

ALKALI METAL NMR AND VIBRATIONAL SPECTROSCOPIC STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

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ABSTRACT

The application of far- and mid-infra-red, Raman, alkali metal n.m.r. and ^{35}Cl n.m.r. techniques to the study of electrolyte solutions in non-aqueous solvents is discussed. The above techniques are very sensitive probes of the environment of ions in solutions. They have been used to detect contact ion pair formation and to determine cationic solvation numbers. ^{23}Na chemical shifts in different solvents, which are strongly influenced by the paramagnetic screening constant, show a linear relationship with Gutmann's donor numbers for these solvents.

I. INTRODUCTION

While most chemical reactions which are carried out in laboratories or in industry, or which occur in living organisms, involve interactions of dissolved chemical species in some solvent, the influence of the solvent on the mechanism and thermodynamics of such reactions remains largely unknown. Only relatively recently chemists, and especially chemists working in non-aqueous solvents, began to appreciate the role of the solvent properties in chemical reactions. Despite this surging interest, our knowledge in this field still remains very rudimentary, owing to the enormous complexity of the problem.

In order to understand the role of the solvent in chemical reactions, we have to know what species are present in our solutions. Only then can we tackle the problem of solute-solute, solute-solvent and solvent-solvent interactions. Yet even a simple solution of a 1:1 electrolyte in a given solvent consists of a number of different species involved in a variety of interactions. For example, both ions will be solvated to some extent. The solvation sphere may be quite complex and consist of several solvent layers. The over-all solvation number of an ion is an unexact quantity and becomes largely a function of the experimental technique. For example, the hydration number of lithium ion has been reported to be as low as 0.065 and as high as 43¹.

Solute-solute interactions result in the formation of ion pairs or of higher aggregates. The extent of ionic aggregation will depend not only on the dielectric constant of the solvent but also on its solvating ability (donicity) as well as on the nature of the ions. Ion pairing can result in contact pairs, solvent shared pairs or solvent separated pairs². Of course, these ion pairs will be solvated in their turn. At higher concentration and/or in solvents of

low dielectric constant and low donicity, ionic triplets, quadruplets, etc., may also form.

Finally, the introduction of a salt into a solvent may affect the solvent-solvent interaction, especially in highly structured solvents such as water or dimethylsulphoxide.

In order to unravel this complex puzzle, we must have the means of identifying the various chemical species present in a given solution. Once all the species are identified, we may then study their interactions and equilibria. Only when such data become available can we begin to understand chemical processes in solutions.

For many years studies of electrolyte solutions were limited to electrochemical measurements or measurements of colligative properties of solutions. Within the last decade, however, spectroscopic techniques and, in particular, mid- and far-infra-red spectroscopy, Raman spectroscopy and n.m.r. spectroscopy have been systematically applied to this problem.

Spectroscopic studies of electrolyte solutions began in the late 1930s, when it was shown that the symmetry of a polyatomic ion in solution may be altered by its interaction with another ion or molecule. For example, the free nitrate ion has a D_{3h} symmetry. Selection rules allow a total of four fundamental vibrations, of which two are doubly degenerate. Three modes are infra-red-active and three are Raman-active. An interaction of the nitrate ion with a cation lowers the symmetry from D_{3h} to C_{3v} or C_{2v} , depending on whether a monodentate or a bidentate 'complex' is formed. The selection rules are altered and the original spectrum is more or less changed. These spectral changes can be used for the identification of species in solutions and for the study of the equilibria between these species. In recent years Plane, Irish, Hester, and Janz have done some very fine work in this field. These studies, however, will not be discussed here in detail, since they are amply covered in two excellent reviews by Irish^{3, 4}.

II. FAR-INFRA-RED STUDIES

Within the last decade a new dimension has been added to spectroscopic studies by the use of far-infra-red spectroscopy. In a study of far-infra-red spectra of tetraalkylammonium salts in benzene Evans and Lo⁵ found a band which could not be assigned either to the solvent or to the salt. The authors assumed that it was due to a cation-anion vibration. As shown in *Table 1*, the calculations, based on a simple 'diatomic' model, agree well with the above assumption.

