Ion–Solvent Interactions. Solvation of the Sodium Ion

Sir:

The importance of specific ion–solvent interactions on the behavior of ionic solutions is now well recognized, as attested to by the great amount of recent work on solvation effects in nonaqueous media,[1–7] but only with the recent work of Kebarle, *et al.*,[8] has it been possible to directly observe the solvation of a cation in the absence of interference by the solvent itself. In their approach, studies are carried out in the gas phase using mass spectrometric methods. This technique permits the determination of previously indeterminant quantities, but at the same time it offers some limitations with regard to both available instrumentation and the types of ions that can conveniently be studied.

We wish to report here the preliminary nmr studies of the interaction of coordinating solvents with sodium tetrabutylaluminate ($NaAlBu_4$) in a saturated hydrocarbon solvent (cyclohexane). Proton magnetic resonance spectroscopy can be used to detect ion–solvent interactions. Such interactions will cause changes in the chemical shift of the participating ^1H nuclei, but the use of the coordinating species as the solvent tends to mask the shifts. $NaAlBu_4$ is soluble in hydrocarbon solvents. Above 62°, the melting point of $NaAlBu_4$, it is miscible in all proportions with cyclohexane. The equivalent conductances of the $NaAl(alkyl)_4$ salts are comparable to those of the tetraalkylammonium salts, thereby substantiating their ionic nature.[6]

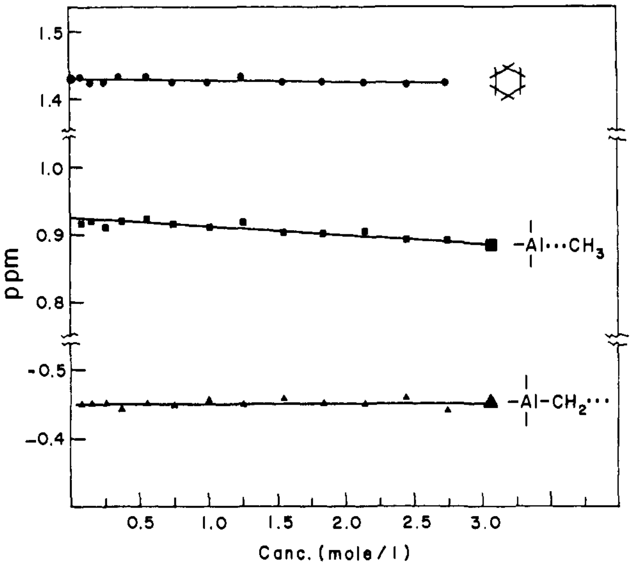

Figure 1. Chemical shifts for proton signals of $NaAlBu_4$ ($\geqslant Al-CH_2\cdots$ and $\geqslant Al\cdots CH_3$) and cyclohexane as a function of $NaAlBu_4$ concentration in cyclohexane.

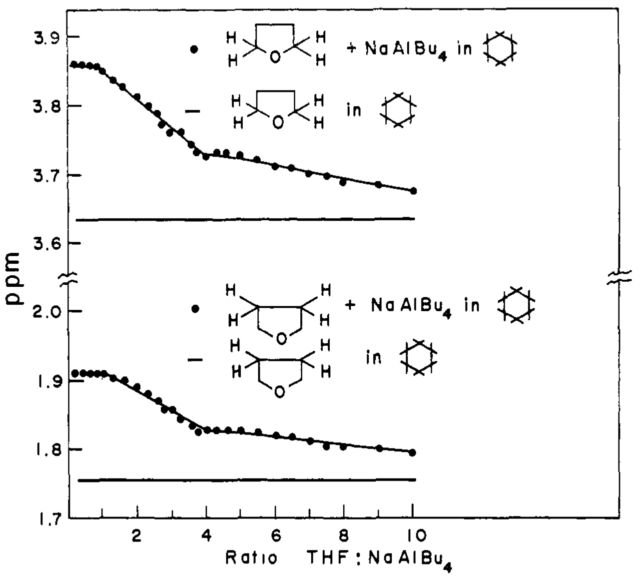

Figure 2. Chemical shifts in the THF proton signals as a function of the mole ratio THF:$NaAlBu_4$.

