APPLICATION OF E.S.R. SPECTROSCOPY TO THE STUDY OF SOLVATION

Martyn C. R. Symons

Department of Chemistry, The University, Leicester, LE1 7RH.

Abstract - The use of e.s.r. spectroscopy as a tool to study solvation
is reviewed. Specific attention is given to the detection of ion-pairs
involving radical anions and cations. The effect of protic solvents on
e.s.r. parameters for radical anions and neutral radicals is discussed
especially for dialkyl nitroxides. The use of ionizing radiation to
generate paramagnetic species in specific environments is also proposed
as a useful method for studying solvation.

INTRODUCTION

Although it is limited to the study of dilute paramagnetic solutes, the technique of e.s.r.
spectroscopy has taken its place amongst other forms of spectroscopy as a useful method for
obtaining structural and dynamic information about solvation. This is especially true in
the field of ion-pair formation, in which e.s.r. spectroscopy stands out as the most power-
ful technique for learning about their presence, structure, and energetics (1-3). It is
also of considerable use for probing dynamic processes in which different species have
life-times in the region of 10^{-6}—10^{-9} s, which is a range that is not readily accessible by
other techniques. Hence, for example, the extensive use of dialkyl nitroxides as "spin-
labels" in biological studies (4,5).

In this Review, attention will be focused upon the study of radicals, neutral or charged.
Transition-metal complexes are omitted because the field is very large and because the
majority of studies involve inner-sphere solvation. Nevertheless, the study of such com-
plexes by e.s.r. spectroscopy can give useful information about solvation (6,7).

ION-PAIRS AND CLUSTERS

Although it was appreciated that ion-pairs could have a range of possible structures (8),
very little direct information about such structures existed before the discovery by Weismann
and his co-workers (9) that the e.s.r. spectra of certain radical-anions in low polarity
solvents contained hyperfine features characteristic of the alkali-metal gegen ions. These
were described as ion-pairs rather than molecules because the anions retained their symmetry,
as indicated by their e.s.r. spectra, and hence specific σ-bonding to a particular atom of
the anion was ruled out. Furthermore, the addition of a more polar solvent led to the
appearance of e.s.r. features of the normal anion with no contribution from the gegen ions.
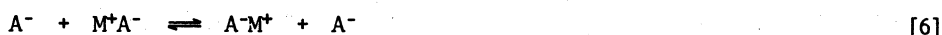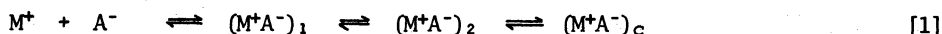
Further studies have confirmed and extended the original observations (1,2,10-15), and a
remarkably detailed insight into the nature of ion-pairs has been forthcoming. Some salient
features are now summarised.

Radical Anions: Cation Hyperfine Coupling
The reason why alkali metal nuclei frequently give rise to detectable hyperfine coupling is
because slight electron-transfer from the paramagnetic anions, which are, of course, power-
ful electron donors, takes place into the outer s-orbital of the cation, and hence even a
small transfer gives an easily detectable coupling. For example, for the Na^+—benzophenone
anion pair, a splitting of 1.125 G corresponds to ca. 0.36% transfer. This is typical,
although values as great as ca. 4% transfer have been detected. Various detailed mechanisms
for spin-transfer have been proposed (2,3). One important factor is the extent of overlap
facilitating charge transfer. If the preferred site for the cation is at or near a node in
the unpaired electron's wave function, direct transfer is inhibited. Another of the factors
that will control the extent of spin-transfer for a given pair of ions is the extent to
which they are solvated, since strong solvation will hold back the electron and block its
arrival as well as tending to separate the ions. Once a true "solvent-shared" ion pair (8)
has been formed, electron-transfer will be prevented, at least for most insulating solvent

molecules. The presence of such ion pairs may still give rise to a detectable modification of the e.s.r. spectrum of the anions but this is not such an immediately compelling effect.

So long as metal ion hyperfine coupling can be detected, a variety of equilibria can be studied and often their rates and even their activation energies and entropies can be estimated from line-width effects. Examples of such equilibria are:

$$M^+ + A^- \;\rightleftharpoons\; (M^+A^-)_1 \;\rightleftharpoons\; (M^+A^-)_2 \;\rightleftharpoons\; (M^+A^-)_c \qquad\qquad [1]$$

$$M^+ + A^-M^+ \;\rightleftharpoons\; M^+A^- + M^+ \qquad\qquad [2]$$

$$M^+ + A^-M^+ \;\rightleftharpoons\; M^+A^-M^+ \qquad\qquad [3]$$

$$M^+A^- \;\rightleftharpoons\; A^-M^+ \qquad\qquad [4]$$

$$A + M^+A^- \;\rightleftharpoons\; A^-M^+ + A \qquad\qquad [5]$$

$$A^- + M^+A^- \;\rightleftharpoons\; A^-M^+ + A^- \qquad\qquad [6]$$

$$A^- + M^+A \;\rightleftharpoons\; A^-M^+A^- \qquad\qquad [7]$$

Equilibrium I

In Process I $(M^+A^-)_1$ represents the ion-pair with maximum solvation, the limiting form being the contact ion-pair $(M^+A^-)_c$. If the equilibria between successive ion-pairs, $(M^+A^-)_i \;\rightleftharpoons\; (M^+A^-)_j$ are fast on the e.s.r. time-scale, then studies will generally only detect an average type of ion-pair. Alternatively if these equilibria are relatively slow, the contact ion-pair will be well defined, but it may be difficult to distinguish between other ion-pairs and the solvated anions. I stress, however, that the extrusion of solvent molecules on ion-pairing need not always occur as a series of well defined jumps. Thus one can envisage a more continuous ebb and flow process such as that in Scheme (I) with no specific
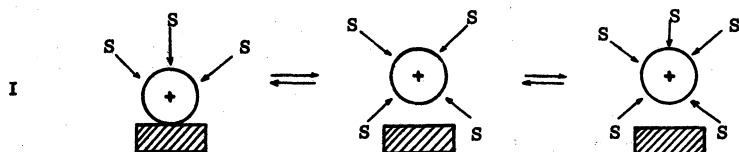
route involved. The best defined unit is likely to be the solvent shared ion-pair in which the shared solvent molecule is amphoteric, but even here, a range of possibilities exist, because of the non-linearity of the bonding functions.

Evidence that different types of ion-pairs are sometimes involved is strong (2). Hirota (21) found that lithium anthracenide in diethyl ether gave spectral features for the normal ion-pair showing cation hyperfine coupling together with a species showing no cation coupling, but having proton splittings that were different from the normal solvated ion values.

A more definitive study is that of Höfelmann et al. (22), for sodium naphthalenide in tetrahydropyran. Contact ion-pairs $[A(^{23}Na^+) = 1.23 \text{ G}]$ together with another type of ion-pair $[A(^{23}Na^+) = 0.38 \text{ G}]$ were detected when tetraglyme was added to the solution. Excess glyme gave only the latter species.

