The Study of Ion–Solvent and Ion–Ion Interactions by Magnetic Resonance Techniques

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Recently the standard techniques for studying ions in solution have been supplemented by spectroscopic techniques, in particular ultraviolet, infrared, and magnetic resonance methods, and in this Review we wish to call attention to some of the ways in which magnetic resonance can shed light on the problems of ionic solvation and interactions between ions in solution. The variables from which information is sought include (i) chemical shifts or *g*-value variation, (ii) the appearance of new resonance lines, (iii) variations in spin–spin hyperfine coupling, (iv) line widths and shapes.

Often these pieces of information are merged. For example, different species may be present in a solution which should in principle give rise to different resonances, but the exchange of nuclei between these species may be so rapid that only a single merged line is detected. The former situation is described as 'static' and will be treated initially, even though the bulk of the results may apply to the 'dynamic' case.

Sometimes chemically interesting information is derived directly from n.m.r. and e.s.r. measurements. At other times a knowledge of the chemistry of the system is required before an understanding of the resonance phenomena can be achieved. Both aspects will be discussed in this Review, but mathematical derivations will be omitted and the more physical aspects of relaxation phenomena largely ignored. Details of the instruments and experimental procedures are also omitted. Knowledge of the theory underlying the resonance phenomena will be assumed. Acid–base equilibria are also outside the scope of this Review.

No attempt is made to cover the literature fully, and our choice of illustrative examples is somewhat arbitrary. Fortunately, a recent review by Hinton and Amis[1] on the applications of n.m.r. to ionic solvation covers recent literature very fully; kinetic aspects of the subject have also been comprehensively discussed.[2]

Of the techniques under consideration, n.m.r. has been the more extensively applied to the study of ions in solution. We therefore devote the first half of the Review to the n.m.r. applications, while the second half treats the more limited, but nevertheless fruitful, applications of e.s.r.

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[1] J. F. Hinton and E. S. Amis, *Chem. Rev.*, 1967, **67**, 367.

[2] A. Loewenstein and T. M. Conner, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 280; C. S. Johnson, 'Advances in Magnetic Resonance', vol. 1, Academic Press, New York, 1965, p. 33.

1 Nuclear Magnetic Resonance

A. Shifts.—If a nucleus experiences a range of different bonding interactions then separate resonances will be observed over a range of frequencies; but if interchange between these states is rapid a single resonance, which is the weighted mean of the individual resonances, will be detected. Resonance frequencies are a function of medium effects on the induced diamagnetic or paramagnetic currents of the electrons associated with the nucleus. For example, an effective gain of associated electrons will increase the shielding of a nucleus and cause a shift of the resonance to high field.

(i) *Solvent nuclei: general.* In an electrolyte solution solvent molecules will be in a variety of environments which may, somewhat arbitrarily, be divided into primary solvation shells of the ions, secondary solvation regions, and bulk solvent where solvent molecules are effectively out of range of ionic influences. If exchange of solvent molecules (or atoms) between these various environments were slow ($\tau_{\frac{1}{2}} >$ *ca.* 10^{-4} sec.) five peaks (or multiplets) could be expected in the n.m.r. spectrum of a solvent nucleus. In practice the secondary solvation sphere merges into bulk solvent, and solvent exchange between these environments and with primary solvation shells of anions is fast, so that these four resonances are time-averaged to a single peak whose shift from the pure solvent resonance reflects the mean effect of the different environments of the primary anion and secondary solvation spheres. Rates of solvent exchange with cation primary solvation shells are also often fast, in which case only one averaged resonance will be seen. However, in certain instances, especially at low temperatures, a separate resonance due to solvent bonded to cations may be resolved; for example, Mg^{2+} in methanol at $-75°$.[3] From relative peak areas the cation solvation number can be determined. An alternative method for determining these solvation numbers is from molal shifts (cf. ref. 4).

