Table V. Bond Distances and Angles in Phosphirane

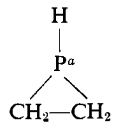
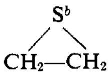
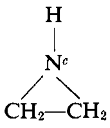
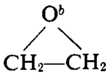
Bond distances, Å		Bond angles, deg	
C-P	1.867	C_1-P-C_2	47.4
P-H_P	1.428	H-P-ring plane	95.7
C_1-C_2	1.502	H_{cis}-C-H_{trans}	114.4
C_1-H_{cis}	1.092	H_P-P-C	95.2
C_1-H_{trans}	1.093	∠C-C-H_{cis}	118.0
P-H_{trans}	2.527	∠C-C-H_{trans}	117.5
P-H_{cis}	2.562	∠H_{cis}-C-ring plane	123.9 ± 0.5
H_P-H_{cis}	2.570	∠H_{trans}-C-ring plane	121.7 ± 0.5

The CPC angle of 47.4° indicates that the P-C orbitals on the phosphorus are also nearly pure p type since the phosphorus orbitals engaged in the bonding with the carbon atoms will strive for maximum overlap with the carbon orbitals,[12] and, since a 90° angle signifies pure p orbitals (assuming only s,p hybridization), it appears that the phosphorus orbitals bonding with the carbon atoms are nearly pure p type.

The lone pair is thus located in a hybrid orbital which is nearly pure 3s and presumably not highly oriented, *i.e.*, unpolarized. If we assume that the lone-pair bond moment is approximately 0.8 D larger in the nitrogen compounds than in the analogous phosphorus compound, all the differences between the dipole moments can be accounted for. For example, dipole moments of phosphine (0.55 D), PF_3 (1.02 D), and phosphirane (1.12 D) then differ from NH_3 (1.47 D), NF_3 (0.28 D), and ethylenimine (1.89 D) by approximately 0.8 D when the lone-pair bond moment is added and the signs of the dipoles are taken into account.

A comparison of bond lengths and bond angles for phosphirane, ethylene sulfide, ethylenimine, and ethylene oxide is given in Table VI.

Table VI. Comparison of Bond Lengths (Å) and Bond Angles (Degrees) for Phosphirane, Ethylene Sulfide, Ethylenimine, and Ethylene Oxide

				
r(C-C)	1.502	1.472[d]	1.480	1.472
r(C-H)	1.093	1.078	1.083	1.082
r(C-X)	1.867	1.819	1.488	1.436
r(X-H)	1.428		1.000	
∠CXC	47.4	48.50[e]	60.0	61.4
∠HCH	114.4	116.0	116.7	116.6
∠CCH	117.5			
∠C-CH_2	149.5	151.70	159.4	159.5
∠HXC	95.2			
∠HXC_2	95.7		112.0	

[a] This work. [b] Reference 2[b]. [c] Reference 3. The ethylenimine structure has not been completely done by isotropic substitution. [d] Taken from Figure 10 of ref 2b. The reported value of 1.492 Å in Table XIV of ref 2b appears to be a typographical error. [e] Recalculated from the original data in ref 2b.

Acknowledgment. We acknowledge the help of Dr. R. L. Poynter in certain phases of this work, Dr. A. W. Adamson for the use of Fluke power supply for the Stark effect measurements, and to Dr. Lise Nygaard for suggestions on our calculations.

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[12] C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1961, pp 194–195.

Spectroscopic Studies of the Solvation of Alkali Metal Ions in Dialkyl Sulfoxide Solutions[1]

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Abstract: Infrared spectra of a large number of alkali metal salts have been obtained in the 5000–100-cm^{-1} spectral region in dimethyl sulfoxide, dipropyl sulfoxide, and dibutyl sulfoxide. In all cases, a band was obtained in the 500–100-cm^{-1} region whose frequency is characteristic of the cation and the solvent but not of the anion. The results indicate that these low-frequency bands are due to the vibrations of the cations in a solvent cage. The study of ν_{S-O} indicates that the solvent dipoles are oriented with the oxygen atom in direct proximity to the metal. Bands obtained with DMSO-d_6 and with NH_4-d_4 show predictable spectral shifts related to the change in the reduced mass of the vibrating system.