In the fast-exchange region, the e.s.r. spectra for two types of ion pair with different cation hyperfine coupling would be expected to exhibit selective broadening of the individual features (B-N-N-B) as depicted in Fig. 1. [Differences in the $\langle g \rangle$ and $\langle A \rangle$ values for the
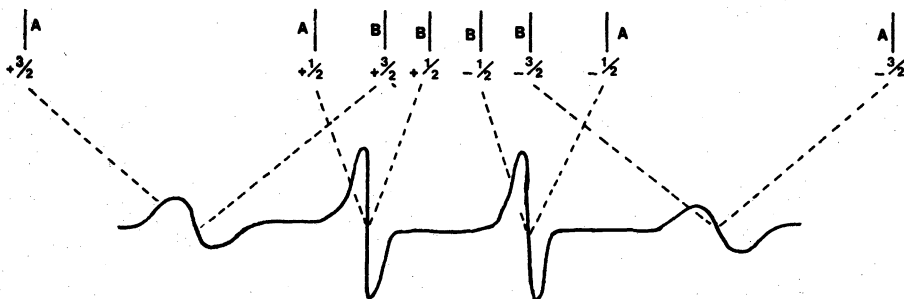
Fig. 1. Predicted hyperfine features for a cation having $I = {}^3/_2$ in equilibrium between two different types of ion-pair, A and B.

anions would make this an asymmetric effect.] Such effects have been observed for several systems (14,22,24).

In these studies, especially those involving a second solvent such as the chelating glymes, the two types of ion pair clearly differ in the extent of solvation. A different situation arises when there are two different 'binding' sites in the anion. Again, two different types of ion-pair should be detectable in the slow exchange regime and an average with suitable line-broadening in the fast exchange region. The latter situation was observed for 2,6-dimethyl-p-benzosemiquinone (25,26), there being a clear preference for the less hindered carbonyl oxygen.

Stevenson and co-workers have studied a range of ion-pair equilibria using hexamethylphos-phoramide (HMPA) as solvent (27,28). This solvent strongly solvates cations but anions are only very weakly solvated: the tendency to form ion-pairs is such that anions with high negative charge density on a functional group (C=O or NO_2) form ion-pairs in the absence of added electrolyte but others give only the free anions unless salts (iodides or chlorates) are added. They report $\Delta G°$, $\Delta H°$ and $\Delta S°$ values for the ion-pair process, and for p-benzo-semiquinone anions (27), and compare these with those reported for dimethoxyethane solvent (29). One possible disadvantage of the method in which extra salt is added is that the new anions (X^-) are in excess, and the equilibria such as

$$M^+ \; + \; X^- \; \rightleftharpoons \; M^+X^- \tag{8}$$

$$\text{and} \; M^+X^- \; + \; A^- \; \rightleftharpoons \; M^+A^- \; + \; X^- \tag{9}$$
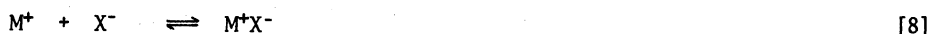
must be considered, as well as the possible formation of triple ions.

In their studies of p-substituted nitrobenzene anions in HMPA these workers (28) found that the ion-pairing equilibria were strongly affected by the σ^+ constant of the substituent. Both the forward and reverse rates are modified, both falling as the negative charge on the nitro-group increases (28).

Equilibrium 2
Process (2), the bimolecular analogue of (1), is readily detectable because it causes an uncertainty in the nuclear quantum number for M^+. This leads to broadening and, ultimately, loss of hyperfine structure, the resulting spectrum in the fast exchange region being almost indistinguishable from that of the solvated anions alone. The line-width increments lead directly to rates.

Anions with two binding sites
However, if the anion has more than one equivalent binding site, as for the semi-quinones or dinitrobenzene anions, process (3) may occur. The triple ion is, of course, a reasonable reactive intermediate for (2) (18), but is unlikely to be detectable for normal systems. However, if the anion has two binding sites the triple ion in (3) may have sufficient stability to give rise to separate resolved features including hyperfine components characteristic of two equivalent cations (19,20). [See § Triple Ions and Ion Clusters.] As expected, the spectral features for the anions within such triple ions are once more typical of the normal, symmetrical species, whereas for the ion-pair they reflect the asymmetry induced by the single perturbing cations.

Equilibrium (4) is another manifestation of such asymmetry. When there are two equivalent sites, the cation can migrate from one to the other at a rate sufficiently great to modify the e.s.r. spectrum. Typically, at low temperature the spectrum may be that of the asymmetric anion, whilst that at ambient temperature may be that of the symmetric anion. At intermediate temperatures selective line broadening occurs because only alternate lines are different for the two limits (see Fig. 2). From this broadening the rate of migration can be calculated. The spectra reveal that it is a single cation that is responsible for the spectral changes, since its contribution to the hyperfine coupling is unaffected.

One advantage of the e.s.r. method is that many processes occur at rates that strongly affect line-widths. This is true for most intramolecular cation migrations (2). One example that has been very thoroughly studied is that of the anthraquinone radical anion (30). Values for $\Delta G°^{\ddagger}$, $\Delta H°^{\ddagger}$ and $\Delta S°^{\ddagger}$ have been obtained for sodium and potassium ion migrations in THF over a wide temperature range, and the effect of adding DMF to these solutions has also been examined. The broad features that transpire are:

    i) Activation energies are small (3-4 kcal. mol^{-1}), with values for K^+ slightly larger than those for Na^+.

    ii) $\Delta S°^{\ddagger}$ values are relatively large and negative, with those for Na^+ (ca. -17 eu) greater in magnitude than for K^+ (ca. -9 eu).
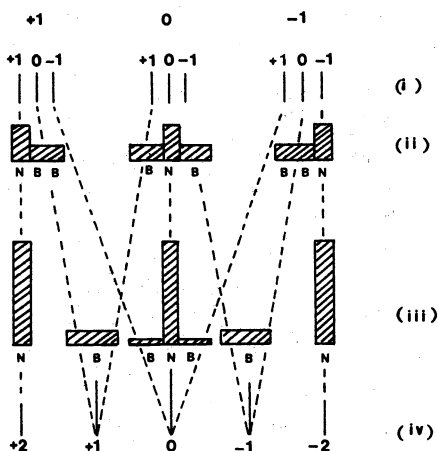
Fig. 2. Hyperfine features for a radical anion with two equivalent ^{14}N nuclei (I = 1). (i) On association with a cation which induces a fluctuation in the ^{14}N hyperfine coupling the coupling constants of the two ^{14}N become different. (ii) Slow exchange. (iii) Intermediate exchange. (iv) Fast exchange. (N = narrow, B = broad.) If exchange occurs at a slow rate this will broaden as in (ii), and if it is fast they will exhibit alternate broadening as in (iii).

iii)   Added DMF reduces the magnitude of $\Delta S^{o\ddagger}$, resulting in a marked increase in migration rate.