In most instances only a single averaged line is detected and the individual molar ionic shifts are deduced from the overall salt shifts by making some quite arbitrary assignment, a popular one being that the shift due to NH_4^+ is zero. It does not seem to have been realised that a link, however tenuous, can be forged between these averaged results and the low-temperature resolved lines discussed above. Thus for magnesium perchlorate in methanol the cation shift can be directly estimated and thence the anion shift derived. In this case the shifts are comparable in magnitude, but opposite in sign.[5] From these results it should be possible by appropriate extrapolations to obtain values for many other ions. However, differences between cation shifts or anion shifts can be meaningfully compared, and this is done in Figure 1 for ions in water[6] and ammonia.[7]

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[3] J. H. Swinehart and H. Taube, *J. Chem. Phys.*, 1962, **37**, 1579.

[4] M. Alei and J. A. Jackson, *J. Chem. Phys.*, 1964, **41**, 3402.

[5] R. N. Butler, E. A. Phillpott and M. C. R. Symons, *Chem. Comm.*, 1968, 371.

[6] (*a*) H. G. Hertz and W. Spalthoff, *Z. Elektrochem.*, 1959, **63**, 1096; (*b*) M. S. Bergqvist and E. Forslind, *Acta Chem. Scand.*, 1962, **16**, 2069; (*c*) Z. Luz and G. Yagil, *J. Phys. Chem.*, 1966, **70**, 554.

[7] A. L. Allred and R. N. Wendricks, *J. Chem. Soc.* (*A*), 1966, 778.

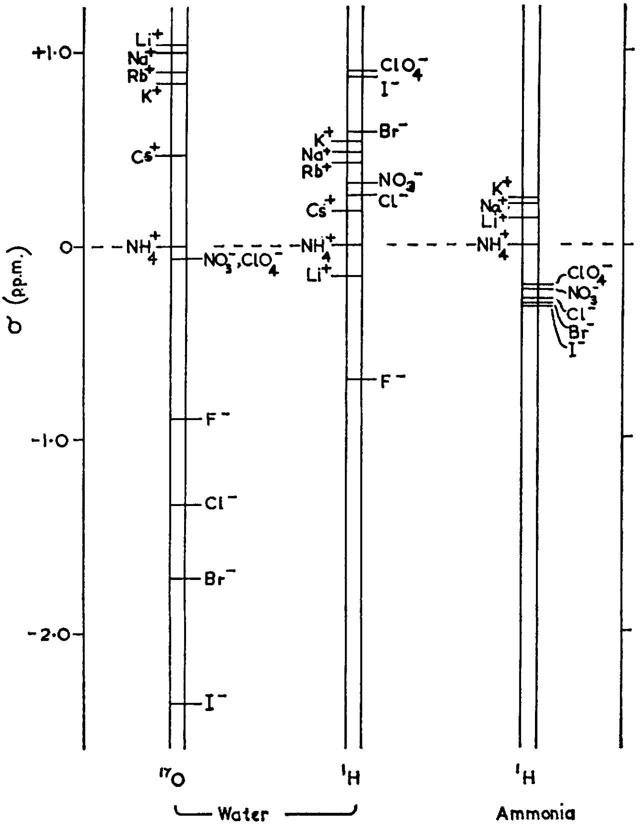

Figure 1 *Ionic molal shifts for* ^1H *and* ^{17}O *resonances of water, and* ^1H *resonances of ammonia, in electrolyte solutions. The ionic molal shift for the ammonium ion has been arbitrarily taken as zero in all cases*

Shoolery and Alder,[8] and most subsequent workers, have discussed shifts for electrolytes in water in terms of two opposing contributions: a low-field shift arising from polarisation of water molecules and a high-field shift from hydrogen-bond breaking. Assignation of high-field shifts to structure-breaking is fully consistent with the increasing high-field shift of the proton resonance of pure water as the temperature is raised and with the proton chemical shift of water vapour.[9] (The shift for ice protons relative to those of water is unknown because the resonance line is too broad. A recent claim that the line is relatively narrow near 0° has been discredited;[10] a small number of protons in an unknown

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[8] J. N. Shoolery and B. J. Alder, *J. Chem. Phys.*, 1955, **23**, 805.

[9] W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, 1958, **28**, 601; E. R. Malinowski, P. S. Knapp, and B. Feuer, *J. Chem. Phys.*, 1966, **45**, 4274.

