Dependence of the ^{14}N Hyperfine Coupling for *p*-Dinitrobenzene Anions in Alcohols upon the Concentration of Alkylammonium Ions

By J. OAKES and M. C. R. SYMONS*
(*Department of Chemistry, The University, Leicester,* LE1 7RH)

WE wish to call attention to two facets of the results of our e.s.r. studies of *p*-dinitrobenzene anions in a wide range of solvents. Since our preliminary studies,[1] we have found that there is a marked dependence of the ^{14}N hyperfine coupling upon the concentration of added alkylammonium salts. This is shown in the Figure for added tetra-n-butylammonium salts together with the very different dependence upon added alkali-metal alkoxides.

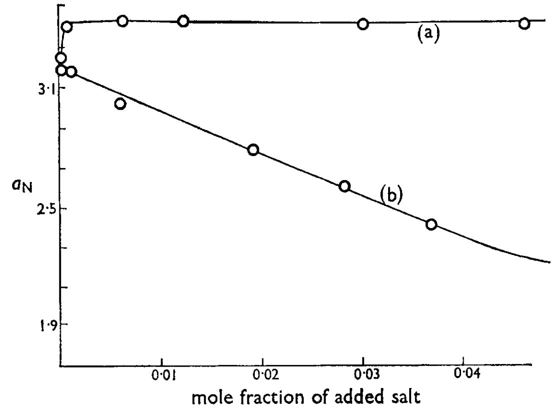

FIGURE. *Dependence of the ^{14}N hyperfine coupling constants for* p-*dinitrobenzene anions in dry ethanol upon the concentration of added salts.*

(a) *Sodium and potassium ethoxide,*

(b) *tetra-n-butylammonium bromide and perchlorate.*

These changes show that cation–anion interactions are important in such good solvents as methanol and ethanol, unless the total ionic strength is kept far lower than is normal practice for e.s.r. studies.

The other important practical aspect arises because it is commonly assumed that hyperfine coupling constants are not affected appreciably by ion-pairing with large alkylammonium ions. This convenient assumption is based upon results such as those of Adams *et al.*[2] who found no dependence of the hyperfine coupling constant for *p*-chloronitrobenzene anions upon the concentration of added alkylammonium salts in contrast with the effect of alkali and alkaline-earth cations.

Our results suggest that the polarising effect of alkylammonium ions is similar to that of aprotic solvent molecules such as dimethylformamide and considerably less than that of protic solvents such as methanol.

The more rapid and far smaller shift in the opposite direction induced by sodium ions is almost certainly caused by the formation of solvent-shared ion-pairs, the net effect being a reinforcement of the polarisation by alcohol molecules.

Added alkali-metal ions induce a marked line-width alternation, but alkylammonium ions do not. This confirms that ion-pairs are formed by the alkali-metal ions and that preferential bonding to the nitro-groups occurs more strongly in these ion-pairs than in those involving alkylammonium ions.

(*Received, January* 18*th*, 1968; *Com.* 067.)

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[1] M. J. Blandamer, J. M. Gross, and M. C. R. Symons, *Nature*, 1965, **205**, 591; J. M. Gross and M. C. R. Symons, *Mol. Phys.*, 1965, **9**, 287; *Trans. Faraday Soc.*, 1967, **63**, 2117.

[2] T. Kitagawa, T. Layloff, and R. N. Adams, *Analyt. Chem.*, 1964, **36**, 925.