The key factor is the large negative entropy, which for this solvent, which bonds strongly to the cations only, means that the cations are more strongly solvated in the transition state. This is to be expected since the anion-cation bond has to be severed cleanly prior to the making of the new bond at the second oxygen site. Indeed, a reasonable model might well be one of displacement by an incoming solvent followed by migration and subsequent replacement of a solvent molecule by the second oxygen (Scheme II). Since solvent is bound
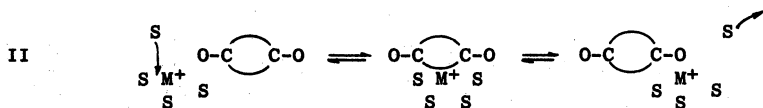
more weakly to K^+ than to Na^+ $|\Delta S^{o\ddagger}|$ is reduced. The nett contribution to $\Delta H^{o\ddagger}$ is then slightly greater on balance for K^+.

The effect of added DMF must also be understood in terms of cation solvation. This is a stronger cation solvator than THF and hence even at low concentrations will be preferentially bonded to the cations in the ion-pairs. This will have the effect of weakening the cation-anion interaction and reducing the need for extra solvation in the transition state.

Solvation versus Ion-Pair Formation
The main factor involved in all these studies of ion-pairs is that of solvation, upon which the electrostatic attraction of cations and anions is superimposed. It is important to realise that the highly localised hydrogen bonds between solvent molecules such as alcohols or amides and an anion may be more effective in stabilising (and possibly perturbing) that anion than a cation such as Na^+ or even Li^+. Protic media are generally also basic media, and thus both cations and anions are strongly solvated. Solvent shared ion-pairs are quite acceptable since neither ion is desolvated, but contact ion-pairs are improbable except in very concentrated solutions, or when both anion and cation have a low surface charge density. Aprotic solvents, however, do not bind strongly to anions, so an anion can readily replace a solvent molecule as a ligand on the cation, the strength of bonding of the solvent and anion being comparable in many cases.

These considerations are illustrated by results for various nitro-aromatic anions (31). The hyperfine coupling to ^{14}N is extremely sensitive to environment. Thus bonding of cations or protic solvent molecules to the oxygen atoms pulls negative charge onto oxygen and increases the spin density on nitrogen. A rough guide to the results is given for $PhNO_2^-$ in Scheme

III. Thus the perturbing power of the alcohols is greater even than that of Li^+. This

	R_2O	R_2O	R_2O	EtOH	R_2O	E_2OH	EtOH	
SOLVENT	├	├	├	├	├	├	├	→ $PhNO_2^-$ (^{14}N)
CATION	R_4N^+	Cs^+	Na^+	R_4N^+	Li^+	NIL	Na^+	
	10	11		12		13	14	(GAUSS)

III (label for the scheme above)

arises, presumably, because several alcohol molecules contribute to the effect. As expected, $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ for ethereal solutions, and these all perturb the anions more than R_4N^+ ions in ethers, which in our view, represents the unperturbed anions.

Addition of R_4N^+ salts to the alcohol solvate results in unwilling displacement of ROH by R_4N^+, which plays the role of an aprotic solvent, causing a steady fall in $a(^{14}N)$. In contrast sodium ions cause a small increase in $a(^{14}N)$. This, we suggested, means that solvent shared ion-pairs cause a slightly greater perturbation by strengthening one of the hydrogen bonds to oxygen (31).

Solvation of Ion-Pairs
Quite apart from the possibility of different types of ion pair (contact, solvent shared, etc.), we expect the e.s.r. parameters of ion-pairs, M^+A^-, to be solvent sensitive. Oakes and Symons (32) explored this possibility using various substituted semiquinones in a range of solvents. Several generalisations were extracted from the data.

   i)   There was a steady fall in calculated spin-density on the cations on going
        from Li^+ to Cs^+, for all solvents. This is normal and reflects the electron
        affinity changes or surface charge-density changes.

  ii)   The hyperfine coupling to M^+ fell on cooling. This again is normal and is
        explained in terms of a preferential binding site for M^+ on or near a nodal
        surface for the unpaired electron, with increasing migration from this site
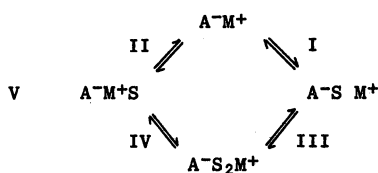   with increasing temperature (see Scheme IV).

IV
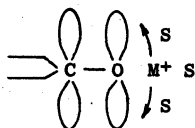
 iii) $A_{iso}(M^+)$ falls on going from durosemiquinone to the unsubstituted anion.
        This, we suggest, arises because the in-plane site is sterically difficult or
        even impossible to occupy in the methylated site, thus forcing the cation
        into the out-of-plane site which gives better overlap and more transfer of
        spin.

  iv)   The metal hyperfine coupling falls on going from t-pentanol to ethereal
        solvents. (Simple alcohols gave dissociation of the ion-pairs, or solvent
        shared ion-pairs, too rapidly.) This is, at first sight surprising, since
        solvent shared ion-pairs would be expected and these should give small or
        zero metal coupling. However, in view of the bulky nature of the solvent
        such structures may be improbable. We suggest that solvation occurs at the
        site not occupied by the cations, thus minimising the perturbation and
        increasing the spin-density on the carbonyl group near the cation (Scheme IV).
        This is supported by the proton hyperfine coupling which moves closer to the
        unperturbed values in the alcoholic media.

It is interesting to compare these results with those of Nakamura et al. (33), who studied the e.s.r. spectra of alkali salts of fluorenone in mixed protic and aprotic media. The ^{13}C hyperfine coupling for the carbonyl carbon increased rapidly for all except the Li^+ salt on the addition of alcohol to ethereal solutions, the increases falling in the order MeOH, EtOH, iPrOH. The form of these curves suggests that one solvent molecule is initially involved, and the increase in $a(^{13}C)$ shows that this is hydrogen bonded to the carbonyl oxygen atom. In order for this to occur, some movement of the cation out of the radical plane must occur for steric reasons, and this is indeed proven by the initial increase in $a(M^+)$. The different behaviour of $a(^{13}C)$ for the lithium salt was explained in terms of solvation of Li^+ by the alcohol.

These workers (33) were able to explain their results for $a(^{13}C)$ and $a(M^+)$ quantitatively

using Scheme V and the four equilibrium constants for these processes. The fit of all the

$$
\begin{array}{c}
\text{A}^-\text{M}^+ \\
\text{II} \nearrow \qquad \nwarrow \text{I} \\
\text{V} \quad \text{A}^-\text{M}^+\text{S} \qquad \qquad \text{A}^-\text{S M}^+ \\
\text{IV} \nwarrow \qquad \nearrow \text{III} \\
\text{A}^-\text{S}_2\text{M}^+
\end{array}
$$

data is surprisingly good. One significant conclusion was that perturbation by the second solvent molecule (ROH) was much less than that of the first. Further solvation resulted in a new species with no coupling to M^+, presumably the fully solvated anion.

In another interesting study of the solvation of ion-pairs, Chen et al. (34) added DMF to various alkali metal aromatic ketyls in ethers. Invariably, $a(M^+)$ increased as one DMF molecule became bound to the complex. Further solvation resulted in dissociation, in a one step process, not involving solvent separated or shared ion-pairs. As stressed above, this is expected for aprotic media since, once a solvent molecule has been inserted between the ions, there is no bonding left to hold them together other than weakened electrostatic forces. However, that $a(M^+)$ should increase prior to dissociation is not an obvious result. Since one DMF molecule has become bonded to the cation, and since this interaction is relatively strong, the anion-cation interaction must be weakened. In that case, thermal migration away from the in-plane site would be greater, and hence the coupling could increase, as observed. This result fits in with the increased rate of migration when DMF is added, that was discussed in 'Anions with two binding sites'.

