siderably improves. Hopefully, the study of the rotational isomerism of a variety of molecules in aqueous systems will contribute to that understanding.

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Spectroscopic Studies of Alkali Metal Ions in Dimethyl Sulfoxide and 1-Methyl-2-pyrrolidone[1]

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Abstract: The solvation of lithium and sodium ions in dimethyl sulfoxide (DMSO) and 1-methyl-2-pyrrolidone (1M2PY) has been studied by the nmr and the far-infrared spectroscopic techniques. Mole ratio study of the NaAl(But)$_4$–DMSO and the NaAl(But)$_4$–1M2PY systems in 1,4-dioxane solutions indicates that the solvation numbers of the Na^+ ion in DMSO and in 1M2PY are 6 and 4, respectively. Infrared spectra of the tetrabutylaluminate and nitrate anions in solutions of these salts as well as the influence of isotope substitution of ^{6}Li in the lithium salts on the vibration frequency of the far-infrared band are consistent with the view that in the above solvents the anions do not enter into the inner solvation shell of the alkali cations.

Far-infrared spectra of electrolyte solutions in various nonaqueous solvents have been recently reported by several investigators.[3–5] This relatively new technique promises to be very useful in the elucidation of the structure of electrolyte solutions.

Similar work which was carried out in our laboratory[6] has shown that solutions of alkali metal salts in dimethyl sulfoxide (DMSO) and in 1-methyl-2-pyrrolidone (1M2PY) exhibit an infrared band in the 450–100 cm^{-1} spectral region whose frequency is dependent only on the nature of the cation and on the solvent. Similar bands have been observed by Edgell and coworkers[3] in tetrahydrofuran (THF) solutions of alkali salts, but in this case the frequencies of the far-infrared bands were also dependent on the nature of the anion, thus indicating that the bands may be due to the vibrations of ion pairs, or that at least the anion entered into the inner solvation shell of the alkali cations. In contrast to THF ($D = 7.4$), both DMSO and 1M2PY are polar solvents with the relatively high dielectric constant values of 46.4[7] and 32[8] and the dipole moments of 3.9[9] and 4.09[10] D, respectively. It would be expected, therefore, that in these solutions the concentrations of ion pairs will be much lower than in THF.

Previous studies have shown that the lithium ion has a solvation number of 2 in DMSO[6b] and of 4 in 1M2PY.[6d] Attempts to obtain the solvation number of Na^+ ion were unsuccessful due to the limited solubility of common sodium salts in solvent mixtures. Schaschel and Day, however, have reported a nmr study of the solvation number of sodium in ethers using sodium tetrabutylaluminate as the solute.[11] This salt has high solubility in organic solvents.

This work was undertaken to study the solvation number of the sodium ion in the two solvents DMSO and 1M2PY as well as to extend the infrared spectral measurements to a more thorough study of the role of the anions in the solutions.

Experimental Section

Reagents. The sources and the purification procedures for DMSO, 1M2PY, and 1,4-dioxane have been described in previous publications.[6] The water content, as determined by the Karl Fisher titration was less than 0.005 *M* for all solvents.

Lithium-6 metal was obtained from Union Carbide Oak Ridge Laboratory, Oak Ridge, Tenn. The assay which was furnished with the metal showed 95.6% ^{6}Li and 4.4% ^{7}Li. In order to prepare ^{6}Li salts, the metal was first added to water. The resulting base solution was then neutralized with a reagent grade acid with the desired anion. The salt solutions were crystallized and dried at 200°.

The method of Schaschel and Day[11] was used to prepare sodium tetrabutylaluminate. Tri-*n*-butylaluminum was obtained from K & K laboratories. The salt was prepared by adding tri-*n*-butylaluminum to an excess of metallic sodium dispersed in *n*-heptane which was previously dried over sodium wire. After refluxing for several hours, the mixture was filtered through a fine porosity filter stick to remove excess sodium and aluminum. The solvent was then removed by vacuum evaporation. The resulting white product was recrystallized twice from *n*-heptane at approximately $-80°$. The final purified product melted at $65 \pm 1°$. The capillary tube was filled with dried deoxygenated nitrogen before the salt was introduced. All manipulations which involved Al(But)$_3$ or NaAl(But)$_4$ were performed in a drybox under a dry nitrogen atmosphere.

