

Studies of Solvation Shell Changes from the Nuclear Magnetic Resonance Linewidth of ^{23}Na

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Summary Addition of polyglycol dimethyl ethers or macrocyclic polyethers to a solution of sodium tetraphenylboron ion-pairs in tetrahydrofuran strongly broadens the ^{23}Na n.m.r. line, indicating that the tetrahydrofuran solvation shell is replaced by the complexing agent.

THE solvation state of ions or ion-pairs frequently affects their physical properties *e.g.* their optical and e.s.r. spectra, and reactivity. In mixtures of solvating agents, preferential complexation with the ionic species may occur, and the composition of the solvation shell becomes an important variable. ^1H N.m.r. spectra are useful in the identification of the solvent species complexed to an ion or ion-pair, especially when the ionic entity is either paramagnetic¹ or exhibits strong diamagnetic anisotropy.² However, in many cases the proton shifts of the ion solvation shell molecules are small or masked by the solvent.

We report that the addition of small quantities of alkali complexing reagents to solutions of salts such as sodium tetraphenylboride markedly affects the linewidth of the

^{23}Na n.m.r. signal, indicating a change in the solvation shell around the Na^+ ion. For nuclei with spin quantum number $I > \frac{1}{2}$, particularly for Na which has a comparatively large quadrupole moment, the linewidth $(1/T_2)_Q$ is largely determined by quadrupole relaxation [equation

$$\left(\frac{1}{T_2}\right)_Q = \frac{3}{40} \frac{2I + 3}{I^2(2I - 1)} \left[\frac{e^2 Qq}{\hbar}\right]^2 \left(1 + \frac{\kappa^2}{3}\right) \tau_r \quad (1)$$

(1)],³⁻⁵ where τ_r refers to the rotational correlation time characterizing the tumbling motion of the ion or ion-pair, eQ is the nuclear electric quadrupole moment, eq denotes the largest value of the electric field gradient, and κ is the asymmetry parameter.

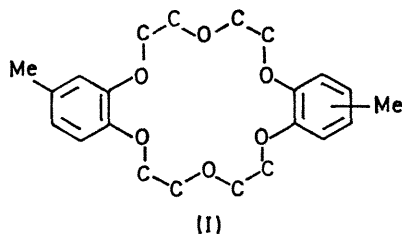
By combining the expression $\tau_r = 4\pi\eta a^3/3RT$ (η is the solution viscosity and a is the radius of the ionic species approximated by a sphere) with equation (1), equation (2) ($\kappa = 0$)^{4,5} is obtained.

$$\left(\frac{1}{T_2}\right)_Q \approx \left(\frac{e^2 Qq}{\hbar}\right)^2 a^3 \frac{\eta}{T} \quad (2)$$

We measured the linewidth of the ^{23}Na n.m.r. signal of a

0.2M-tetrahydrofuran (THF) solution of NaBPh_4 as a function of temperature, then added 0.2M-hexaethylene-glycol dimethyl ether ($\text{MeO}[\text{CH}_2\text{CH}_2\text{O}]_6\text{Me}$ or glyme 7) (I) or 0.2M-dimethyldibenzo-18-crown-6 (II) and repeated the measurements. The ^{23}Na resonance signal was obtained on a Varian DP 60 EL spectrometer at a frequency of 15.1 MHz, and operating in the high resolution mode. With the crown compound present the spectrometer was operated in the wide line mode. The chemical shifts were measured with an AEG gaussmeter, using a 1M-aqueous NaCl solution as standard.

Changes in the ^{23}Na chemical shift from 5.7 p.p.m. (NaBPh_4 -THF) to 9.2 p.p.m. [NaBPh_4 -(I)-THF] to 14.9 p.p.m. [NaBPh_4 -(II)-THF] were observed, all shifts being upfield from NaCl and measured at 40 °C. The shifts are comparable to those found for NaBPh_4 in pure tetraglyme⁵ and indicate a change in the solvation shell around the Na^+ ion. Such alkali n.m.r. shifts have also been reported⁶ for sodium and lithium salts on changing the solvent medium and can be correlated with the solvating ability of the



respective solvents. The Figure shows changes in the linewidths, as $1/T_2$ vs. η/T plots. The viscosities, η , (measured with an Ubbelohde viscometer) are those of the 0.2 M-salt solutions in the absence or presence of the complexing agent. The large change in the ^{23}Na linewidth of the NaBPh_4 salt on addition of an equimolar quantity of (I), and even larger change on addition of (II) is evidence that in the solvent separated NaBPh_4 ion-pair⁷ the THF solvation shell around the Na^+ ion is replaced by (I) or by (II). Studies with small quantities of tetraglyme show similar behaviour and addition of more than an equimolar quantity of (I), after correction for the increased viscosity, does not lead to further line broadening, indicating the formation of 1:1 complexes between the crown compound or glymes and the NaBPh_4 .

Two factors may be responsible for the increased linewidth, *viz.*, a change in the rotational correlation time τ_r of the ion-pair on changing the solvation shell around the Na^+ ion, or a change in the electric field gradient at the Na nucleus. We suggest that the latter factor is the more important one. The overall size of the solvated ion-pair does not change significantly when the THF solvation shell is replaced by either (I) or (II). Viscosities of the 0.2M- NaBPh_4 solutions are nearly identical in the absence and presence of the complexing agent. However, in

the THF-separated ion-pair the oxygen atoms are nearly spherically distributed around the Na^+ ion. This is probably not the case for compound (I) and certainly not for (II) which derives its strong alkali complexing property

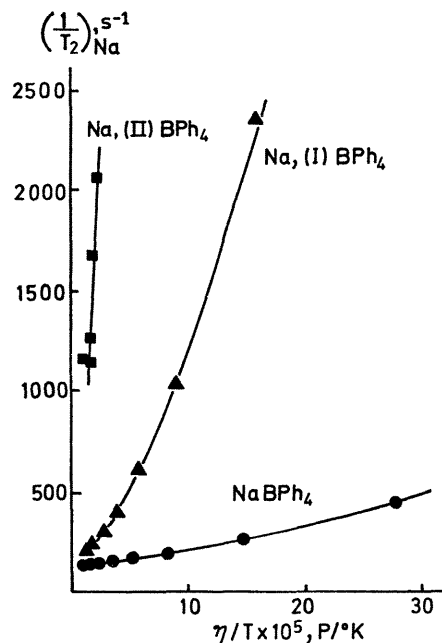


FIGURE. Changes in the linewidth $1/T_2$ of the ^{23}Na n.m.r. signal of sodium tetraphenylboride on addition of equimolar quantities of alkali complexing agents. Concentration of all species: 0.2M. For 0.5M- NaBPh_4 solutions, the $1/T_2$ value was found to be the same as for 0.2M- NaBPh_4 at corresponding η/T values.

largely from the fact that the polyether ring can assume a nearly planar conformation, with the Na^+ ion situated in the hole of the polyether ring.⁸ This non-spherical type of solvation would strongly increase the electric field gradient contributed by the lone electron pairs of the oxygen atoms at the Na nucleus. The small curvature in the linewidth plots may indicate that slight changes take place in the solvated ion-pair structure as the temperature is lowered, *e.g.*, an increased ordering around the Na^+ ion.

This method is useful in the study of ion and ion-pair solvation, especially in cases where ^1H n.m.r. studies do not provide conclusive evidence. Also, the complexation of certain crown compounds with sodium ions or ion-pairs may be slow enough^{2b} for a kinetic study to be made from the change in the linewidth of the ^{23}Na n.m.r. signal.

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