At the same time Edgell and co-workers⁶ observed far-infra-red bands

Table 1. Cation-anion vibrations in benzene solutions⁵

Salt	$\nu_{\text{obs}}(\text{cm}^{-1})$	$\nu_{\text{calc}}(\text{cm}^{-1})$
$(n\text{-C}_4\text{H}_9)_4\text{NCl}$	120 ± 3	
$(n\text{-C}_5\text{H}_{11})_4\text{NCl}$	119 ± 3	119
$(n\text{-C}_4\text{H}_9)_4\text{NBr}$	80 ± 4	83
$(n\text{-C}_5\text{H}_{11})_4\text{NBr}$	80 ± 4	

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

Table 2. Frequencies of far-infra-red bands for alkali ion vibrations in tetrahydrofuran⁶

Salt	$\nu(\text{cm}^{-1})$	Salt	$\nu(\text{cm}^{-1})$
LiCo(CO) ₄	413	LiBPh ₄	412
NaCo(CO) ₄	192	LiNO ₃	407
KCo(CO) ₄	142	LiCl	387
		LiBr	378
		LiI	373

arising from the motion of the alkali cation in tetrahydrofuran solutions of lithium, sodium and potassium tetracarbonyl cobaltate and pentacarbonyl manganate. The data, shown in Table 2, indicate that the frequency of the bands is largely dependent on the nature of the cation and, to some extent at least, on the anion. The data suggested that the vibrating species are ion pairs or higher aggregates.

Far-infra-red spectra were obtained for a large number of alkali salts in a polar and highly solvating solvent, dimethylsulphoxide⁷. Again far-infra-red bands were observed which could not originate from the solvent or the salt. The frequencies of these bands, however, are strongly dependent on the nature of the cation but are completely independent of the anion (Table 3). The bands are quite broad and the integrated intensity is directly proportional to the concentration of the salt. The relative intensity, however, decreases with increasing mass of the cation.

It was assumed that in this case the band is indicative of a vibration of the cation in a solvent cage. Isotopic substitutions of ⁶Li⁺ and ND₄⁺ for ⁷Li⁺ and NH₄⁺, respectively, as well as of d₆-DMSO indicate unambiguously that both the cation and the solvent participate in the observed vibration.

Table 3. Absorption bands of alkali metal salts in dimethylsulphoxide⁷

Salt	$\nu(\text{cm}^{-1})$	Salt	$\nu(\text{cm}^{-1})$
LiCl	429	KBr	153
LiBr	429	KI	153
LiI	429	KNO ₃	154
LiNO ₃	429	KSCN	153
LiClO ₄	429		
		RbBr	125
NH ₄ Cl	214	RbI	123
NH ₄ Br	214	RbNO ₃	125
NH ₄ I	214	RbClO ₄	122
NH ₄ NO ₃	214		
NH ₄ ClO ₄	214	CsI	110
NH ₄ SCN	214	CsClO ₄	109
NaCl	199		
NaBr	199		
NaI	198		
NaNO ₃	206		
NaClO ₄	200		
NaSCN	200		
NaBPh ₄	198		

While in dimethylsulphoxide solutions the frequencies of the 'solvation bands' are strictly independent of the anion, the same situation does not prevail in all solvents, especially in solvents of low donicity and/or low dielectric constant. For example, in 1-methyl-2-pyrrolidone solutions all lithium salts, except for the chloride, show bands at 398 cm^{-1} ⁸. Repeated measurements on lithium chloride solutions, however, show that for this salt the solvation band occurs at 377 cm^{-1} , or 21 cm^{-1} lower than that of other lithium salts. Similar observations were made in other solvents where, generally, salts with polyatomic anions show a constant frequency while some halides deviate by $10\text{--}15\text{ cm}^{-1}$ from the above values (*Table 4*).

Table 4. Alkali ion solvation bands in different solvents (cm^{-1})

	DMSO	Me ₂ CO	1-Me-2-Pyr	PC	4MePy
Li ⁺	429	425 (409)	398 (377)	397 (383)	390
NH ₄ ⁺	214	—	207	184	290
Na ⁺	200	195	204	186	178 (172)
K ⁺	153	140	140	144	—
Rb ⁺	125	—	106	115	—
Cs ⁺	110	—	—	112	—
	Py	2Cl-Py	HOAc	MeNO ₂	
Li ⁺	385	355 (340)	390	340–370	
NH ₄ ⁺	196	—	—	—	
Na ⁺	182 (170)	—	—	—	
K ⁺	—	—	—	—	
Rb ⁺	—	—	—	—	
Cs ⁺	—	—	—	—	

It seems reasonable to assume that the change in the frequency of the solvation band is due to a change in the nature of the solvent cage around the cation. A simple explanation of this change would be that a small counter-ion, such as a halide ion, replaces a solvent molecule in the inner solvation shell, forming a solvated contact ion pair. The cation, in such cases, vibrates in a cage composed of solvent molecules *and* a counter-ion.