The importance of solvation phenomena in the mechanism of reactions in solutions is patently obvious and needs no emphasis. Historically a variety of experimental techniques have been used in the determination of solvation numbers of ions. These include studies of various physicochemical properties of solutions such as refractive index, freezing and boiling points, vapor pressure, surface tension, density, specific heat, ionic transport numbers, and solubility studies. These classical techniques have been adequately reviewed by Bockris.[2]

In recent years the application of nuclear magnetic resonance spectroscopy to investigations of solvation phenomena has become quite widespread. In most cases this technique has been used in studies of transition metal ions. An excellent recent review thoroughly covers the literature to 1966.[3]

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[1] Taken in part from the Ph.D. Thesis of B. W. Maxey, Michigan State University, 1968.

[2] J. O'M. Bockris, *Quart. Rev.* (London), 3, 173 (1949).

Applications of infrared spectroscopic techniques to the study of the solvation phenomenon have been less extensive. Edgell and coworkers[4] have reported absorption bands of alkali metal salts of tetracarbonylcobaltates and pentacarbonylmanganates in tetrahydrofuran which they attributed to the vibrations of ion pairs since the positions of the bands were dependent both on the nature of the cation and of the anion. On the other hand, our preliminary studies on the spectra of alkali metal salts in dimethyl sulfoxide[5] indicated that the positions of the bands depended only on the nature of the cation and were completely independent of the nature and the mass of the anion. Thus the results were more indicative of the vibration of solvated cations than of ion pairs.

The use of dimethyl sulfoxide (DMSO) as a nonaqueous solvent has been studied quite thoroughly by earlier investigators. The solvent has a broad liquid range, 18.4–189°, a relatively high dielectric constant of 46.4[6] and a high dipole moment of 3.9 D.[7] It is an excellent solvent for many inorganic and organic compounds.[8,9]

Spectroscopic studies of alkali metal and ammonium ion solvation in this laboratory have been extended to a wide variety of solvents. This paper presents information obtained from solution studies of these salts solvated by dimethyl, dipropyl, and dibutyl sulfoxides as well as some pertinent results of an nmr study of some DMSO–alkali ion solutions.

Experimental Section

Reagents. Dimethyl sulfoxide was obtained from the J. T. Baker Chemical Co., as Baker Analyzed reagent. It was refluxed for several hours over barium oxide and then vacuum distilled through a 1-m packed column. The center fraction was collected and subjected to repeated fractional crystallizations. The water content of the final product (determined by Karl Fischer titration) was <0.005 *M* and melting points of various batches of DMSO prepared during the course of this investigation were in the 18.4 ± 0.2° range; the literature value is 18.4°.[9] It should be noted that even with repeated fractional freezings it is quite difficult to remove the last traces of water.

Dipropyl sulfoxide (DPSO) and dibutyl sulfoxide (DBSO) were obtained from the Aldrich Chemical Co., Inc. These compounds were dried over barium oxide and then repeatedly fractionally crystallized until the initial intense yellow coloration had been completely removed. They were stored over barium oxide. The melting points of the final products were respectively 25–27 and 32–33° (lit. mp 24.5–25.5[10] and 30–31° [11]). Infrared spectra of the purified materials showed no evidence of contamination by sulfones or other sulfoxides.

1-Pentanol, Baker Analyzed, was stored for several days over anhydrous calcium sulfate, then decanted, and distilled slowly. The first 15% of the distillate was discarded. The water content of the center fraction was less than 0.005 *M*. A higher water concentration resulted if the calcium sulfate was not removed from the solvent prior to distillation. Barium oxide could not be used as a drying agent due to its reaction with the alcohol.

Isotopically pure (99.5%) DMSO-d_6 was obtained from Mallinkrodt Chemical Works and was used without further purification; ammonium-d_4 bromide was obtained from the Isomet Corp. as 98% isotopically pure material and was also used as received. All of the alkali metal salts, with the exception of the tetraphenylborates, were commercially available reagent grade products. Ammonium iodide had a yellow tint and was purified by recrystallization from a water–ethanol mixture while the other salts were used without purification other than drying. The tetraphenylborates were prepared by the addition of a stoichiometric amount of sodium tetraphenylborate to an aqueous solution of a metal chloride followed by washing, filtrating, and vacuum drying of the resulting precipitate.