[10] J. Clifford, *Chem. Comm.*, 1967, 880.

state give rise to this line which has a frequency close to that from gaseous molecules.) The ^{17}O resonance of water is also shifted to high-field by increasing temperature or by dilution with an inert (non-hydrogen-bonding) solvent.[6c]

Shifts for electrolyte solutions imply that 1 : 1 electrolytes have a predominantly structure-breaking effect; the opposite direction of shifts for other electrolytes implies dominance of polarisation. Proton ionic shifts[5] (Figure 1) for the halide ions are increasingly to high-field going from fluoride to iodide. This is consistent with the decrease in polarisation as the ionic radius increases, but may indicate some increase in structure-breaking also. For the alkaline earth ions ($Mg^{2+} \rightarrow Ba^{2+}$) a similar shift to high-field with increasing ionic radius is observed. The greater polarisation effect of the dipositive alkaline earth cations than of the unipositive alkali metal cations is reflected in the lower-field of the former series. Figure 1 also shows ionic shifts in liquid ammonia solution. These are much smaller than those in aqueous solution, and the order of effects of halide ions on solvent proton shifts is reversed. Differences in proton-shift behaviour between these two solvent systems are ascribed to the smaller degree of hydrogen bonding in liquid ammonia.[7]

The ^{17}O n.m.r. spectra of diamagnetic salts in water consist of one line, both for the rapidly and slowly exchanging cation cases. If cobalt(II) perchlorate is added, in most cases the resonance merely shifts, but in the cases of the Al^{3+}, Ga^{3+}, and Be^{2+} the ^{17}O n.m.r. spectrum then consists of a large broad shifted peak and a small residual peak at the original position. [If dysprosium(III) is used instead of cobalt (II), there is still a large shift but little broadening of this peak.[4]] For fast-exchange cations all the water in the system is exchanging rapidly between bulk solvent and the solvation shells of the cobalt(II) and the diamagnetic cations, giving an average paramagnetic shift for all the water. But for Al^{3+}, Ga^{3+}, and Be^{2+} the slowly exchanging water in their primary hydration spheres does not come directly under the influence of the paramagnetic ion, hence the small residual peak. Solvation numbers for Al^{3+} and Be^{2+} have been estimated from peak areas in these experiments.[11]

Again it is not yet possible to determine absolute values for cation or anion shifts but, as for proton shifts, ^{17}O molar shifts can be arbitrarily separated into self-consistent sets of ionic shifts[6c] (Figure 1). It is interesting to compare trends for ^{17}O and for ^{1}H shifts for certain series of ions. For instance, the order of halide shifts is exactly reversed in the two cases, presumably because of the differences in hydrogen-bonding interaction. Ion–water interactions appear to be more important than structure-breaking effects for ^{17}O shifts.

(ii) *Solvent nuclei: mixed solvents.* For slow-exchange diamagnetic cations in binary solvent mixtures it should be possible to detect separate resonances arising from both solvents co-ordinated to the cations, apart from the resonances for the bulk solvent. In solutions of aluminium chloride in, for example, aqueous dimethylformamide, dimethyl sulphoxide,[12] and *N*-methylacetamide,[13] signals

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[11] R. E. Connick and D. Fiat, *J. Chem. Phys.*, 1963, **39**, 1349.
[12] A. Fratiello and D. P. Miller, *Mol. Phys.*, 1966, **11**, 37.
[13] J. F. Hinton and E. S. Amis, *Chem. Comm.*, 1967, 100.

from the organic solvent bonded to the Al^{3+} cation have been detected. Moreover, in aluminium perchlorate solution in aqueous acetonitrile a series of peaks in the proton n.m.r. spectrum can convincingly be assigned to the series of solvated Al^{3+} cations containing 1—6 molecules of primary solvating water.[14]