In solvents of very low dielectric constant or with very low solvating ability, even polyatomic anions influence the frequencies of the solvation band. It was shown above (*Table 2*) that in tetrahydrofuran the frequencies of lithium solvation bands vary for each anion. Similar results have been recently obtained by us in nitromethane solutions⁹. The frequency of the lithium solvation band is strongly dependent on the nature of the anion. Thus, for lithium perchlorate the band is at 370 cm^{-1} , while for the iodide it is at $\sim 340\text{ cm}^{-1}$. Evidence will be presented later indicating that despite the high dielectric constant of nitromethane (35.9 at 30°C) its low donor ability results in a very weak cation solvation. Consequently, in these two solvents the anions participate in the observed vibration. Examination of solvation bands in a given solvent, therefore, gives a good indication of the presence or absence of contact ion pairs.

The influence of the environment on the frequency of the cation vibration has also been studied by Tsatsas and Risen¹⁰. The far-infra-red spectrum of

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

sodium tetrabutylaluminum in cyclohexane solutions showed *two* solvation bands, at 195 and 160 cm^{-1} . In tetrahydrofuran solution, however, only one band, at 195 cm^{-1} , was observed. Addition of tetrahydrofuran to a sodium tetrabutylaluminum solution in cyclohexane resulted in the disappearance of the 160 cm^{-1} band as the THF/ NaAlBu_4 mole ratio exceeded 1:1.

It should be noted that Edgell *et al.*⁶ showed that, in general, the far-infrared solvation bands are Raman-inactive, which is indicative of the largely electrostatic nature of the cation-solvent or cation-anion interaction. Tsatsas and Risen, however, found a 202 cm^{-1} Raman band in cyclohexane solutions of sodium tetrabutylaluminum. This band, however, was not observed in tetrahydrofuran solutions, which indicates that in cyclohexane the ion-solvent interaction responsible for the 200 cm^{-1} band has a significant degree of covalent character.

In another study¹¹ Risen and co-workers observed the influence of complexation on the frequency of the solvation band. The solvation bands of the sodium ion in dimethylsulphoxide and in pyridine occur at 200 and 180 cm^{-1} , respectively; for potassium ion the respective frequencies are 150 and 136 cm^{-1} . The addition of a complexing agent, dibenzo-18-crown-6, to sodium and potassium solutions in the two solvents produced a marked change in the spectra. As seen from *Figure 1*, the solvation bands are shifted to

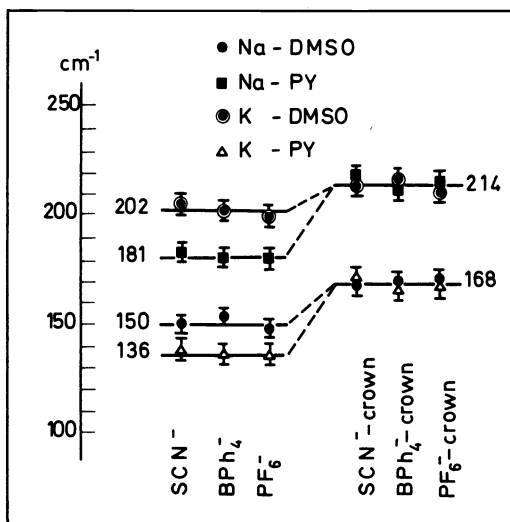


Figure 1. Comparison of the ion motion band frequencies for salts and M^+ -dicyclobenzene-18-crown-6 systems in dimethylsulphoxide and pyridine solutions¹¹

higher frequency and become *independent of the solvent*, as well as of the anion. It is clear that in this case the cation is encased in the ligand and vibrates within the ring formed by the ether oxygens.

So far we have assumed that a perturbation in the frequency of the solvation band is indicative of the formation of contact ion pairs. A question may arise

whether solvent shared or solvent separated ion pairs have any effect on the solvation bands.

A partial answer to this question comes from the study of solvation bands in glacial acetic acid solutions¹². As seen from *Table 5*, all lithium salts

Table 5. Absorption bands of lithium salts in acetic acid solution¹²

Salt	$\nu(\text{cm}^{-1})$ in CH_3COOH	$\nu(\text{cm}^{-1})$ in $\text{CD}_3\text{—COOD}$
LiCl	390 ± 4	365 ± 5
LiBr	391	367
LiI	392	368
LiNO_3	390	366
LiSCN	391	366
LiClO_4	390	366
LiBPh_4	389	362
⁶ LiCl	405 ± 5	
⁶ LiBr	408	
⁶ LiI	410	
⁶ LiNO_3	407	
⁶ LiClO_4	405	

studied in this solvent show a solvation band at $390 \pm 4 \text{ cm}^{-1}$. Yet acetic acid is a solvent of very low dielectric constant (6.3 at 25°C) in which the electrolytes should be largely ion paired. A reasonable explanation seems to be that in this case we have solvent shared or solvent separated ion pairs. This assumption is supported by ⁷Li n.m.r. studies (see below).