Infrared Spectra. Spectra in the 5000–650-cm^{-1} spectral region were obtained on Beckman IR-5 or IR-7 spectrophotometers. Spectra in the 650–32-cm^{-1} region were obtained on a Perkin-Elmer 301 spectrophotometer.

Liquid cells for all spectral regions were of the demountable type available from the Barnes Engineering Co., Stamford, Conn. Sodium chloride windows were used for the 5000–650-cm^{-1} spectral region and polyethylene windows for the lower frequency region. Most far-infrared solution spectra were obtained using an equal pathlength of pure solvent in the reference beam. Those spectra obtained using sheet polyethylene as reference were corrected for absorption due to the solvent.

While the purified solvent was essentially anhydrous, it was subsequently established that moisture did not affect the spectra. Thus, although precautions were taken not to excessively expose the solutions to air, it was found to be unnecessary to use a drybox for the preparation of solutions.

Results and Discussion

Infrared Spectra in DMSO. Infrared spectra of DMSO have been studied in detail by several investigators. Using the assignments of Horrocks and Cotton,[12] who have performed a complete vibrational analysis of dimethyl sulfoxide, the bands which are of primary interest to our study are the S–O fundamental stretching mode at 1055 cm^{-1}, two C–S–O bending modes (a symmetric deformation at 382 cm^{-1} and an antisymmetric mode at 333 cm^{-1}), a C–S–C deformation at 308 cm^{-1}, and a methyl torsional mode predicted at approximately 200 cm^{-1}. The spectrum of DMSO has been obtained from 5000 to 32 cm^{-1} in this laboratory. The S–O stretching mode and the two C–S–O deformations were observed as sharp, strong bands. The C–S–C deformation was observed as a very weak band but no evidence of the methyl torsional mode was obtained. A new broad band was observed at 80 cm^{-1} which we assign to dipole–dipole vibrations among the solvent molecules. Such bands have been observed in other polar solvents.[13] No other new bands were observed.

The spectra of alkali metal salts in DMSO were obtained. The only bands that appear in the solution spectra which cannot be attributed to either DMSO itself or to the anion present are tabulated in Table I. Typical examples are illustrated in Figure 1. All solutions were scanned from 5000 to 80 cm^{-1} and some to 40 cm^{-1}. Concentrations of 0.1–2 *M* were employed. The frequencies of the new bands were independent of salt concentration within this range. Small amounts of water, up to 7%, did not affect the frequencies. The intensities of the bands were directly proportional to the

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(3) J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

(4) (a) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, *J. Am. Chem. Soc.*, **88**, 1815 (1966); (b) W. F. Edgell, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, No. R-149; (c) W. F. Edgell, J. Lyford, and J. Fisher, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, No. S-136; (d) W. F. Edgell, personal communication.

(5) B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967).

(6) J. J. Lindberg, J. Kenttamaa, and A. Nissema, *Suomen Kemistilehti*, **B34**, 156 (1961).

(7) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(8) D. Martin, A. Weise, and H. J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967).

(9) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(10) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

(11) S. Searles and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).

(12) W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

(13) R. J. Jakobsen and J. W. Brasch, *J. Am. Chem. Soc.*, **86**, 3571 (1964).

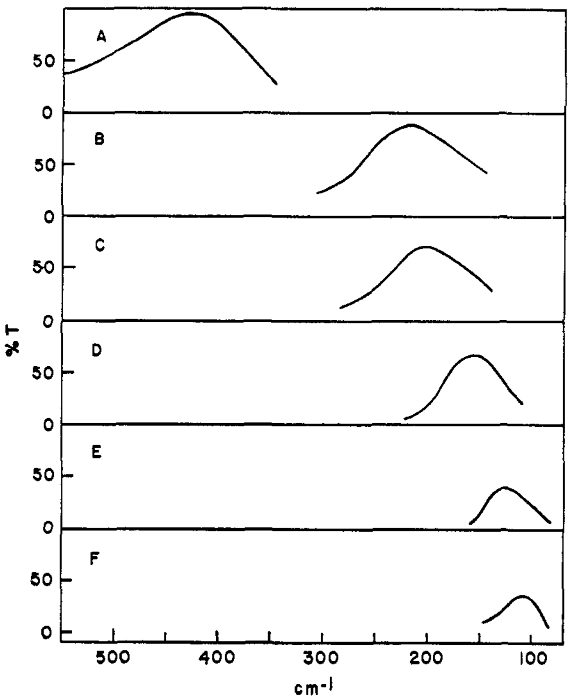

Figure 1. Absorption spectra of alkali metal cations in DMSO solutions: A, Li^+; B, NH_4^+; C, Na^+; D, K^+; E, Rb^+; F, Cs^+.