Triple Ions and Ion Clusters

Solutions of electrolytes in low dielectric solvents tend to form ion aggregates even at low concentrations. E.s.r. spectroscopy is capable of defining at least two such species clearly. Thus $M^+A^-M^+$ ions, if they have a sufficiently long life will show hyperfine coupling to two equivalent cations, whilst $A^-M^+A^-$ ions will usually be in a triplet-state which also has a characteristic spectrum.

The former species were discovered by Gough and co-workers (19,20), for anions having two equivalent functional groups. It had been clear for some time that such anions would be most likely to give $M^+A^-M^+$ units, which are the natural transition intermediates for cation exchange in the presence of excess cations. However, our own attempts to prepare such species involved the use of added alkali halides, especially sodium iodide. Gough et al.'s success came from the use of sodium tetraphenylboride. For this salt there can be no bonding between the parent cations and anions, so the possibility of bonding to the vacant sites of the radical anions becomes attractive and does in fact lead to stable triple ions. Warhurst and his co-workers (35) have examined the role of the iodide ions in systems containing added sodium iodide, and have concluded that it is certainly involved in the cation exchange process.

As with much of the early work on ion-pairs, Weissman and co-workers pioneered the study of triplet-state aggregates, by studying the liquid and solid state e.s.r. spectra of species containing divalent cations, $A^-M^{2+}A^-$ (36). For monovalent cation salts, the species detected is $(M^+A^-)_2$ rather than $A^-M^+A^-$, as evidenced by hyperfine coupling from two equivalent cations (37). No doubt $A^-M^+A^-$ ions would be formed in the presence of an excess of $R_4N^+A^-$.

Solid-state spectra, which are generally rather uninformative, except for nitrogen centred anions (38) now give the "mean" separation between the interacting electrons, and some measure of any deviations from axial symmetry (2). Mao et al. (39) have extended these studies, and shown that higher clusters are formed in ethereal solutions which dissociate in more polar media into triple ions, $(R^-M^{2+}R^-)$. For the alkali salts, both $R^-M^+R^-$ and $R^-M^+R^-M^+$ were detected.

Radical Cations in Ion Pairs

Far more attention has been paid to the solvation and ion-pairing of radical anions than to that of radical cations. This is partly because media such as sulphuric acid (40,41) were traditionally used. Also, as was stressed some time ago (1), slight electron-transfer towards cations such as Na^+ results in slight population of their outer s-orbitals, giving rise to a readily detectable isotropic hyperfine coupling. However for A^+X^- ion pairs, electron transfer from X^- leaves unpaired spin in the p-manifold of X^-. This will not, in first order, give rise to any isotropic hyperfine coupling, which will therefore probably remain undetectably small. However, such a charge-transfer configuration will give rise to

a field induced orbital angular momentum and this will in turn give rise to a small positive g-shift.

These predictions have been nicely confirmed in recent work by Goez-Morales and Sullivan (42), who studied the cation of 1,2,4,5-tetramethoxybenzene in a range of solvents including chloroform, methylene chloride, methylcyanide, nitromethane and their higher alkyl analogues. The anion induced g-shifts were much larger for I^- (or I_3^-) than for Br^- (or Br_3^-), as expected, and became greater as the solvent polarity was reduced. These experiments clearly establish the presence of halide ion-pairs, but no further details about these species are available at present.

SOLVATION OF RADICAL ANIONS

By far the most significant change in the e.s.r. spectra of radical anions occurs when solvent molecules can form hydrogen bonds to some specific atom or group. Thus addition of a protic solvent such as an alcohol to a solution of the radical anion in an aprotic solvent has little effect on the e.s.r. spectra of species such as the naphthalene anions, but a marked effect on the spectra of semiquinone anions (43) and nitro-aromatic anions (31). Indeed these solvent induced perturbations may be as great or greater than those induced by cations in ion-pairs (31). Most studies have been devoted to p-benzosemiquinones and aromatic nitro anions, and I consider these in turn.

Semiquinones
Two extremes of solvation can be envisaged. In one, the solvent interacts to stabilise the negative charge equally on the two carbonyl groups, whilst in the other, strong solvation at one carbonyl group pulls the negative charge predominantly to this end of the molecule, leaving the other side largely unsolvated. The former is more likely, and in fact solvent induced asymmetry has not been detected for semiquinones, although it has for m-dinitro-benzene anions in water, (see § Aromatic Nitro Anions).

If one considers an isolated anionic carbonyl group, $R_2C=O^-$, then hydrogen bonding to oxygen will tend to stabilise the form $R_2C-O^-\cdots HA$, thus forcing the unpaired electron more onto carbon. This should result in an increase in $\underline{a}(^{13}C)$ and a fall in $\underline{a}(^{17}O)$. For the semi-quinones this occurs at both carbonyl groups simultaneously, and the expected changes in the coupling to ^{13}C and ^{17}O are indeed observed (44-46). The ring proton hyperfine coupling is effectively "buffered" and is relatively insensitive to such changes. Values of a_{iso} (^{13}C) or (^{17}O) are a linear function of the Z-value (47) of a range of solvents for p-benzosemi-quinone (48), (Fig. 3). This means, indeed, that protic solvents are very much more
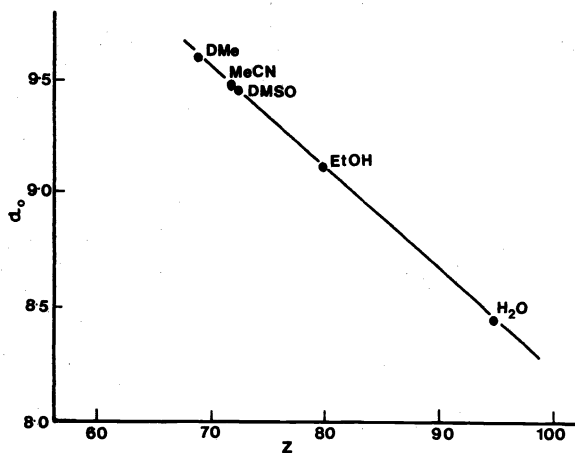

Fig. 3.   Dependence of the ^{17}O coupling constant of p-benzosemiquinone upon the Z value of the solvent.

effective in perturbing the anions, water being the most powerful. The reason why such good correlations with Z are observed (Fig. 3.) is probably because in both studies, it is the tendency to pull negative charge towards the solvent molecules that is involved.

The anions of 2,6-dimethylbenzoquinone and other 2,6-disubstituted quinones are of interest since one of the anionic oxygen sites is far more shielded than the other. This is clear from the fact that mono-protonation and cation binding occur almost exclusively at the unhindered oxygen site (49,50), which suggests that solvation may also be asymmetric. This fact makes the hyperfine coupling to the ring protons far more sensitive to changes. In

this case a plot of $\Delta A[= \underline{a}(^1H_{Me}) - \underline{a}(^1H_{ring})]$ gives only a poor correlation with Z, showing that opposing factors are involved. The major additional factor was thought to be steric, bulky solvent molecules giving a greater differential solvation than small molecules, especially water.