$NaAlBu_4$ is prepared by refluxing $AlBu_3$ with a sodium dispersion in *n*-heptane under a N_2 atmosphere. After filtration, the *n*-heptane is removed by vacuum evaporation, leaving the salt which is then recrystallized from *n*-pentane at Dry Ice temperature.

All solvents were distilled over potassium or $LiAlH_4$ and stored in vacuum-tight flasks in a N_2 drybox.

Nmr spectra were obtained with a Varian A-60A (60 Mc/sec) spectrometer. Tetramethylsilane was used as an internal standard.

In a saturated hydrocarbon solvent, where there is no permanent dipole and only C–C and C–H σ bonds are present, the minimum possible ion–solvent interaction should occur. The absence of any significant ion–solvent interaction is verified in Figure 1, where the shifts in the proton signals for the pertinent hydrogen atoms in both the butyl group of $NaAlBu_4$ and in the cyclohexane are plotted as a function of salt concentration. The points at a concentration of 3.06 *M* in the curves for the butyl hydrogen atoms represent the fused salt, and it is seen that only a very slight shift attributable to the large concentration change is observed. A significant shift in the signals from the butyl group would be expected at very low salt concentrations because of the dissociation of ion pairs to free ions, but this range is outside our present experimental capabilities. The proton signal from the cyclohexane is seen to show essentially no shift from that of the pure cyclohexane even at a salt concentration as high as 2.76 *M*. The spectra in Figure 1 are taken at 63°. Equivalent results were obtained at 32°, but the lesser solubility of the salt in cyclohexane at that temperature limits the concentration range to a maximum of approximately 2 *M*.

From the above, we might consider the solvent to act essentially as a dispersing medium for the salt. It is then possible to observe directly the effects of the addition of controlled amounts of coordinating solvents such as tetrahydrofuran (THF), diethyl ether, pyridine, etc. In Figure 2, the shifts in the proton signals for the two types of hydrogen atoms in THF are shown as a function of the mole ratio of THF to $NaAlBu_4$ using cyclo-

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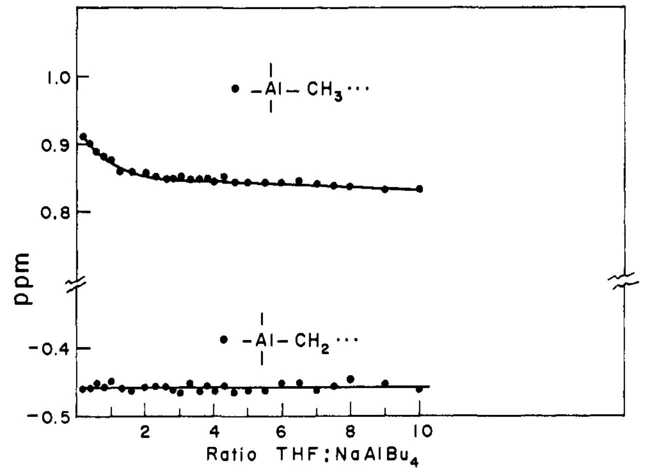

Figure 3. Comparison of the effect of THF on the chemical shifts in proton signals from $>AlCH_2\cdots$ and $>Al\cdots CH_3$.

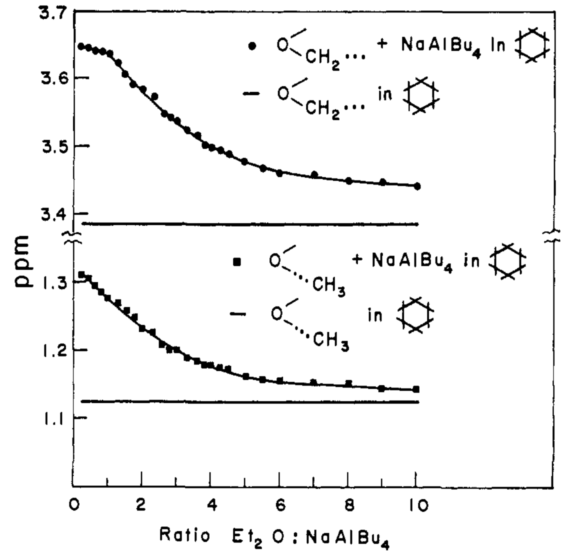

Figure 4. Chemical shifts in Et_2O proton signals as a function of the mole ratio $Et_2O:NaAlBu_4$.