Measurements. Nuclear magnetic resonance measurements were performed on Varian A-60 and A-56/60D spectrometers. A Model 200 AB Hewlett-Packard audio oscillator was used as an

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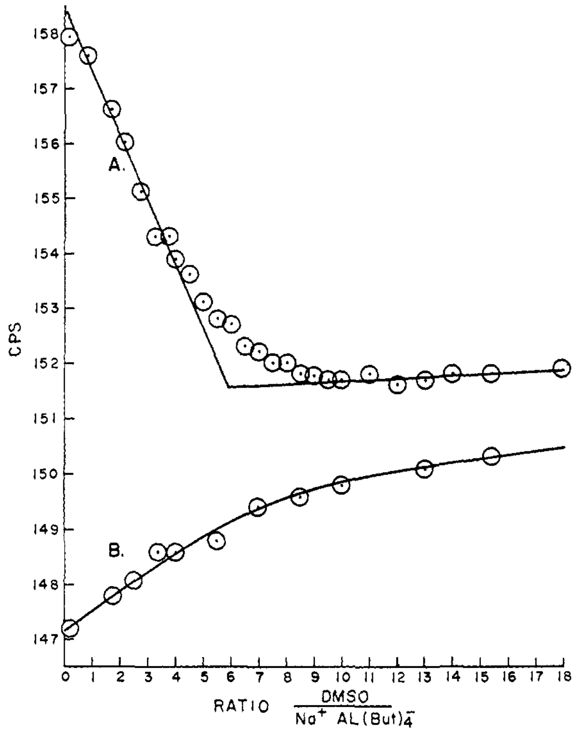

Figure 1. A, chemical shift of DMSO protons *vs.* DMSO/NaAl(But)$_4$ mole ratio; NaAl(But)$_4$ concentration = 0.36 *M*; B, blank.

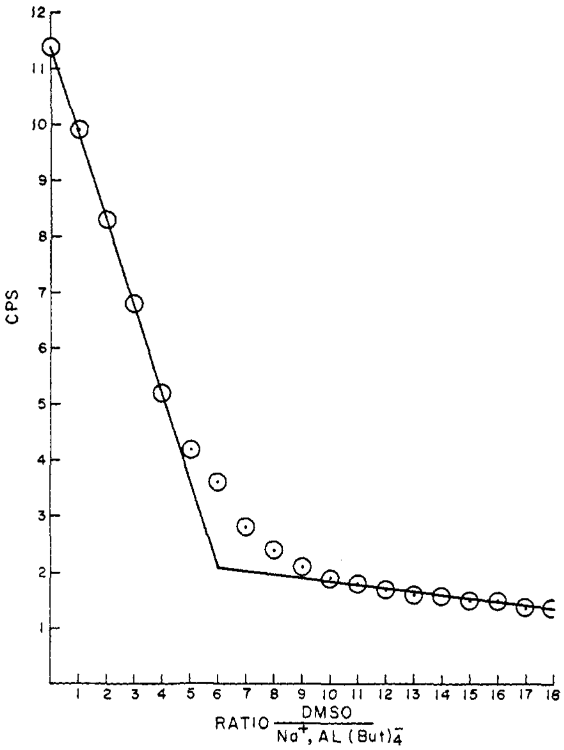

Figure 2. Chemical shift of DMSO protons *vs.* DMSO/NaAl(But)$_4$, base line subtracted.

external audio frequency source for calibration purposes. A Heath Universal Digital Instrument Model no. Eu-805 counter was used to monitor the signal frequency.

Tetramethylsilane was used as an internal standard for all measurements. An external side-band method was used to determine the chemical shifts. In performing the mole ratio experiments, the nmr analytical resonance and reference bands were scanned alternately several times until consistent results were obtained. All experiments were performed at least twice and all sample tubes were equilibrated at 35° before they were placed in the probe.

The far-infrared measurements were made on a Perkin-Elmer 301 spectrophotometer. Polyethylene windows were used for all far-infrared measurements. Teflon spacers on the order of 0.1 to 0.5 mm were used. The mid-infrared spectra were measured with a Perkin-Elmer 237B spectrophotometer.

Results and Discussion

Solvation Number of Na$^+$. Study of the solvation number of the sodium ion in nonaqueous solvents has been hampered by limited solubilities of sodium salts in solvent mixtures. In this respect sodium tetrabutylaluminate looked promising since it is quite soluble in hydrocarbons.[11] Unfortunately, NaAl(But)$_4$, 1M2PY, and hydrocarbon solvents such as cyclohexane, benzene, or heptane do not form completely miscible systems when the concentrations of the sodium salts are sufficiently high for the nmr measurements. As in previous experiments,[6d] dioxane was used as the "inert" solvent. It was shown previously that dioxane does not interact appreciably with 1M2PY and, in general, it is a poorer solvating medium than DMSO or the amides.[12,13] While it is impossible to assume that dioxane does not have any influence on the solvation equilibria, it seems reasonable to assume that in comparison to DMSO or 1M2PY its solvating ability would be quite small.