Aromatic Nitro Anions
As we have stressed above, hydrogen bonded protic solvents cause a major electronic perturbation to the nitro group, causing $\underline{a}(^{14}N)$ to increase. Stevenson and Echegoyen (51) have used methylacetylene as a proton donor with p-dinitrobenzene anions in hexamethylphosphoramide (HMPA), and have estimated the enthalpy of hydrogen bonding from the e.s.r. results. Stevenson and his co-workers have found that HMPA is an excellent solvent for such studies (28,29,51) since ion-pairing is not extensive, but can usually be induced by the addition of salt. This solvent does not interact significantly with the anions, but solvates alkali cations strongly.

The enthalpy $(\Delta H_t°)$ for bond formation was -1.74 kcal M^{-1}, this being somewhat less negative than the value for bonding to HMPA itself (-2.69 kcal M^{-1}), obtained from n.m.r. data.

In an extension of this work, Stevenson et al. (52) used methanol as hydrogen bond donor, and varied the substituent in para-substituted nitrobenzene anions, again using HMPA solvent. A linear correlation between $\ln K_{eq}$ and the σ^+ values for their substituents was observed. Hence they deduced that these anions responded to substitution in the same way as correspondingly substituted phenoxide anions, as might be expected.

We conclude that solvation of radical anions is weak in aprotic solvents but, provided there are functional groups with basic sites, protic solvents form hydrogen bonds of sufficient strength to perturb the anions in a readily detectable way. When two functional groups are present, they are generally solvated equivalently. However, this is not the case in the special instance of m-dinitrobenzene anions (53-55).

In aprotic solvents, these anions are symmetrical, as symmetry considerations predict. However, when ion-pairs are formed they become asymmetric in a catastrophic fashion (56), such that $\underline{a}(^{14}N_1) \gg \underline{a}(^{14}N_2) \sim 0$. In a crude sense this can be pictured as a switch to the mono nitro structure, the other NO_2 group behaving as a neutral substituent. In alcoholic media, a line-width alternation is observed even though ion-pairing is insignificant. This must mean that there is a rapid switching from strong to weak solvation at both nitro groups occurring out of phase. In the unique case of water, however, the slow exchange situation is found, with $\underline{a}(^{14}N_1) \gg \underline{a}(^{14}N_2)$. We deduced from the line-widths obtained from such spectra that the mean lifetime of these asymmetric solvates is ca. 4.5 μs at 282 K. Addition of t-butyl alcohol caused an initial increase in this lifetime followed, in the 0.04 mole fraction region by a rapid fall. This is, in my view, one of the most dramatic examples of the special role of water structure yet discovered.

SOLVATION OF NEUTRAL RADICALS

Although stable nitroxide radicals have been widely exploited as "spin-labels" in biological systems, their use as probes to study solvation has not been extensive. Recently, Jolicoeur and Friedman (57,58) have reported the effect of varying solvent upon the two nitroxides usually known as TEMPO (2,2,6,6-tetramethyl-piperidine-N-oxide) and OTEMPO (2,2,6,6-tetramethyl-4-piperidone-N-oxide). They concentrated upon line-width effects, distinguishing between a uniform broadening induced by spin-rotation relaxation (T_J) and an asymmetric broadening ascribed to modulation of the g and A tensor components by the rotational motion (T_c).

We have carried out similar studies using di-t-butyl nitroxide (DTBN), but have focused attention primarily on changes in $A(^{14}N)$ (59). Line-width studies are rendered difficult by the fact that unresolved hyperfine coupling to many protons makes a major contribution for all but the most viscous solvents or highest temperatures. The difficulty is that $A(^1H)$ also varies with solvation, increasing in magnitude as $A(^{14}N)$ falls. We have used a computer simulation method coupled with selected use of the $\underline{d}^{18}$ nitroxide to overcome this problem.

Trends in ^{14}N Hyperfine Coupling Constants
Some trends in $A(^{14}N)$ are displayed in Fig. 4. All these changes can be understood in terms of the hydrogen-bonding equilibrium:
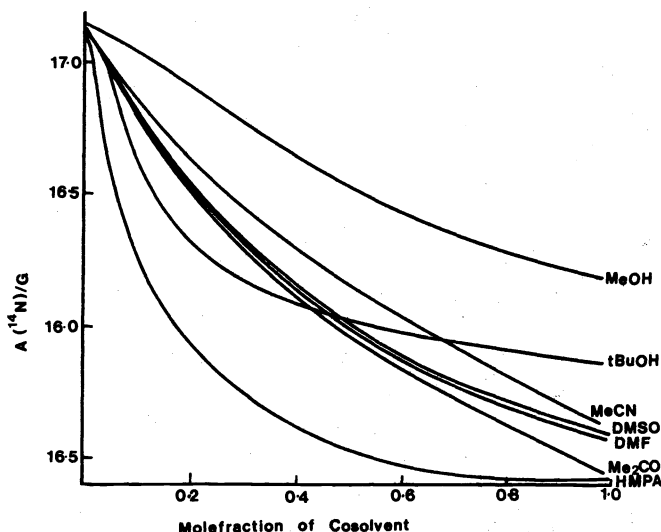
$$R_2NO \text{----} H\overset{|}{O}H \text{----} + B \; \rightleftharpoons \; R_2NO \; + \; B \text{----} H\overset{|}{O}H \text{----} \; . \qquad [10]$$
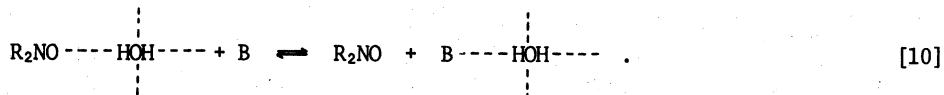
Fig. 4. Hyperfine coupling constants (^{14}N) for DTBN in aqueous solutions as a function of the mole-fraction (M.F.) of added co-solvents. [MeOH = methanol, t-BuOH = t-butyl alcohol, MeCN = methylcyanide, DMSO = dimethylsulphoxide, Me$_2$CO = acetone, HMPA = hexamethylphosphoramide and DMF = dimethylformamide.]

A(^{14}N) is a maximum in aqueous solution, for which this equilibrium is assumed to be constrained completely to the left hand side. Interaction with aprotic solvents is dipolar in nature and A(^{14}N) is then relatively insensitive to changes. The major difference between R$_2$NO as a probe and anions such as PhNO$_2^-$ is its low basicity. Thus as [B] increases hydrogen bonds are rapidly lost. This could be viewed as preferential solvation by the aprotic solvent, but in our view this is a completely misleading description. It is the strong affinity of the basic aprotic solvent for hydrogen bonds that removes water from the nitroxide, and it is the loss of such bonding, not the gain of aprotic solvent molecules that causes A(^{14}N) to fall.