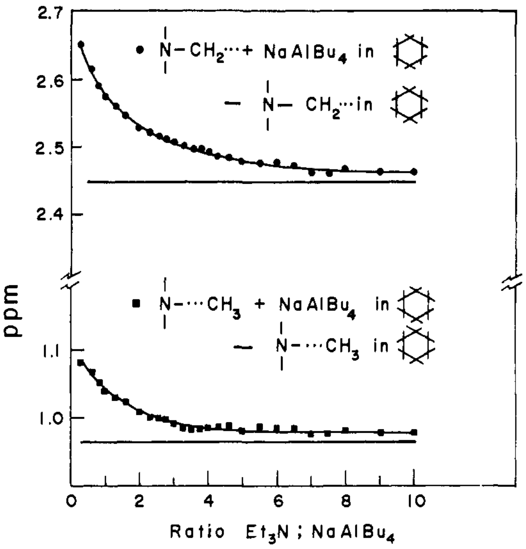

Figure 5. Chemical shifts in Et_3N proton signals as a function of the mole ratio $Et_3N:NaAlBu_4$.

hexane as a solvent. In this study the salt concentration is 0.265 *M*. Measurements were also made at salt concentrations of 0.09, 0.157, 0.96, and 2.00 *M* with substantially the same result. The α- and β-methylene signals of THF in cyclohexane are seen to be constant at respectively 3.64 and 1.75 ppm. With $NaAlBu_4$ present, both signals shift downfield, the chemical shift being an average value of the complexed and uncomplexed ether because of rapid equilibration between the two forms.

Here it can be seen that, up to a ratio of 1:1 THF: $NaAlBu_4$, the shift relative to the unperturbed THF in cyclohexane is very nearly constant. This implies that all of the THF molecules below this ratio see essentially the same environment. We interpret this to be a complex with the sodium ion. Complexation with the sodium ion rather than the aluminum is substantiated in Figure 3. Here the $>Al-CH_2\cdots$ proton signal is unaffected by the addition of THF whereas that of the $>Al\cdots CH_3$ shows a marked dependence. Coordination of the THF to the aluminum should cause a significant shift in the $>Al-CH_2\cdots$ proton signal. The same dependence is noted with diethyl ether. Using triethylamine as a coordinating species, the $>Al\cdots CH_3$ signal is masked. However, the $>Al-CH_2\cdots$ signal is unaffected again, indicating complexation with the sodium ion. The shift in the $>Al\cdots CH_3$ proton signal is most probably due to a change in the nature and extent of ion pairing, that is, the formation of free ions and solvent-separated ion pairs.

As the ratio of THF to salt is further increased, a distinct break is noted at a ratio of 4:1, showing the existence of a four-coordinated species. This can qualitatively be interpreted in terms of the over-all equilibrium expression

$$[Na\cdot THF]^+ + 3THF = [Na\cdot 4THF]^+$$

in which we have assumed the 1:1 complex to be totally in the complexed form, but the distinct nature of the break at a ratio of 4:1 implies a considerable stability of the 4:1 species. In Figures 4 and 5, analogous plots are shown for diethyl ether and triethylamine. The diethyl ether shows a stable 1:1 complex, but no further well-defined coordinated species is observed as in the case of the THF. The triethylamine is seen to form a much weaker complex toward the sodium ion than either THF or Et_2O.

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E. Schaschel, M. C. Day
Department of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803
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Photochemistry of *t*-Butyl Alkyl Ketones in Solution

Sir:

It has been recognized for some time that aliphatic ketones can undergo several distinct types of photochemical reactions. The effects of structure and spin multiplicity of excited states on the competition between these types of reactions, however, are still not completely understood. We have investigated the