Figure 1 shows the influence of the variation in the DMSO/Na$^+$ mole ratio on the chemical shift of the DMSO methyl protons. It is seen (curve A) that the two straight lines of the plot intersect at a DMSO/Na$^+$ mole ratio of 6. Plot B shows the chemical shift in the DMSO–dioxane system without the presence of the salt. It is seen that there is some interaction between DMSO and dioxane. In order to make an accurate correction for the latter interaction, the dissociation of the sodium ion–DMSO solvate must be known so that the concentration of the uncomplexed DMSO would be taken into account. Since this value is unknown, a maximum correction was made by subtracting the base line as shown in Figure 2. While the shape of the mole-ratio plot changes, the mole-ratio value of 6:1 at the break point does not change. The curvature of the experimental points near the break shows that the solvate is dissociated to some extent at the 6:1 mole ratio of 1M2PY to the sodium ion. However, if the assumption is made that the bulky Al(But)$_4^-$ anion is essentially unsolvated, then the data indicate that the sodium ion is solvated by six molecules of DMSO.

Figure 3 shows the results of the 1-methyl-2-pyrrolidone nmr mole-ratio experiment. The break occurs at a 4.3:1 mole ratio, which implies a solvation number of 4 for sodium ion in 1M2PY, although the presence of higher solvates cannot be ruled out. In this case the base line does have zero slope and no corrections to the mole-ratio line are necessary. Figure 4 shows the behavior of the dioxane protons as a function of the 1M2PY/NaAl(But) ratio. Obviously 1M2PY and dioxane do not exhibit a detectable interaction. With salt present there is only a slight shift in the dioxane protons as shown in line A, Figure 4.

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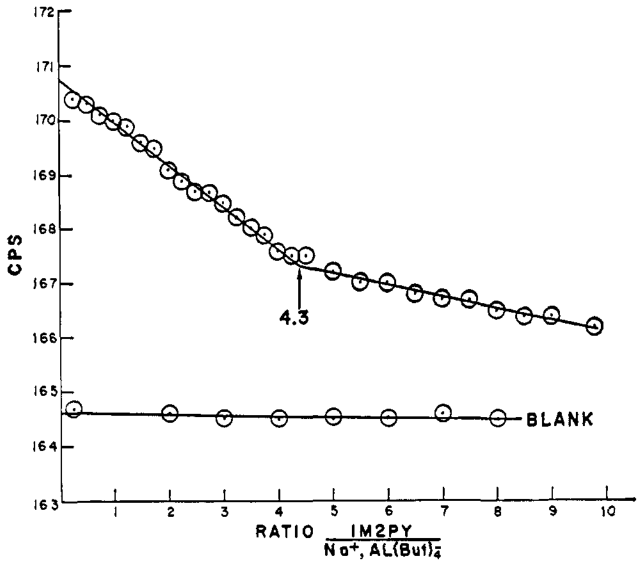

Figure 3. A, chemical shift of N-methyl protons of 1M2PY *vs.* 1M2PY/NaAl(But)$_4$ mole ratio; concentration NaAl(But)$_4$ = 0.38 *M;* B, blank.

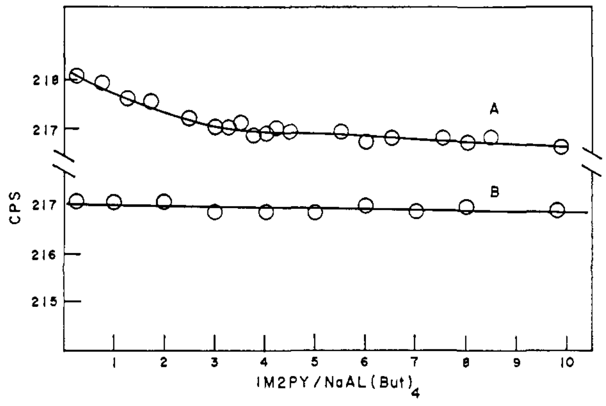

Figure 4. A, chemical shift of dioxane protons *vs.* IM2PY/NaAl-(But)$_4$ mole ratio; NaAl(But)$_4$ concentration = 0.38 *M;* B, blank.

Influence of the Anions. In order to determine what role the anion might have in producing a shift in the N-methyl proton resonance of 1M2PY, a large amount of the bromide ion was added in the form of tetrahexylammonium bromide and the shift of the N-methyl resonance was plotted as a function of the 1M2PY/Br$^-$ mole ratio. The results are shown in Figure 5. No effect of the bromide anion was observed. Admittedly Br$^-$ and Al(But)$_4^-$ may produce different effects, but Br$^-$ ion would be expected to be solvated much more than Al(But)$_4^-$.