The trend to lower A(^{14}N) values on adding methanol could be caused by weaker H-bonding, or by an increase in the concentration of non-H-bonded nitroxide. Since methanol is a relatively strong proton-donor, we favour the latter explanation, and this is supported by recent solid-state studies which suggest the presence of two types of nitroxide in methanol glasses at 77 K (59). The reason for this trend can be understood in terms of the presence, in methanol, of a huge excess of weakly basic "lone-pairs" of electrons, not involved in hydrogen-bonding. We have recently obtained evidence, from infrared studies, that under conditions that form (OH)$_{free}$ groups in water, methanol forms a weakly bonded (OH)$\cdot$ group (60,61), having, we suggest, the structure:
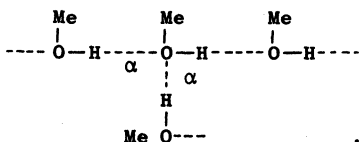
The two bonds labelled α in this structure will be much weaker than the remainder and give rise to the new infrared absorption. We suggest that formation of such units competes with hydrogen bonding to R$_2$NO molecules to such an extent that only ca. 50% are hydrogen bonded in pure methanol.

The trend for t-butyl alcohol is particularly interesting (Fig. 5). There is an initial plateau in which A(^{14}N) doesn't change appreciably, but this is progressively lost on heating. Then there is a rapid fall in A(^{14}N), the limiting value being nearly reached in the 0.4 M.F. region. (This value is less than that for methanol because of steric restrictions.) The plateau and its temperature sensitivity is thought to be characteristic of the unique ability of water to form cages about large spherical hydrocarbon groups (62,63). Such cage formation is typified by results for aqueous t-butyl alcohol, and is expected for DTBN. Thus, until there is insufficient water for these cages, the nitroxide is not greatly affected. However, once this region (ca. 0.64 M.F.) is passed, cage sharing is thought to
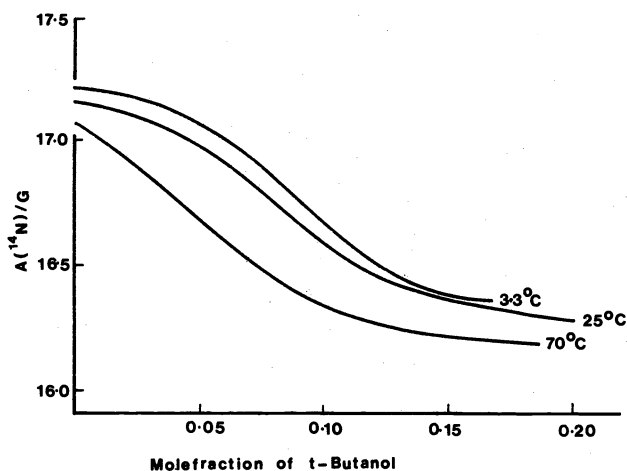
Fig. 5.   Hyperfine coupling constants (^{14}N) for DTBN in aqueous solutions
containing t-butyl alcohol at 3.3°, 25° and 70°C.

set in, and this is reflected in the rapid fall in A(^{14}N). Dispersion of the cages leaves
the residual water preferentially solvating the alcohol molecules.

Trends in Line-widths
Above ambient temperatures, symmetrical broadening reflects control by T_J. The trends follow
closely those for A(^{14}N) and we have suggested that this arises because the H-bonded mole-
cules make little contribution because of their lack of rotational freedom. However, the
non-bonded molecules have the required freedom, and contribute to a width that depends, in
the usual way, upon Δg, viscosity and temperature (64). This is well illustrated by the T/η
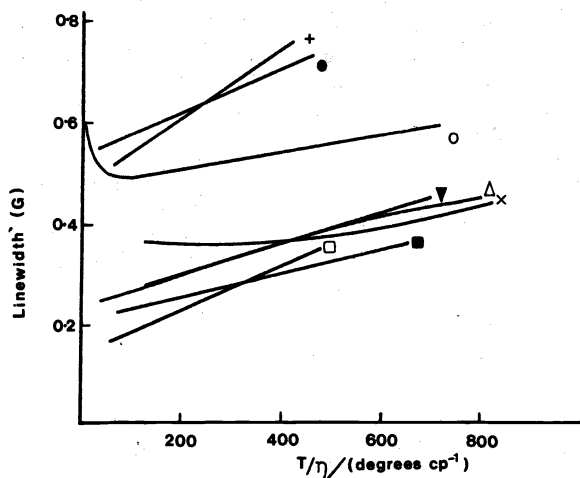plots in Fig. 6.

Fig. 6.   Linewidths (ΔH and W_H) for DTBN and TEMPO in various solvents as a
function of T/η.   +DTBN/DMSO, •DTBN/Heptane, oDTBN/MeOH, W_H for ■DTBN/MeOH,
×DTBN/Water, ▼d^{18} DTBN/CD$_3$OD, W_H for △TEMPO/EtOH, W_H for □TEMPO/DMSO.

For most solutions at ambient temperature, changes in asymmetric broadening were too small to
monitor accurately. However, at low temperatures such broadening is significant for some
systems (Fig. 7). A question arises about the source of this broadening. When it occurs
without significant change in A(^{14}N), as in aqueous glycerol solutions, then it must reflect
increases in T_c. However, when it correlates with rapid changes in A(^{14}N), as for example,
in the aqueous t-butyl alcohol system, the broadening may well stem in part from the H-
bonding equilibrium. This is because of changes in g_{av} and A_{iso} indicated in Fig. 8. The
data are not sensitive enough to allow a clear distinction between these two broadening
mechanisms. We conclude that estimation of T_c from asymmetric broadening in systems when
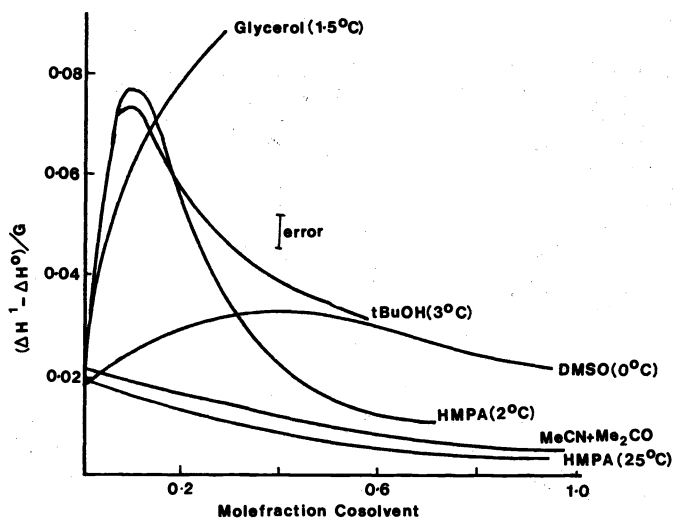A(^{14}N) is intermediate in value between that for fully H-bonded and non-bonded molecules

Fig. 7. Linewidth difference $(\Delta H^{-1} - \Delta H^0)$ for aqueous DTBN as a function of the M.F. of added co-solvents at ca. 0°C. Glycerol, HMPA, tBuOH, Me$_2$CO, MeCN, DMSO, HMPA at 25°C.
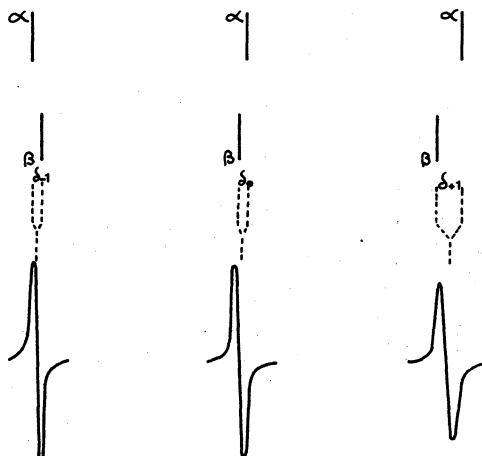
Fig. 8. Simulation of an exchange broadened spectrum for DTBN in water + HMPA mixture containing equal concentrations of hydrogen-bonded (α) and "free" (β) DTBN.

could give very misleading results.