We can conclude, therefore, that the far-infra-red spectrum of ionic vibrations is sensitive only to the nearest neighbours of the cation. At this time, at least, it allows us to differentiate between contact ion pairs and ions with only solvent molecules in the inner solvation shell. It cannot distinguish between free solvated cations and solvent shared or solvent separated ion pairs.

Far-infra-red spectra of alkali salts were studied in a number of non-aqueous solvents. The positions of the solvation bands are shown in *Table 4*. Frequencies given parenthetically represent the cases where one or at most two anions (invariably halides) displace the frequency of the ion-solvent vibration.

As seen from *Table 4*, the frequencies of the solvation bands are strongly influenced by the nature of the solvent but the solvent influence decreases with increasing mass of the cation. For the lithium ion the observed frequency range is from 429 cm^{-1} in dimethylsulphoxide to 340 cm^{-1} in nitromethane solutions. As a simple approximation we can consider that aside from ion pair formation the vibrational frequency is influenced by three factors: the mass of the vibrating system, the geometric configuration of the solvation shell and the strength of the ion-solvent interaction. Unfortunately, at this time it is impossible to separate the influence of these three factors. It should be noted, however, that the solvating ability of a solvent has a perceptible influence on the solvation band frequency. For example, the inductive effect of the substituent groups seems to be operating in 4-methylpyridine, pyridine

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

and 2-chloropyridine, where the frequencies of the Li^+ solvation bands are 390, 385 and 355 cm^{-1} , respectively. The most solvating solvent, dimethylsulphoxide, shows the highest frequency of 429 cm^{-1} , while the last solvating, nitromethane, has the lowest frequency of 340 cm^{-1} .

Only a few attempts have been made to study the solvation band in mixed solvents. As the solvent composition is changed, the frequency of the solvation band varies gradually from the characteristic of one solvent to that characteristic of the other. The rate of frequency change is related to the respective solvating abilities of the two solvents. It is seen from *Figure 2* that

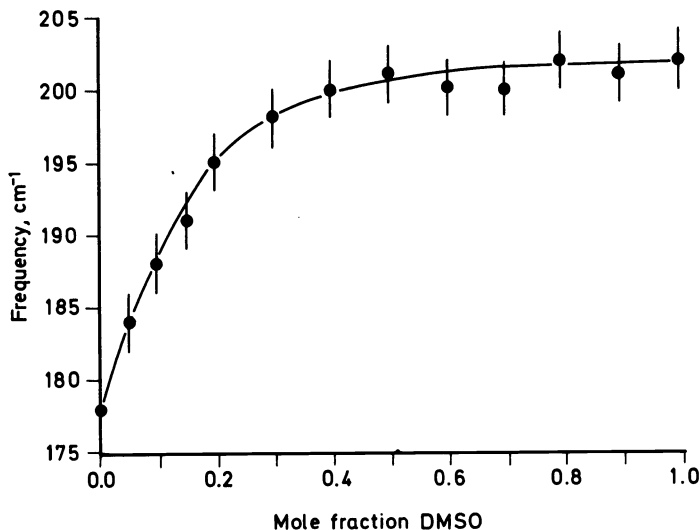


Figure 2. Variation in the frequency of the sodium solvation band in dimethylsulphoxide-pyridine mixtures¹³

in dimethylsulphoxide-pyridine mixtures the frequency characteristic of the sodium ion in pure dimethylsulphoxide is reached at relatively small mole fractions of this solvent—that is, the cationic inner solvation shell is composed entirely of dimethylsulphoxide molecules when the mole fraction of dimethylsulphoxide is ~ 0.5 ¹³. In other words, there is a strong preferential solvation of the sodium ion by dimethylsulphoxide.

III. MID-INFRA-RED AND RAMAN SPECTRA

It has been pointed out above that useful information can also be obtained from the vibrational spectra of the solutions in the mid-infra-red spectral region. For example, the study of the symmetric stretch of the perchlorate ion at 934 cm^{-1} (A_1) of lithium perchlorate in nitromethane-acetone mixtures shows this band to be quite narrow and symmetrical as long as the acetone/ Li^+

mole ratio is greater than or equal to 4¹⁴. Below this ratio, however, the band begins to broaden and shift. It seems reasonable to assume that this behaviour is a manifestation of a $\text{Li}^+ - \text{ClO}_4^-$ interaction. Since it only occurs at mole ratios of acetone/ Li^+ below 4, the data seem to indicate that the solvation number of lithium in acetone solutions is 4. This technique, therefore, can be used to obtain reliable values of cationic solvation numbers. Of course, this number refers only to the inner solvation shell of the ion.