Figure 5 illustrates that at low values of the 1M2PY/NaAl(But)$_4$ ratio the terminal methyl protons of the tetrabutylaluminate anion undergo a shift. The relative behavior of the anion protons is very similar to that reported by Schaschel and Day.[11] Figure 6 shows the nmr spectra of the terminal methyl protons and the methylene protons not bonded to the aluminum atom in solutions with DMSO/NaAl(But)$_4$ ratios of 0.25:1 and 18:1. Although there are some differences between the two spectra there certainly are no extensive changes. This evidence supports the idea of minimum anion solvation.

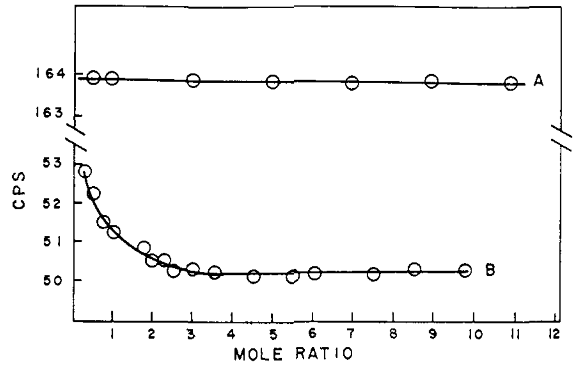

Figure 5. A, chemical shift of N-methyl protons of 1M2PY *vs.* 1M2PY/(Hex)$_4$NBr mole ratio; salt concentration = 0.38 *M;* B, chemical shift of the terminal methyl protons of tetrabutylaluminate anion *vs.* 1M2PY/NaAl(But)$_4$ concentration = 0.38 *M.*

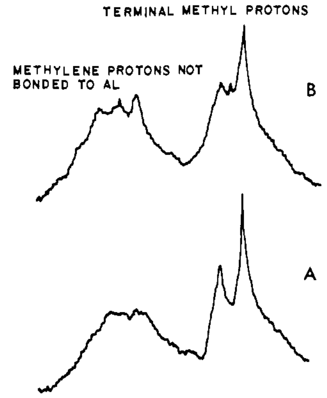

Figure 6. Nmr spectra of terminal methyl protons and methylene protons not bonded to the aluminum atom in tetrabutylaluminate anion; salt concentration = 0.36 *M:* A, DMSO/NaAl(But)$_4$ ratio of 0.25:1; B, DMSO/NaAl(But)$_4$ ratio of 18:1.

Infrared Studies. Solutions of NaAl(But)$_4$ in DMSO and 1M2PY exhibit cation solvent bands at 195 and 206 cm^{-1}, respectively. These frequencies correspond, within experimental error, to those found with more familiar salts such as sodium perchlorate, sodium iodide, and sodium tetraphenylborate.[6] The far-infrared Na–DMSO cation–solvent band changes in appearance as the concentration of DMSO in DMSO–dioxane mixture is decreased. Figure 7 shows the spectra of NaAl(But)$_4$ in pure dioxane and in pure heptane. The absence of strong absorption in the dioxane solution in the 200-cm^{-1} region indicates a lack of strong ion–solvent interaction since sodium ion–solvent interactions are usually observed in this region. The appearance of the Na$^+$–DMSO band occurs at about the same frequency in the presence of dioxane as in pure DMSO. Even at the relatively low 5.5:1 DMSO/NaAl(But)$_4$ ratio the Na–DMSO band is still evident. In pure dioxane and at very low DMSO/NaAl(But)$_4$ ratios the sodium solvent band in DMSO gives way to a much broader absorption which may be due to the formation of ion pairs. The broad absorption is also observed with heptane as solvent. The absorption data in Figure 7 should not be taken as quantitative. A summary of the far-infrared absorption studies in various pure and mixed solvents is tabulated in Table I.