concentrations of the respective salts. Attempts were made to observe the spectra of some tetraalkylammonium salts in DMSO in the 650–50-cm^{-1} region but no absorption bands were detected.

Table I. Absorption Bands of Alkali Metal Salts in Dimethyl Sulfoxide, Dipropyl Sulfoxide, and Dibutyl Sulfoxide

Compd[a]	ν_{max}, cm^{-1}		
	DMSO	DPSO	DBSO
LiCl	429 ± 2	416 ± 4	426 ± 3
LiBr	429 ± 2	421 ± 4	425 ± 3
LiI	429 ± 2	420 ± 4	425 ± 3
$LiNO_3$	429 ± 2	421 ± 4	425 ± 3
$LiClO_4$	429 ± 2	421 ± 4	426 ± 3
NH_4Cl	214 ± 5	221 ± 4	
NH_4Br	214 ± 4	222 ± 3	226 ± 3
NH_4I	214 ± 4	223 ± 3	225 ± 3
NH_4NO_3	214 ± 4	223 ± 3	226 ± 3
NH_4ClO_4	214 ± 4	224 ± 3	226 ± 3
NH_4SCN	214 ± 4	224 ± 3	225 ± 3
NaCl	199 ± 5		
NaBr	199 ± 5	216 ± 5	
NaI	198 ± 3	219 ± 3	219 ± 5
$NaNO_3$	206 ± 3	218 ± 5	219 ± 7
$NaClO_4$	200 ± 3	217 ± 3	221 ± 5
NaSCN	200 ± 3	221 ± 3	224 ± 5
$NaPh_4B$	198 ± 3	220 ± 7	226 ± 5
KBr	153 ± 3		
KI	153 ± 3	156 ± 3	152 ± 5
KNO_3	154 ± 3		
$KClO_4$		153 ± 4	
KSCN	153 ± 3	154 ± 4	155 ± 5
KPh_4B		153 ± 3	154 ± 4
RbBr	125 ± 4		
RbI	123 ± 3	123 ± 6	
$RbNO_3$	125 ± 4		
$RbClO_4$	122 ± 4		
CsI	110 ± 4		
$CsClO_4$	109 ± 4		

[a] Concentrations range from 0.2 to 2 *M*.

The observed bands in the alkali metal salt solutions could be ascribed to ion-pair vibrations similar to the cases described by Edgell,[4] or to vibrations between an ion pair and the solvent or to vibrations of solvated cation or anion.

If the vibration were due to a contact or a solvent-separated ion pair, the observed frequencies should be dependent on the mass of the anion as observed by Edgell and coworkers in tetrahydrofuran solutions and by Evans and Lo[14] who observed ion-pair vibrational bands in benzene solutions of tetraalkylammonium halides. In the last case, observed spectral shifts in changing the anion were very close to those predicted on the basis of the corresponding change in the reduced mass of the vibrating system.

Existence of ion pairs in concentrated solutions of electrolytes in DMSO has been somewhat debated. Sears, *et al.*,[9] report that at concentrations $\leq 7 \times 10^{-3}$ *M* of various sodium, potassium, and tetraalkylammonium salts, electrical conductance studies indicate complete dissociation of the salts.

Gasser and coworkers have studied concentrated solutions of lithium chloride, rubidium iodide, and cesium iodide in DMSO. Evaluation of activity coefficients of these electrolytes led the authors to the conclusion that ion association occurs in solutions with concentrations larger than 1×10^{-2} *M* but their electrical conductance data do not support these conclusions.[15]

In order to check for possible influence of the anion on the frequencies of the observed bands, we carried out the following four studies.