For solutions of fast-exchange cations in some mixed solvents, for instance aqueous pyridine[15] and aqueous *N*-methylformamide,[12] variation of proton shift with solvent composition indicates solvation by both components. But in other cases such as aqueous alcohols[12] a lack of shift variation over only a limited range of solvent composition does not rule out solvation by the organic component (Figure 2). Recent measurements in aqueous dioxan indicate some solvation of the perchlorate anion by the dioxan.[16] The relative magnitudes of shifts for different protons in the organic solvating molecule can yield information about bonding to the cation. In aqueous pyridine bigger displacements of the β- than of the γ-proton lines are consistent with the expected solvation at the nitrogen atom and consequent polarisation.[15] In aqueous dimethylformamide the carbonyl proton resonance is displaced more than that for the methyl protons by addition of salts. This has been interpreted in terms of preferential interaction between the cations and the oxygen atom rather than the nitrogen atom of the dimethylformamide.[12]

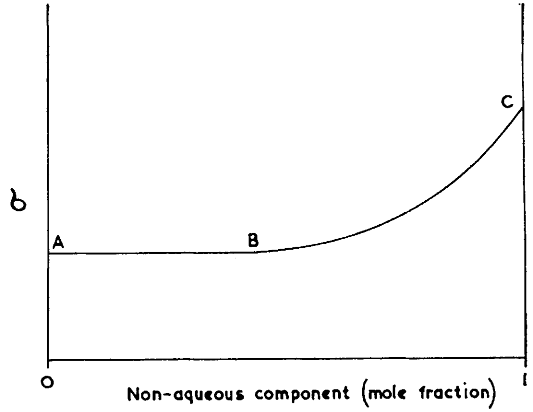

Figure 2 *Hypothetical variation of solvent chemical shift due to solute with mole fraction composition of a binary aqueous solvent mixture. Such a plot could arise from preferential solvation by water; if observations are made only in the region A to B then no indication of solvation by the non-aqueous component is obtained, whereas such solvation is indicated by observations over the whole range A to C*

(iii) *Solvent nuclei: solutions containing paramagnetic ions.* Very much larger solvent shifts can often be detected when paramagnetic ions are involved. When there is hyperfine coupling between a nucleus and an unpaired electron

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[14] L. D. Supran and N. Sheppard, *Chem. Comm.*, 1967, 832.
[15] A. Fratiello and E. G. Christie, *Trans. Faraday Soc.*, 1965, **61**, 306.
[16] J. F. Hinton, L. S. McDowell, and E. S. Amis, *Chem. Comm.*, 1966, 776.

the nuclear resonance is split into a doublet, but because of the very large magnetic field associated with unpaired electrons these lines are so far removed from a normal resonance that they are not detected. If, however, reorientation of the electron in the magnetic field is rapid, as is the case for example for $Co(OH_2)_6{}^{2+}$, a weighted averaged line will be detected, shifted from the normal solvent resonance because of the Boltzmann distribution of the electron spin states. Such shifts are called contact or Knight shifts; as they are very large compared with normal chemical shifts they can be of great use in separating broad overlapping resonances (see, *e.g.*, p. 279 and refs. 4 and 11).

The situation is otherwise very similar to that discussed above for diamagnetic ions. If solvent molecules have a long life-time in contact with a rapidly relaxing paramagnetic ion, then their nuclear resonance will be greatly shifted up- or down-field, depending on the sign of the effective spin-density at this nucleus (contact shift), or upon the anisotropy of the *g*-tensor (pseudo-contact shift). From the shift it is often possible to calculate hyperfine coupling constants, but care must be taken to make proper allowance for the pseudo-contact shift. However, irrespective of the source of the shift, the area under the resonance line can give a good estimate of the solvation number, for example of Co^{2+} in methanol at low temperatures,[17] and the effect of temperature on line-widths can give detailed kinetic information. Moreover, detailed information about solvation in mixed solvents can be obtained; for example, peaks in the low-temperature proton n.m.r. spectrum of Co^{2+} in methanol containing traces of water can be assigned[17] to water and *cis*- and *trans*-methanol molecules in $[Co(MeOH)_5(OH_2)]^{2+}$. If the electron spin relaxation is too slow (*e.g.*, for Mn^{2+}), no nuclear resonance will be detected from bound solvents and only the bulk solvent line will be detected.

As the rate of exchange of co-ordinated solvent increases, the usual line broadening and shift towards the weighted-mean frequency occurs, until a single shifted line results (see Figure 4). This applies irrespective of the rate of electron spin relaxation. In contrast with the situation for diamagnetic ions, the overall shift can now safely be assigned to the effect of the paramagnetic cation only since Knight shifts are so large. Specific examples are cited in ref. 1; further discussion is deferred until line-widths in these systems are considered.

