion-pairs present in these solutions.

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[1] G. Atkinson and C. J. Hallada, *J. Amer. Chem. Soc.*, 1962, **84**, 721.
[2] P. K. Das, *J. Indian Chem. Soc.*, 1959, **36**, 613.
[3] E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, 1960, **82**, 5801.
[4] J. B. Hyne, *J. Amer. Chem. Soc.*, 1963, **85**, 304.
[5] J. L. Walter and Sr. M. Rosalie, *Analyt. Chem.*, 1965, **37**, 45.
[6] A. Fratiello and D. C. Douglass, *J. Chem. Phys.*, 1963, **39**, 2017.