1. Spectra were obtained of ammonium thiocyanate (the most soluble of our salts in DMSO) with the concentration varied from 0.05 to 7.0 *M*. Thus the mole ratio of DMSO:NH_4^+ was varied from ~350:1 to 1:1. The data are given in Table II. The frequency of the 214-cm^{-1} band found in dilute solutions of ammonium salts does not shift significantly up to a 1:1 mole ratio, with increasing concentration of the salt nor are new absorptions observed. However, at a mole ratio of 1:1 a slight broadening and frequency shift is observed which may be indicative of increasing ion pairing or of a changing stoichiometry.

Table II. Infrared Absorption Data: NH_4SCN in DMSO (cm^{-1})

Concn, *M*	ν_{CN}	δ_{SCN}	ν_{SO}	δ_{CSO}	$\nu_{NH_4^+-DMSO}$
0.05			1055	330, 378	214
0.10	2055	464	1055		214
0.25	2055	464	1054		214
0.50	2057	463	1051	330, 378	212
1.0	2056	464	1047		216
3.0	2058	468	1030		212
5.0	2060	467	1025		215
7.0	2060	468	1020	338, 386	208 (broad)

2. The effect of increasing the anion concentration without increasing alkali-cation concentration was investigated by addition of tetraalkylammonium halides to solutions of lithium and ammonium halides. Such additions did not change the frequencies or intensities

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(14) J. C. Evans and G. Y-S. Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

(15) J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.*, **61**, 922 (1965); M. D. Archer and R. P. H. Gasser, *ibid.*, **62**, 3451 (1966); J. M. Crawford and R. P. H. Gasser, *ibid.*, **63**, 2758 (1967).

of the observed bands. For example, a 0.5 *M* solution of lithium iodide and a solution of 0.5 *M* LiI + 0.5 *M* Pr_4NI both gave bands at 430 cm^{-1} of equal intensities. Similar results were obtained at 214 cm^{-1} with solutions 0.4 *M* NH_4Br, 0.4 *M* NH_4Br + 0.4 *M* Bu_4NBr, and 0.4 *M* NH_4Br + 1.0 *M* Bu_4NBr.

3. The spectra of the complex anions SCN^- and NO_3^- were investigated as a function of DMSO:salt mole ratio. In all cases from highly dilute solutions to saturation, representing mole ratios of 1:1 for DMSO:NH_4SCN and approximately 3:1 for DMSO:$LiNO_3$, the anion spectra did not undergo significant change (Tables II and III). If it can be assumed that strong association between an anion and a metal cation or a solvent molecule will distort the symmetry of the anion and, therefore, perturb its ir spectrum, it can be concluded that no such strong interaction is occurring in these solutions.

Table III. Infrared Absorption Data: $LiNO_3$ in DMSO (cm^{-1})

Concn, *M*	ν_{2,NO_3^-}	ν_{3,NO_3^-}	ν_{SO}	δ_{CSO}	ν_{4,Li^+-DMSO}
0.10	830	1340	1055	330, 379	429
0.50	827	1343	1054		428
1.0	829	1343	1050	332, 380	428
2.0	830	1340	1044		429
4.0	830	1340	1035	333, 382	430

4. Solutions of sodium nitrate and of lithium bromide were prepared in benzene–DMSO mixtures in order to decrease the dielectric constant of the medium and the positions of the Na^+–DMSO bands were determined. The results are shown in Table IV. We would expect that with the decreasing dielectric constant the extent of ion-pair association would increase. It is seen, however, that the frequency of the observed band is constant within the experimental error of the measurements. Even more significant is the fact that the intensity of the band was found to be independent of the DMSO:benzene ratio. If the observed band was due to an ion-pair vibration, drastic decrease in the dielectric constant of the medium should result in an increase in the concentration of ion pairs and, therefore, in the intensity of the observed band.

Table IV. Absorption Bands of Alkali Metal Salts in DMSO–Benzene Mixtures

Compd	Concn, *M*	Solvent[a]	Dielect constant[b]	ν_{max}, cm^{-1}
$NaNO_3$	1.0	DMSO	46.4	206 ± 3
$NaNO_3$	0.60	2:1 C_6H_6–DMSO	14.5	205 ± 3
LiBr	0.05	DMSO	46.4	431 ± 3
LiBr	0.10	2:1 C_6H_6–DMSO	14.5	433 ± 3
LiBr	0.05	4:1 C_6H_6–DMSO	8.4	429 ± 3
LiBr	<0.05 (satd)	5:1 C_6H_6–DMSO	6.9	428 ± 3

[a] Volume ratios. [b] J. J. Lindberg, J. Kenttamaa, and A. Nissema, *Suomen Kemistilehti*, **B34**, 156 (1961).