There is a marked increase in asymmetric broadening in the 0 to 0.04 M.F. region of aqueous t-butyl alcohol that must reflect an increase in T_c since $A(^{14}N)$ hardly changes. We suggest that this is like a fall in temperature, reflecting the increased local structure induced by the added alcohol. No such excessive broadening was observed for methanol + t-butyl alcohol solvents. This conclusion is in sharp contrast with that of Jolicoeur and Friedman, who suggested that R$_2$NO radicals experience an unusual freedom in low-temperature water (58).

INFORMATION FROM RADIATION STUDIES

Cation-anion interactions of the type observed with ion-pairs discussed above is frequently detected for radicals formed in ionic solids by ionizing radiation (3,65,66). These studies have helped in the task of deducing details of geometry for ion-pairs since for single crystal studies radical orientations are frequently known. Another significant way in which one can learn about matrix effects is by studying a given radical in a range of different salts and solvents. In a limited range of studies (67,68), we concluded that neutral molecules (NO$_2$) formed from anions (NO$_2^-$ or NO$_3^-$) interact only weakly with their environment, whereas radical anions (CO$_2^-$, SO$_3^-$, PO$_3^{2-}$) interact strongly, their e.s.r. parameters (A$_{iso}$,

2B) being strongly dependent upon the surrounding crystal field.

It is also possible to study the solvation of monatomic cations in this way, perhaps the most informative being Ag^+. There is considerable controversy regarding the way this ion is solvated, certain studies suggesting only minor solvation by water, for example (69). When solutions containing Ag^+ are frozen to glasses and exposed to ^{60}Co γ-rays they readily form Ag^o centres whose e.s.r. spectra comprise a well defined doublet of doublets, (Fig. 9).
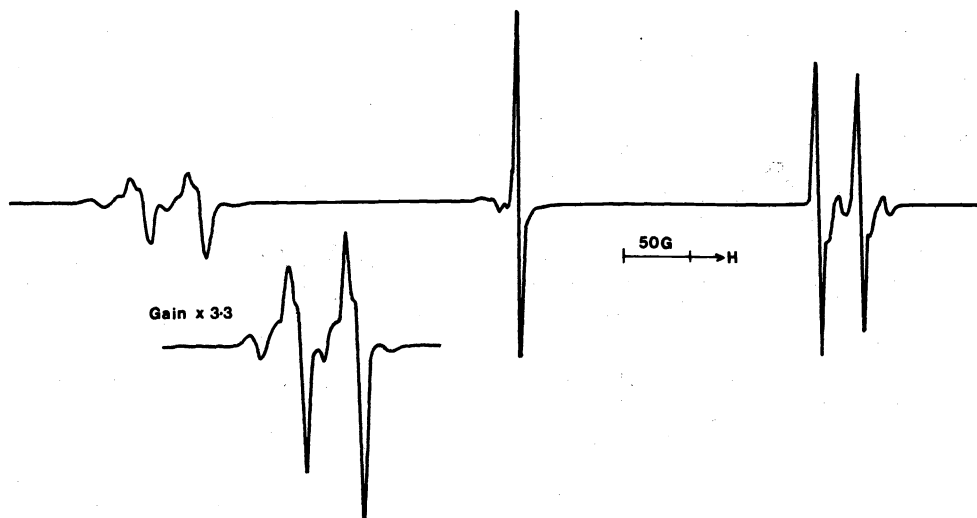

Fig. 9.   First derivative e.s.r. spectrum for an aqueous glass containing Ag^+ after exposure to ^{60}Co γ-rays at 77 K, showing hyperfine features to ^{107}Ag and ^{109}Ag assigned to various types of solvated atoms.

[^{109}Ag and ^{107}Ag have I = -$^1/_2$ and nearly equal abundancies: ^{107}Ag having the smaller magnetic moment.]

For basic solvents such as DMSO or HMPA, only one form of Ag^o dominates the spectrum, but the hyperfine coupling is greatly reduced from the gas-phase value (Table) in a manner that reflects the basicity or donicity of the medium (70).

However, for methanolic, and even more markedly, for aqueous glasses, a wide range of subtly but clearly diff.rent species are formed. Their relative abundancies depend upon the time of irradiation, degree of annealing above 77 K, and concentration and nature of other additives, but not on the nature of the gegen ions.

We postulate that this distribution of Ag^o centres reflects a distribution of Ag^+ solvates for these protic media. This is supported by the fact that 'free' silver atoms are not detected on annealing, which would have been expected if desolvation were involved. In this connection, it is interesting to recall that when electrons are trapped in alcohol glasses at 77 K, e.s.r. and optical spectroscopy show that solvation is almost complete, and certainly extensive. These results can be compared with those for the same systems at 4.2 K, which show that solvation is initially minor (71,72). On warming solutions irradiated at 77 K the spectra change irreversibly to those found at 77 K. Thus solvation in glasses can be "switched on" by the acquisition of charge, but loss of charge does not lead to the reverse process.

CONCLUDING COMMENT

This Review would not be complete without some reference being made to the complimentary use of n.m.r. spectroscopy in the study of paramagnetic radical ions. This aspect of the subject has been studied in depth by de Boer and his co-workers (73-75).