One of the vibrational modes of acetone which occurs at 789 cm^{-1} is quite sensitive to solvent-cation interactions. As a lithium salt is progressively added to the solution, the intensity of the 789 cm^{-1} band decreases but there is a concomitant growth of a new band at 804 cm^{-1} ⁹. It seems reasonable to assign this band to an acetone vibration displaced by its interaction with the lithium ion. A series of acetone solutions in nitromethane were prepared and the integrated intensities of the 789 cm^{-1} band were obtained. A plot of the integrated intensity versus concentration gave a straight line. In another series of solutions, this time containing variable mole ratios of lithium perchlorate and acetone, the 789 and 809 cm^{-1} bands were computer-resolved and the respective areas integrated. Knowing the concentrations of bound and free acetone, the *average* solvation number of the lithium ion, n , can be calculated

$$\bar{n} = \frac{(\text{Me}_2\text{CO})_{\text{total}} - (\text{Me}_2\text{CO})_{\text{free}}}{(\text{Li}^+)_{\text{total}}}$$

A plot of \bar{n} versus concentration is shown in *Figure 3*. It is seen that the values tend towards a limiting number of 4.

In a recent series of papers Edgell and co-workers used the vibrational spectrum of cobalt tetracarbonyl anion ($\text{Co}(\text{CO})_4^-$) as a probe of the ionic environment¹⁵. The C—O stretching frequency at $\sim 1900\text{ cm}^{-1}$ was monitored in several solvents as a function of salt concentration and temperature. In

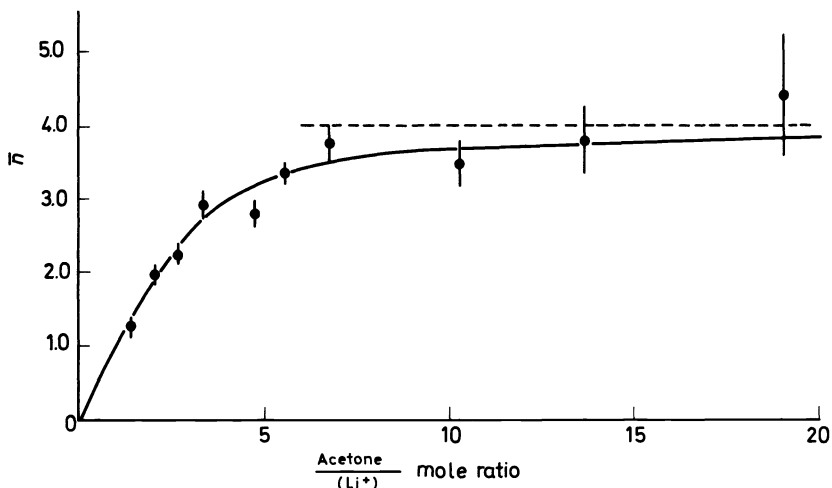


Figure 3. Variation of the average inner solvation number of Li^+ ion in acetone-nitromethane mixtures as a function of acetone/ Li^+ mole ratio

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

dimethylsulphoxide, dimethylformamide, hexamethylphosphoramide, acetonitrile, pyridine and nitromethane only a single absorption band was obtained. Extremely careful computer resolution of the band shape did not indicate a complex structure, with the exception of a very weak band at the low-frequency side assigned to the ^{13}C solvent species. On the other hand, in tetrahydrofuran and piperidine solutions additional bands were observed at the high- and low-frequency side of the main band. The behaviour of the two new bands indicates that they reflect the same environment, presumably a contact ion pair.

IV. ^{23}Na NMR STUDY OF ELECTROLYTE SOLUTIONS

In recent years the use of n.m.r. in the study of electrolyte solutions has become quite popular. Proton n.m.r. has been widely used for the studies of ionic interactions in solutions as well as for the determination of solvation numbers. For example, at low temperatures exchange between bulk water molecules and those in the inner solvation shell of a cation is slower than the n.m.r. time scale and, therefore, two separate resonances are observed for the free and bound water. Measurements were usually made in water-acetone mixtures so as to be able to attain low temperatures and it has been