(iv) *Solute nuclei.* There are nuclei of spin $\geqslant \frac{1}{2}$ for all the alkali metals and all the halogens, so it is possible to study the whole range of alkali halides in solution. Magnitudes of chemical shifts increase greatly from lithium[18] through to caesium,[19] and similarly increase with increasing size for the halogens (Table). However, the sensitivity of chemical shift to solvent decreases rapidly as ionic size increases; lithium[18] and fluoride[20] resonances are very solvent-sensitive, caesium[20] practically unaffected.

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[17] Z. Luz and S. Meiboom, *J. Chem. Phys.*, 1964, **40**, 1058.

[18] G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller, and W. K. Musker, *Inorg. Chem.*, 1966, **5**, 554.

[19] C. Deverell and R. E. Richards, *Mol Phys.*, 1966, **10**, 551.

[20] A. Carrington, F. Dravnicks, and M. C. R. Symons, *Mol. Phys.*, 1960, **3**, 174.

Chemical shifts, in p.p.m., of alkali-metal nuclei in 3-*molal aqueous solutions of alkali halides* (*from ref.* 19)

CsI	−57	CsI	−57
RbI	−21	CsBr	−36
KI	−6	CsCl	−23
NaI	−1		

In aqueous solutions of alkali halides the chemical shift of the alkali metal increases with concentration. Up to about 4 molal concentrations the shift varies linearly with activity, implying that interionic interactions are important in determining the magnitude of the shift. Indeed the lack of solvent-sensitivity of the caesium resonance compared with the large shifts produced by varying the nature and concentration of anions[19, 20] underlines the significance of these interionic interactions. The increasing magnitude of chemical shift with cation or anion size rules out a simple electrostatic explanation of these shifts. A more likely rationalisation of the observed shifts emerges from comparison of alkali halide solutions and the respective crystals, illustrated for rubidium bromide in Figure 3.

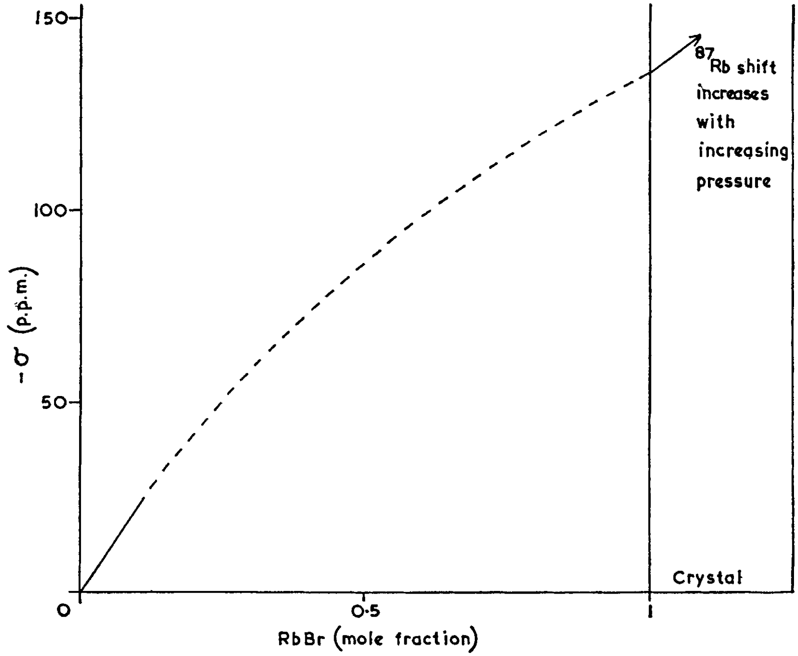

Figure 3 *Variation of* ^{87}Rb *chemical shift with mole fraction in aqueous rubidium bromide solution. This Figure relates this variation to the chemical shift value in the crystal, and variation of chemical shift with pressure in the crystal*

(————), experimental results;