REFERENCES

1. M. C. R. Symons, J. Phys. Chem., 71, 172 (1967).
2. H. Sharp and M. C. R. Symons, Ions and Ion-Pairs in Organic Reactions, M. Szwarc. Ed., Wiley, New York, N.Y. (1972).
3. E. de Boer and E. Sommerdijk, Ions and Ion-Pairs in Organic Reactions, M. Szwarc. Ed., Wiley, New York, N.Y. (1972).
4. T. J. Stone, T. Buckman, P. L. Nordio and H. M. McConnell, Proc. Natl. Acad. Sci., 54, 1010 (1965).
5. C. L. Hamilton and H. M. McConnell, Structural Chemistry and Molecular Biology, Eds. A. Rich and N. Davidson, W. H. Freeman & Co., San Francisco, p.115 (1968).
6. R. Wilson and D. Kivelson, J. Chem. Phys., 44, 154 (1966).
7. C. M. Guzy, J. B. Raynor and M. C. R. Symons, J. Chem. Soc. (A)., 2791 (1969).
8. T. R. Griffiths and M. C. R. Symons, Mol. Phys., 3, 90 (1960).
9. F. C. Adam and S. I. Weissman, J. Amer. Chem. Soc., 80, 1518 (1958).
10. N. M. Atherton and S. I. Weissman, J. Amer. Chem. Soc., 83, 1330 (1961).
11. P. J. Zandstra and S. I. Weissman, J. Amer. Chem. Soc., 84, 4408 (1962).
12. A. H. Reddoch, J. Chem. Phys., 43, 3411 (1965).
13. J. M. Gross and J. D. Barnes, J. Chem. Soc. (A)., 2437 (1969).
14. K. Höfelmann, J. Jagur-Grodjinski and M. Szwarc, J. Amer. Chem. Soc., 91, 4645 (1969).
15. T. A. Claxton, W. M. Fox and M. C. R. Symons, Trans. Faraday Soc., 63, 1 (1967).
16. W. M. Gulick and D. H. Geski, J. Amer. Chem. Soc., 88, 4119 (1966).
17. J. Gendell, J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 37, 2832 (1962).
18. D. H. Chen, E. Warhurst and A. M. Wilde, Trans. Faraday Soc., 63, 2561 (1967).
19. T. E. Gough and D. R. Hindle, Canad. J. Chem., 47, 1698; 3393 (1969).
20. T. E. Gough and D. R. Hindle, Trans. Faraday Soc., 66, 2420 (1970).
21. N. Hirota, J. Amer. Chem. Soc., 90, 3603 (1968).
22. K. Nakamura and Y. Deguchi, Bull. Chem. Soc. Japan, 40, 705 (1967).
23. N. Hirota, J. Phys. Chem., 71, 127 (1967).
24. A. Crowley, N. Hirota and R. Kreilick, J. Chem. Phys., 46, 4815 (1967).
25. T. A. Claxton, J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 64, 596 (1968).
26. T. A. Claxton and J. Oakes, Trans. Faraday Soc., 64, 607 (1968).
27. G. R. Stevenson and A. E. Alegria, J. Phys. Chem., 77, 3100 (1973).
28. G. R. Stevenson and L. Echegoyen, J. Phys. Chem., 77, 2339 (1973); A. E. Alegria, R. Concepcion and G. R. Stevenson, J. Phys. Chem., 79, 361 (1975).
29. R. D. Allendoerfer and R. J. Papez, J. Phys. Chem., 76, 1012 (1972).
30. K. S. Chen, T. Takeshita, K. Nakamura and N. Hirota, J. Phys. Chem., 77, 708 (1973).
31. J. Oakes, J. Slater and M. C. R. Symons, Trans. Faraday Soc., 66, 546 (1970).
32. J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 66, 1 (1970).
33. K. Nakamura and N. Hirota, J. Amer. Chem. Soc., 6919 (1973).
34. K. S. Chen, S. W. Mao, K. Nakamura and N. Hirota, J. Amer. Chem. Soc., 93, 6004 (1971).
35. J. C. Bailey, P. R. Colau and E. Warhurst, J.C.S. Faraday I., 69, 570 (1973).
36. N. Hirota and S. I. Weissman, J. Amer. Chem. Soc., 86, 2537 (1964).
37. N. Hirota, J. Amer. Chem. Soc., 89, 32 (1967).
38. W. M. Fox, J. M. Gross and M. C. R. Symons, J. Chem. Soc. (A)., 448 (1966).
39. S. W. Mao, K. Nakamura and N. Hirota, J. Amer. Chem. Soc., 96, 5341 (1974).
40. A. Carrington, F. Dravnieks and M. C. R. Symons, J. Chem. Soc., 947 (1959).
41. S. I. Weissman, E. de Boer and I. Conradi, J. Chem. Phys., 25, 796 (1956).
42. G. Goez-Morales and P. Sullivan, J. Amer. Chem. Soc., 96, 7232 (1974).
43. J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 64, 2579 (1968).
44. E. W. Stone and A. H. Maki, J. Chem. Phys., 36, 1944 (1962).
45. E. W. Stone and A. H. Maki, J. Amer. Chem. Soc., 87, 454 (1965).
46. E. A. C. Lucken, J. Chem. Soc., 4234 (1964).
47. E. M. Kosower, J. Amer. Chem. Soc., 80, 3253; 3261 (1958).
48. T. E. Gough and M. C. R. Symons, Trans. Faraday Soc., 62, 269 (1966).
49. T. A. Claxton, J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 63, 2125 (1967).
50. P. S. Gill and T. E. Gough, Trans. Faraday Soc., 64, 1997 (1968).
51. G. R. Stevenson and L. Echegoyen, J. Amer. Chem. Soc., 96, 3381 (1974).
52. G. R. Stevenson, L. Echegoyen and H. Hidalgo, J. Phys. Chem., 79, 152 (1975).
53. C. J. W. Gutch and W. A. Waters, Chem. Comm., 39 (1966).
54. W. E. Griffiths, C. J. W. Gutch, G. F. Longster, J. Myatt and P. F. Todd, J. Chem. Soc. (B)., 785 (1968).
55. D. Jones and M. C. R. Symons, Trans. Faraday Soc., 67, 961 (1971).
56. C. J. W. Gutch, W. A. Waters and M. C. R. Symons, J. Chem. Soc. (B)., 1261 (1970).
57. C. Jolicoeur and H. L. Friedman, Ber. Bunsenges Physik. Chem., 75, 248 (1971).
58. C. Jolicoeur and H. L. Friedman, J. Solution Chem., 3, 15 (1974).
59. E. Smith and M. C. R. Symons, J.C.S. Faraday I, in press (1976).
60. M. C. R. Symons, Phil. Trans. Roy. Soc., (1975).
61. I. Strauss and M. C. R. Symons, Chem. Phys. Letters, 39, 471 (1976).
62. M. C. R. Symons and M. J. Blandamer, Hydrogen-Bonded Solvent Systems, Ed. A. K. Covington and P. Jones, Taylor & Francis, London (1968).

63.   D. N. Glew, D. H. Mak and N. S. Rath, Chem. Comm., 264 (1968).
64.   P. W. Atkins, Electron Spin Relaxation in Liquids, Ed. L. T. Muus and P. W. Atkins,
       Plenum Press, New York, p.279 (1972).
65.   D. W. Ovenall and D. H. Whiffen, Mol. Phys., 4, 135 (1961).
66.   P. W. Atkins, N. Keen and M. C. R. Symons, J. Chem. Soc., 2873 (1962).
67.   M. C. R. Symons, J. Chem. Soc. (A)., 1998 (1970).
68.   J. H. Sharp and M. C. R. Symons, J. Chem. Soc. (A)., 3075 (1970).
69.   J. W. Akitt, J.C.S. Dalton, 175 (1974).
70.   R. D. Brown and M. C. R. Symons, unpublished results.
71.   D. R. Smith and J. J. Picroni, Canad. J. Chem., 45, 2723 (1967).
72.   H. Hase, T. Warashina, M. Noda, A. Namiki and T. Higashimura, J. Chem. Phys., 57,
       1039 (1972).
73.   G. W. Canters and E. de Boer, Mol. Phys., 26, 1185 (1973).
74.   B. M. P. Hendriks and E. de Boer, Mol. Phys., 29, 129 (1974).
75.   B. M. P. Hendriks and E. de Boer, Pure & Applied Chem., 40, 259 (1974).