In regard to the interaction of cation and anion to form ion pairs, D ke,[14] *et al.*, have reported that the

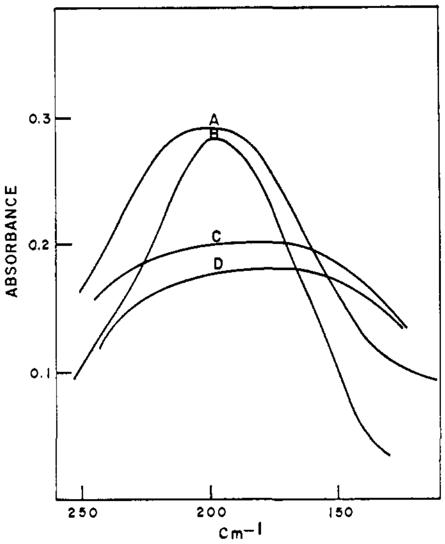

Figure 7. Far-infrared spectra: A, DMSO/NaAl(But)$_4$ of 5.5; B, DMSO/NaAl(But)$_4$ of 18; C, NaAl(But)$_4$ in dioxane; D, NaAl(But)$_4$ in *n*-heptane. Salt concentration = 0.36 *M*.

ion pair formation constants of sodium iodide and sodium tetraphenylborate in 1M2PY are all zero, since the data fit the Fuoss-Onsager equation for unassociated electrolytes. The salt concentrations for the conductance study were on the order of 10^{-3} *M*.

Table I. Infrared Spectra of NaAl(But)$_4$ in Various Solvents from 320 to 170 cm^{-1}

Solvent	Concn of NaAl(But)$_4$, *M*	ν_{max} of the Na$^+$–solvent band, cm^{-1}
DMSO	0.5	195
DMSO:NaA(But)$_4$, 18:1	0.5	197
DMSO:NaAl(But)$_4$, 5.5:1	0.5	200
1M2PY	0.5	206
DMSO:dioxane, 50:50	0.25	195
1M2PY:dioxane, 50:50	0.25	206
Dioxane	0.8	Broad absorption
Heptane	0.4	Broad absorption

Table II. Infrared Absorption Data: LiClO$_4$ in 1M2PY with But$_4$NNO$_3$

Solutes	Concn, *M*	ν_2, NO$_3^-$, cm^{-1}	ν_3, NO$_3^-$, cm^{-1}	ν, Li$^+$–1M2PY, cm^{-1}
LiClO$_4$	0.1			399
But$_4$NNO$_3$	0.6	835	1343	
But$_4$NNO$_3$	0.05	Too weak	1345	
But$_4$NNO$_3$+ LiClO$_4$	0.6 0.05	834	1343	397
But$_4$NNO$_3$+ LiClO$_4$	0.6 0.6	837	1343	399
But$_4$NNO$_3$+ LiClO$_4$	0.05 0.6	Too weak	1347	399

The addition of an anion in the form of tetraalkylammonium salt to a solution of an alkali ion salt conceivably could have an effect on the far-infrared cation solvent band. Tetrabutylammonium nitrate was employed for this purpose. Since lithium ion would be more likely to form ion pairs than sodium ions, lithium salts were used in the anion study. The nitrate ν_2 and ν_3 bands as well as the cation-solvent band were observed as the NO$_3^-$/LiClO$_4$ ratio was varied from 0.05:0.6 to 0.6:0.05 or from about 0.08:1 to 12:1. The results are tabulated in Table II. No frequency changes outside of experimental error were observed. These results seem to support the concept that the cation-solvent bands are due to vibration of the cations in the solvent cage rather than to the ion pair vibrations.

Isotopic Shift of ^{6}Li. In an earlier paper[6d] we reported that lithium bromide, iodide, nitrate, perchlorate, and triocyanate in 1M2PY solutions all showed an infrared band at 398 cm^{-1}. The behavior of lithium chloride was anomalous in that the band occurred at 377 cm^{-1}. We have expanded these studies to include the same salts (with the exception of the thiocyanate) with the ^{6}Li isotope. Table III lists the band maxima obtained. The change in frequency is from 398 cm^{-1} for the naturally occurring ^{7}Li salts to 420 cm^{-1} for the ^{6}Li salts, a shift of 22 cm^{-1}. Again the chloride is an exception with the band shifting from 377 to 409 cm^{-1}, or a shift of 32 cm^{-1}.

Table III. Absorption Spectra of ^{6}Li Salts in 1-Methyl-2-pyrrolidone

Salt	ν_{max}
LiClO$_4$	420 ± 4
LiNO$_3$	420
LiI	420
LiBr	420
LiCl	409 ± 6

The simplest model for the observed vibration would be a "diatomic" one involving the stretching vibration of the lithium ion with one solvent molecule.[6a] The calculated frequency, on the basis of Hooke's law, is 426 cm^{-1}, which differs only by 6 cm^{-1} from the observed value. Approximate calculations for a linear "triatomic" model 1M2PY-Li$^+$-1M2PY, or a tetrahedral model with four solvent molecules solvating the lithium ion, gave essentially the same results.

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