(- - - - -), arbitrary interpolation between solution and crystal points

The magnitude and variation of the alkali and halogen shifts in the crystals under varying pressures have been satisfactorily interpreted[21] in terms of the Kondo–Yamashita theory,[22] in which chemical shifts are controlled by overlap repulsive forces between the ions. Increasing proximity of ions leads to increased overlap and repulsion and thus to an increasingly low-field shift. In aqueous solution the resonances shift increasingly downfield as the concentration increases and interionic interactions increase. The plot of shift against mole fraction tends towards the shift for the crystal; moreover, this graph tends in the same direction as that of the shift against pressure trend for the crystal (Figure 3). The Kondo–Yamashita theory thus predicts qualitatively the correct direction and order of magnitude of shifts for a given alkali halide, and the observed largest shifts for largest ions. The anomalous position of lithium among the cations can be understood in terms of tenacious solvation inhibiting interionic interactions in the case of this very small cation.

Concentration-dependence of ^{203}Tl and ^{205}Tl chemical shifts in aqueous solutions of thallium(I) and thallium(III) can be understood in terms of extensive ion-pairing or complex formation.[23–25] The continuous gradation from effects due to fortuitous encounters between ions, through preferential ion-pairing, to complex formation thus leads us beyond our brief into complex chemistry, where the application of n.m.r. to a very wide range of solvent and solute nuclei has proved of great value in elucidating problems of composition, structure, and kinetics.[1, 2]

In mixed aqueous solutions of caesium fluoride ^{19}F shifts correlate linearly with mole fraction composition for many solvent mixtures, such as aqueous methanol and aqueous dimethylformamide. This behaviour implies smoothly changing statistically controlled variation of the fluoride solvation shell as solvent composition varies.[20] As in the case of solvent proton shifts (see Figure 2), lack of variation of ^{19}F shift with composition over a limited range, as in aqueous methyl cyanide and aqueous isopropyl alcohol, does not necessarily indicate lack of solvation of fluoride by the organic component.

Solvent composition dependence of ^{7}Li shifts[18] has in several cases indicated solvation by both components of a binary solvent mixture. Lithium ions are particularly satisfactory for such studies since solvent effects on shifts are relatively large and correlate well with Kosower's solvent polarity factor, *Z*.[26]

Considerable information about interactions of tetra-alkylammonium, anilinium, and similar salts in solution has been obtained by studying the proton resonances of the cations. The differences in shift behaviour of the various protons for anilinium salts in non-polar solvents[27] and for quaternary ammonium salts

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[21] R. Baron, *J. Chem. Phys.*, 1963, **38**, 173; D. Ikenberry and T. P. Das, *J. Chem. Phys.*, 1966, **45**, 1361, and refs. therein.

[22] J. Kondo and J. Yamashita, *J. Phys. and Chem. Solids*, 1959, **10**, 245.

[23] H. S. Gutowsky and B. R. McGarvey, *Phys. Rev.*, 1953, **91**, 81.

[24] R. Freeman, R. P. H. Gasser, R. E. Richards, and D. H. Wheeler, *Mol. Phys.*, 1959, **2**, 75.

[25] R. Freeman, R. P. H. Gasser, and R. E. Richards, *Mol. Phys.*, 1959, **2**, 301.

[26] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3253.

[27] G. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 1614; G. Fraenkel and J. P. Kim, *J. Amer. Chem. Soc.*, 1966, **88** ,4203.

in nitrobenzene[28] indicate significant ion-association with the anion in close proximity to the nitrogen atom of the cation. Also the observation that the 1-methylene and *ortho*-ring proton shifts of 1,4-diethylpyridinium salts are a function of the nature and concentration of anion in deuteriochloroform solution demonstrates significant ion association in this system.[29]

B. Line-widths and Shapes.—A large number of factors govern the width of an n.m.r. line, which is usually treated in terms of two time constants, T_1, the spin-lattice or longitudinal relaxation time, and T_2, the spin-spin or transverse relaxation time. T_1 is a measure of the interaction between spin energy and thermal motion of the molecule and its surroundings; it governs the degree of saturation. When this interaction is very efficient, leading to rapid spin inversion, each spin state has a very short lifetime and there is uncertainty-principle broadening of the resonance line. On the other hand, T_2 is associated with variations in the relative energies of the spin states. In both cases it is the time-dependence of some interaction acting on the spins that causes the relaxation. One important factor controlling line-widths will therefore be a fluctuation of position and orientation of solvent molecules relative to an ion or other solvent molecules. This coupling may be direct, through magnetic fields, or indirect, *via* electric fields, if the nucleus has a quadrupole moment.