The results of these experiments all indicate that the anion is not significantly involved in the vibrating species. The source of the infrared activity must, therefore, be due to species containing only the cation and the solvent.

It can be seen from Table I that the band frequencies show a marked dependence on the cation but no such dependence on the anion. This fact is made most evident, for example, by comparing the frequency obtained for sodium tetraphenylborate to the frequency for sodium chloride. The positions of the bands are virtually identical even though the anion masses differ by nearly a full order of magnitude giving strong indication that the observed bands are due to cation–solvent vibrations.

We have previously reported[5] some rough calculations (taking Na^+–solvent vibration as reference) which indicated that, with the exception of the lithium ion, the frequencies of the new bands were a predictable function of cation mass. These calculations required the assumption that the force constant of the cation–solvent bond did not vary with change of cation. The results of these calculations, made for the asymmetric stretch of a linear "triatomic" model for reasons stated below, are shown in Table V. As pointed out at the time, this assumption may not be valid. However, using ND_4Br and DMSO-d_6 it is possible to calculate directly the effect of changing cation and solvent masses since isotopic substitution should not affect the force constants. Using the same model as a basis for calculation, it is possible to predict a frequency shift for the 430-cm^{-1} band of lithium–DMSO solutions to 416 cm^{-1} for lithium–DMSO-d_6 solutions. In the same manner, a shift to lower frequency of 19 cm^{-1} is calculated for the 214-cm^{-1} band of ammonium solutions upon changing from NH_4^+ to ND_4^+. The spectrum of 0.5 *M* LiI solution in DMSO-d_6 showed a shift of the observed band to 421 ± 2 cm^{-1} while a spectrum of ND_4Br in normal DMSO showed a shift of 14 ± 3 cm^{-1} from the band for NH_4Br. The observed shifts are in reasonable agreement with the predicted values.

Table V. Calculated and Observed Band Frequencies (cm^{-1})

Cation	DMSO ν_{calcd}	DMSO ν_{obsd}	DPSO ν_{calcd}	DPSO ν_{obsd}	DBSO ν_{calcd}	DBSO ν_{obsd}
Li^+	347	429	384	421	394	425
NH_4^+	223	214	244	223	248	226
Na^+		200		218		223
K^+	160	153	172	154	174	154
Rb^+	120	124	125	123	125	
Cs^+	106	110	106		106	

Further evidence of cationic coordination was obtained by a study of the fundamental S–O stretching frequency (Tables II and III). If the coordination were due to a dipolar attraction of a cation to DMSO, it would be to the negative dipole on the oxygen atom. Such coordination should result in a shift of ν_{SO} to lower frequencies.[16] A significant shift is observed for solutions of greater than 1 *M* salt concentration. In addition, the C–S–O bending modes shifted to higher frequency as salt concentration increased.

The results of our nmr investigations[17] indicate a

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(16) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

(17) B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, 90, 4470 (1968).

1:2 stoichiometry of the type $M(DMSO)_2^+$ for both Li^+ and NH_4^+ in DMSO solutions. Similar measurements on sodium ions indicate either a solvation sphere of ill-defined stoichiometry or the simultaneous existence of more than one well-defined structure. Such studies have not yet been extended to the other alkali metals.

The most likely configuration for the 1:2 solvates is linear triatomic. The far-infrared band for each structure is evidently the highest energy mode, ν_3, the asymmetric stretch. Using the appropriate formulas,[18] one may calculate the force constant of the DMSO–metal bond and the frequency of the ir inactive symmetric stretching mode, ν_1. The force constants so calculated for the lithium and ammonium solvates are, respectively, 3.6×10^4 and 2.2×10^4 dyn/cm. The frequencies for ν_1, which may be Raman active, are, respectively, 88 and 54 cm^{-1}. Very rough estimations for ν_2, the ir active bending mode, are respectively, 40 and 25 cm^{-1}. Dimethyl sulfoxide is not highly transparent in these regions so that these bands may not be observable.