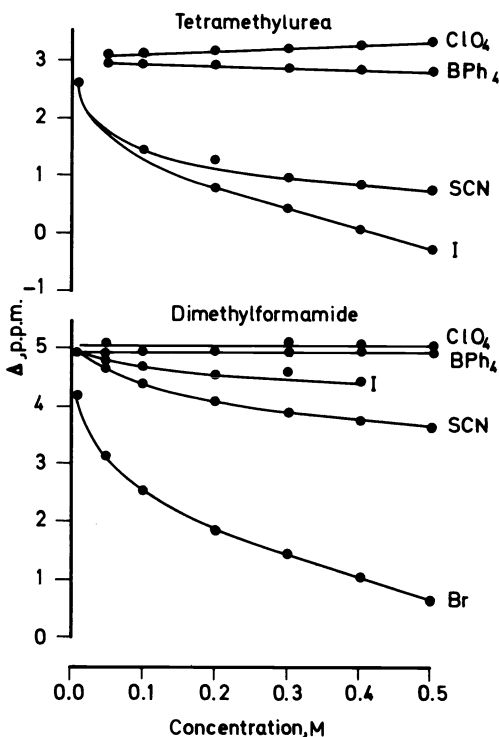


Figure 4. ^{23}Na chemical shifts with respect to 3.0 M aqueous NaClO_4 solution in tetramethylurea and in dimethylformamide¹⁹

assumed that acetone acts as a completely inert diluent. Hydration numbers for a number of transition metal cations were obtained by this technique¹⁶.

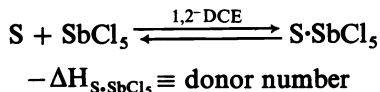
While much useful information has been obtained by proton n.m.r., it seems that the use of alkali metal n.m.r. as well as halogen n.m.r. has been particularly fruitful in the elucidation of the structure of alkali salt solutions in non-aqueous solvents.

The first comprehensive study of sodium iodide solutions in non-aqueous solvents has been reported by Bloor and Kidd¹⁷. Observed chemical shifts were referred to an infinitely dilute aqueous sodium iodide solution. Twelve solvents were used and chemical shifts varied from +9.9 p.p.m. (upfield) shift for acetic anhydride to -13.1 p.p.m. (downfield) for ethylenediamine. Some concentration dependence of chemical shifts was observed. The authors claim a correlation between chemical shifts in different solvents and the aqueous pK_a values of these solvents.

A more detailed study of several sodium ions in a number of non-aqueous solvents has been carried out in our laboratory¹⁸. The experimental results of Bloor and Kidd were confirmed, but the comparison of several different salts indicated that the counter-ions also play an important role in determining the behaviour of the ^{23}Na chemical shifts. In general, in the concentration range of 0.01–0.5 M, sodium perchlorate and sodium tetraphenylborate show no, or very little, concentration dependence. On the other hand, the iodide, bromide and thiocyanate showed a very considerable concentration dependence, the shifts being increasingly more negative with increasing concentration. An example of ^{23}Na chemical shifts in dimethylformamide and tetramethylurea solutions is illustrated in *Figure 4*¹⁹. It is seen that the chemical shifts for all of the salts converge towards the same limiting value at infinite dilution. It seems reasonable to expect that this limiting value represents the chemical shift of free sodium ion in the particular solvent. Concentration dependence of the sodium halides and thiocyanate solutions can be ascribed to the formation of contact ion pairs in these solutions.

A glance at the limiting sodium chemical shifts in different solvents immediately indicates a possible correlation with the solvating ability of these solvents. Thus, nitromethane, the least solvating solvent, has the largest upfield shift, while strongly solvating solvents such as pyridine, dimethylsulphoxide and hexamethylphosphoramide have the most pronounced downfield shifts. It should be noted, parenthetically, that there is no correlation between these chemical shifts and the polarity of the solvents, expressed either as the dielectric constant or the dipole moment.

Unfortunately, we do not have any theoretically based scale for the donor ability of the solvents. There are, however, several empirical scales proposed by various authors to express this quantity. The most promising one is that of Gutmann's solvent donor numbers (or donicity)²⁰. This scale is based on the enthalpy of the 1:1 complex formation between a dilute solution of a given solvent and antimony (v) chloride in 1,2-dichloroethane:



The ability of this scale to predict the behaviour of complex species in non-

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

aqueous solvents has been adequately demonstrated in recent years by Gutmann and co-workers as well as by other investigators. It was of interest to us to see if there is a correlation between these donor numbers and the ^{23}Na chemical shift. The plot, illustrated in *Figure 5*, shows a respectable straight line. It should be noted that at first glance the two parameters should be of