Other factors which can contribute are the anistropy of the chemical shift of a tumbling molecule, spin–rotation coupling, and the effect of paramagnetic materials. Anisotropy is particularly important in ^{19}F resonances. Coupling to magnetic fields generated by rotating molecules is important when rotation is fairly free in a liquid. The greater the frequency of collisions the smaller the correlation time and the less effective is this coupling as a mechanism for relaxation. Thus we can say that motions having any frequency from the resonance frequency down to near zero will affect the line-width through T_2, but only those close to resonance will involve T_1.

(i) *Solvent nuclei.* In principle considerable information relating directly to the correlation times of the solvent molecules in the absence and presence of ions can be extracted from resonance studies of solvent nuclei. The situation has been reviewed in depth by Hertz.[30] We turn to some more specifically chemical aspects by considering an equilibrium in which a given nucleus is transferred between environments in which it resonates at different frequencies. For slow rates of exchange between two sites, two narrow lines are detected. As this rate is increased, for example by an increase in temperature, these individual lines broaden and eventually merge to a single broad line centred on the weighted-mean position. Further increase in rate gives rise to line-narrowing (Figure 4). This behaviour is well exemplified by the case of cobalt (II) perchlorate in methanol.[17] The effect of temperature on shifts and line-widths is summarised in Figure 5.

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[28] R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, 1964, **68**, 1875.

[29] R. J. Chuck and E. W. Randall, *Spectrochim. Acta*, 1966, **22**, 221.

[30] H. G. Hertz, in 'Progress in Nuclear Magnetic Resonance Spectroscopy', vol. 3, ed. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon, Oxford, 1967, p. 159.

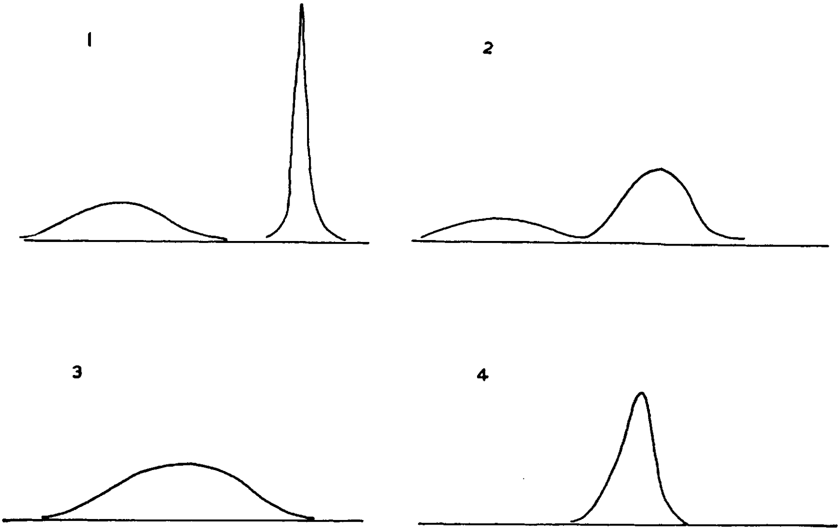

Figure 4 *Variation of* ^{1}H *n.m.r. spectra with temperature for a solution of a cation whose rate of solvent exchange varies from 'slow'* (i.e. $\tau_{\frac{1}{2}} \gg 10^{-4}$ sec.) (1) *through intermediate* (2 *and* 3) *to fast* (4) *as the temperature rises*