Infrared Spectra in Dipropyl and Dibutyl Sulfoxide Solutions. Investigations were extended to these solvents in order to study the effects of decreasing dielectric constant, increasing mass, and increasing electron-donating ability which is dependent on the inductive effect of the alkyl groups. The importance of the inductive effect in determining the complexing abilities of various sulfoxides has been demonstrated.[19]

Just as in the case of DMSO, solutions of alkali metal salts in dipropyl and dibutyl sulfoxides gave a single band characteristic of the cation. The observed frequencies are given in Table I.

In comparing the spectra obtained from DMSO solutions to those obtained for the other sulfoxides, certain trends may be anticipated. In the series from DMSO to DBSO inductive effects will tend to shift a given cation–solvent band to higher energy. The frequency order predicted from such a consideration would be $(n\text{-}C_4H_9)_2SO > (n\text{-}C_3H_7)SO > (CH_3)_2SO$. This effect should be greatest for Li^+ and least for Cs^+ due to differences in their charge to mass ratios.

The effect of increasing solvent mass will follow an order opposite to that for the inductive effect and should be least important for Li^+, due to its very low mass relative to that of solvent molecule, and most important for Rb^+ and Cs^+.

The decreasing dielectric constant encountered in the series from dimethyl to dibutyl sulfoxide might have induced the formation of ion pairs; however, no evidence for ion-pair formation was obtained.

Using the sodium band frequency in each solvent as a reference, we have made estimations of the locations of other cationic vibrations based upon a linear triatomic approximation. The results are presented in Table IV. Due to the known high coordinating ability of Li^+, it is expected that the lithium frequencies should lie at much higher energies than those calculated.

The expected predominance of the inductive effect for Li^+ is observed for the change from dipropyl to dibutyl sulfoxide. The lower frequency in DPSO solutions as compared to that in DMSO was not predicted but may be related to the small size of lithium ion and to as yet unexplained steric effects. Such unpredictable behavior has been observed in sulfoxide complexes of transition metal ions.[20] The deviation for ammonium, though not large, is expected; although the mass of this cation is intermediate to Li^+ and Na^+, its large radius and low charge density will decrease the influence of solvent induction substantially over that for Na^+ resulting in a low observed value. Agreement among calculated and observed values is acceptable for potassium, rubidium, and cesium salts. It is interesting to note that the mass and inductive effects, being in opposition as stated above, exactly balance in the cases of K^+ and Rb^+. Insufficient data are available for cesium salts, but it would be expected that the mass effect would predominate and a shift to lower energy would be observed.

An attempt was made to obtain spectra of solvated cations in 1-pentanol solutions. Due to solubility limitations and to the opacity of the solvent above 350 cm^{-1}, only the salts of sodium and ammonium were studied. In both cases, however, solvent–cation bands were not observed. It appears, therefore, that the 1-pentanol–alkali metal ion interaction is much weaker than in the case of DMSO.

Conclusions

The results obtained in this investigation indicate that the low frequency bands observed in sulfoxide solutions of alkali metal salts are due to the vibrations of cations in a solvent cage or, in the case of lithium and ammonium, the vibrating species is a $M^+(DMSO)_2$ complex.[17] In this cage, the solvent dipole is oriented with the oxygen atom in direct proximity to the metal. Although it is clear that the nature or the mass of the anion does not influence the vibrational frequency of the sulfoxide–metal bond, it cannot necessarily be concluded that the anion is absent from the immediate surroundings. For example, it seems very likely that the 7 *M* solution of ammonium thiocyanate contains cations and anions in close proximity.

This work is being extended to other nonaqueous solvents, both polar and nonpolar. Such studies will not only give further information on the nature of the solvates present in such solutions, but also they could lead to a more quantitative understanding of the solvation and complexation abilities of various solvents.

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(18) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p 172.

(19) (a) P. Klaeboe, *Acta Chem. Scand.*, **18**, 27 (1964); (b) P. Klaeboe and E. Augdahl, *ibid.*, **18**, 18 (1964).

(20) W. F. Currier and J. H. Weber, *Inorg. Chem.*, **6**, 1539 (1967).