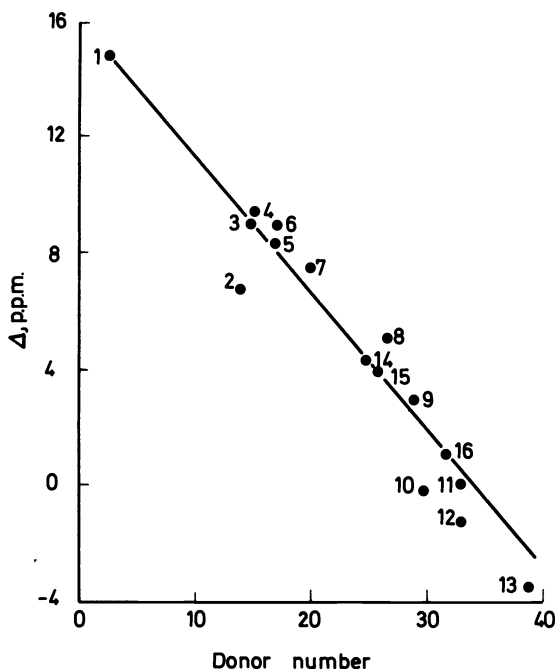


Figure 5. Plot of infinite dilution sodium-23 chemical shifts against the donor number of the solvent: (1) nitromethane; (2) acetonitrile; (3) sulpholane; (4) propylene carbonate; (5) acetone; (6) ethylacetate; (7) tetrahydrofuran; (8) dimethylformamide; (9) tetramethylurea; (10) dimethylsulphoxide; (11) water; (12) pyridine; (13) hexamethylphosphoramide; (14) formamide; (15) methanol; and (16) ethanol

different nature, since the donor numbers reflect a covalent interaction between a donor and an acceptor while ^{23}Na chemical shifts reflect electrostatic ion-dipole interaction. Nevertheless, the agreement seems to be too good to be fortuitous and must indicate a partial electrostatic character of the $\text{S}\cdot\text{SbCl}_5$ bond and/or some degree of covalency in the solvent-cation interaction.

It is interesting to note that the results of the ^{23}Na n.m.r. study underline the importance of the solvent donor ability on the formation of contact ion pairs as previously indicated by Mayer and Gutmann²¹. For example, formamide, with high dielectric constant of 109.5 and a fairly high donor number of 24.7, should be a highly dissociating solvent. Indeed our data show no concentration dependence of the ^{23}Na chemical shift for sodium iodide solutions¹⁹. On the other hand, comparison of the chemical shifts for the same salt in dimethylsulphoxide, sulpholane and propylene carbonate illustrate the importance of solvent donicity. Dimethylsulphoxide and

sulpholane have nearly identical dielectric constants of 46.7 and 44, respectively, but quite different donor numbers of 29.8 and 14.8. There is no concentration dependence of the ^{23}Na chemical shift in dimethylsulphoxide but a very marked one in sulpholane, indicating ion pair formation. Likewise concentration dependence of the chemical shift in NaI solutions in propylene carbonate²² indicates ion pair formation, although the solvent has a high dielectric constant of 65.0 but a relatively modest donor number of 15.1.

Linear relationships between Gutmann's donor numbers and ^{23}Na chemical shifts allows the determination of the former by the n.m.r. measurements. Chemical shifts have been determined for a number of solvents for which the experimental donor numbers are not available and these values have been estimated from the linear plot (Table 6). The ^{23}Na resonances in

Table 6. Limiting ^{23}Na chemical shifts and donor numbers in various solvents^{21, 23}

Solvent	Chemical shift (p.p.m.) ^a	Donor number	Solvent	Chemical shift (p.p.m.) ^a	Donor number
Nitromethane	15.6	2.7	Ethanol	0.35	31.5 ^b
Propylene carbonate	9.4	15.1	Dimethylsulphoxide	0.11	29.8
Sulpholane	9.0	14.8	Pyridine	-1.35	33.1
Acetone	8.4	17.0	Hexamethylphosphoramide	-3.45	38.8
Ethylacetate	8.2	17.1	Hydrazine	-5.4	44 ^b
Tetrahydrofuran	7.1	20.0	Ethylenediamine	-4.1	55 ^b
Dimethylformamide	5.0	26.6	Ethylamine	-4.3	55.5 ^b
Methanol	3.8	25.7 ^b	<i>i</i> -Propylamine	-12.4	57.5 ^b
Tetramethylurea	3.0	29.6	Ammonia	-13.1	59 ^b

^a Measured against aqueous 3.0 M NaClO₄ solution. Corrected for bulk susceptibility.

^b Estimated values from the linear δ against donor number plot.

the basic solvents are strongly shifted downfield, which necessitates an extrapolation of the linear δ_{Na^+} versus donor number plot²³. Thus, we find, for example, that the donor number of liquid ammonia is 59, the highest found thus far. It should be noted, however, that there is, at present, no assurance that the plot maintains its linearity in the region of large downfield shifts.

V. ^7Li AND ^{35}Cl NMR STUDIES

The ^7Li nucleus has a spin of 3/2 and thus is amenable to n.m.r. studies. Despite the fact that the nucleus has a quadrupole moment, the ^7Li resonance lines for Li^+ ion are exceptionally narrow and the chemical shifts can be measured with considerable accuracy. Previous studies by Maciel *et al.*²⁴ and by Akitt and Downs²⁵ in several non-aqueous solvents showed that the frequency of the ^7Li resonance is quite sensitive to the environment. In our recent study²⁶ chemical shifts of lithium salts were measured in 11 non-aqueous solvents against 4.0 M aqueous lithium perchlorate solution as an external reference. Lithium perchlorate, tetraphenylborate, chloride, bromide, iodide and triiodide were used. The data are illustrated in Table 7. The

STUDIES ON SOLVATES IN NON-AQUEOUS SOLVENTS

Table 7. Limiting ^7Li chemical shifts and donor numbers in various solvents²⁶

Solvent	Chemical shift (p.p.m.) ^a	Donor number	Solvent	Chemical shift (p.p.m.) ^a	Donor number
Acetonitrile	2.80	14.1	Acetic acid	0.03	—
Dimethylsulphoxide	1.01	29.8	Dimethylformamide	-0.45	30.9
Propylene carbonate	0.61	15.1	Tetramethyl-		
Tetrahydrofuran	0.60	20.0	guanidine	-0.63	—
Methanol	0.54	25.7	Acetone	-1.34	17.0
Nitromethane	0.36	2.7	Pyridine	-2.54	33.1

^a Measured against 4.0 M LiClO_4 aqueous solution. Corrected for bulk susceptibility.

range of chemical shifts is much narrower than for ^{23}Na nucleus and varies from +2.80 p.p.m. in acetonitrile to -2.54 p.p.m. in pyridine. In dimethylformamide, dimethylsulphoxide, and methanol the shifts were independent of concentration. Concentration dependence, indicative of the contact ion pair formation, was evident in tetrahydrofuran, nitromethane and tetramethylguanidine solutions.

No concentration dependence was observed in acetic acid solutions, although, as mentioned above, the solvent has a very low dielectric constant and it is natural to expect that there will be a considerable amount of ion association in this medium. It seems reasonable to assume that in this case we have largely solvent separated ion pairs. This assumption is supported by the previously mentioned observation that the frequency of the far-infra-red

Table 8. Line broadening of ^{35}Cl resonance in LiClO_4 solutions

Solvent	Conc. (M)	W_{obs}^a (Hz)	$W_{\text{corr}}^{a,b}$ (Hz)
Acetone	0.00	—	—
	0.26	11	10
	0.52	16	13
	1.00	27	13
Methanol	0.00	—	—
	0.49	19.4	15
	1.00	19.4	14
Tetrahydrofuran	0.00	—	—
	0.26	53	44
	0.49	63	45
	1.44	202	64
Nitromethane	0.00	—	—
	0.26	85	82
	0.51	120	103
	1.01	178	131
	—	—	—
Tetramethylguanidine	0.00	—	—
	1.00	280	51
	—	—	—
Acetonitrile	0.00	—	—
	0.26	15	14
	0.50	27	21
	1.00	26	22

^a Width at half height.

^b Corrected for viscosity.

solvation band of lithium salts in this solvent was found to be independent of the nature of the anion.

The data obtained with ^{35}Cl n.m.r. studies favour the above conclusions. Measurements on lithium perchlorate solutions in various solvents were carried out. In dilute solutions the width at half-height of the ^{35}Cl resonance was 10–20 Hz. As seen from *Table 8*, in nitromethane, tetrahydrofuran and tetramethylguanidine solutions an increase in the salt concentration is accompanied by a considerable broadening of the ^{35}Cl resonance. On the other hand, very little concentration dependence is evident in acetone, methanol or acetonitrile solutions. We feel that this broadening is due to a change in the electric field gradient at the chlorine nucleus as the perchlorate ion interacts with Li^+ to form a contact ion pair.

Similar results were recently obtained by Stengle and co-workers in their studies of metal perchlorate solutions in non-aqueous solvents²⁷.

Contrary to the case of ^{23}Na n.m.r., no correlation was found between ^7Li chemical shifts and Gutmann's donor numbers. It has been shown by several investigators^{17, 28} that while, for the sodium nucleus, the paramagnetic screening constant is much larger than the diamagnetic screening constant, in the case of lithium the two terms are of approximately the same magnitude and tend to cancel each other. Consequently, specific properties of solvent molecules, such as ring currents, become important for lithium chemical shifts.

VI. CONCLUSIONS

It seems that one can conclude from the above discussion that spectroscopic techniques can be very useful in the elucidation of the structure of electrolyte solutions. Both the vibrational spectroscopy and particularly the alkali metal n.m.r. are very sensitive probes of the immediate chemical environment of ions in solutions. The interpretation of the results is not always straightforward and the work done to date has been mostly qualitative. A great deal of additional experimental and theoretical studies is needed before we can understand the role of solvents in chemical reactions.

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