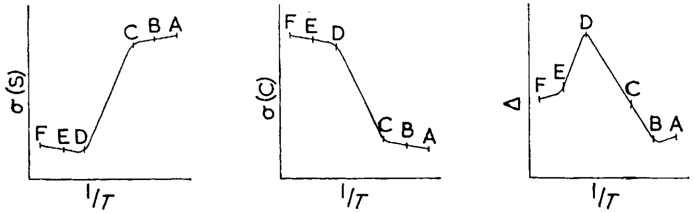

Figure 5 *Variation of proton chemical shift for bulk solvent* [σ (s)], *for solvent bound to cation* [σ (c)] *and variation of line width* (Δ) *for either, with reciprocal temperature* (1/*T*) *for a solution where rates of solvent exchange at the cation vary from much slower to much faster than the n.m.r. frequency*

The points A to F correspond to identical temperatures in each diagram. The section A to B corresponds to exchange rates much lower than the n.m.r. frequency; from B to C both lines broaden; C to D the lines overlap and the peaks approach to coalesce at D; D to E involves exchange narrowing; and beyond E rates of exchange are much faster than the n.m.r. frequency. The steady upfield trend with rising temperature for cation–solvent shifts in the region A to B, and for the averaged solvent shifts E to F, arises from variation of the Boltzmann distribution between the two spin states. Kinetic data and Arrhenius parameters can be obtained from the section B to E

Two pieces of chemical information can be extracted. These are the solvation number of the cation at low temperatures and, from the region $B \rightarrow E$ in Figure 5, rates and thence activation parameters for the solvent exchange. For cobalt(II) in methanol the parallel behaviour of methyl and hydroxyl proton resonances indicates exchange of whole methanol molecules; in contrast the different behaviour of the two proton resonances for methanolic solutions of chromium(III) implies that only the hydroxyl proton exchanges rapidly, the remainder of the methanol molecule remaining, as expected, firmly bound to the cation. Indeed the n.m.r. study showed that proton exchange is faster for methanol co-ordinated to Cr^{3+} than for free methanol, illustrating the electron-withdrawing properties of the cation. This chromium–methanol case illustrates the general desirability of studying solvent exchange processes by monitoring the ligating nucleus, *e.g.*, ^{17}O rather than ^{1}H for water or for alcohols.

The relatively slow electronic relaxation for manganese(II), which precludes observation of bound solvent peaks in solutions of this cation (see p. 281), is, with fast exchange of co-ordinated solvent molecules,[31] the reason for the possible success of Swift and Sayre's method for determining hydration numbers.[32] Determination of solvation numbers by peak-area or molal-shift methods mentioned earlier, is straightforward for slow-exchange cations, but these methods are not applicable to the majority of cations whose rates of solvent exchange are too fast for separate co-ordinated solvent n.m.r. signals to be detectable. Swift and Sayre treat line-widths of averaged proton signals from water containing a diamagnetic cation of unknown hydration number with the Mn^{2+} ion acting as a probe. The method depends on modifying the association time of Mn^{2+} and water, and hence the proton resonance line-width, by addition of the competing cation. In view of the sensitivity of line-widths in Mn^{2+} solutions to added ions and to ionic-strength variations, it has not proved possible to determine hydration numbers of cations directly from solutions containing only Mn^{2+} and the cation of interest, but an empirical relationship has been obtained for relating hydration numbers of cations to the known hydration numbers of Al^{3+} (6·0) and Be^{2+} (4·0). Hydration numbers so determined are lower than expected, for instance for Ca^{2+} (4·3), Cd^{2+} (4·6); only for larger cations is the octahedral value of 6·0 approached [Ba^{2+} (5·7)]. The marked similarity of values for cations of similar size (*e.g.*, Ca^{2+}, Cd^{2+}; Ba^{2+}, Pb^{2+}), and the increase with increasing ionic radius, are considered to arise from a balance between six-co-ordination of cations and four-co-ordination in water itself. Smaller ions may be more readily accommodated geometrically into the water structure. Despite objections to the physical basis of the method[33] the empirical relationship gives consistent results.[34] It may be noted that recent ultrasonic[35] and ^{7}Li n.m.r.[36] studies support Swift and Sayre's values. The surprising values are those of zero for both H^+ and NH_4^+ cations; those values are likely to be accidental consequences of the definition of hydration number and the fact that protons are common to cation and solvent. This method of determining solvation numbers has been extended from aqueous solution to liquid ammonia, in which the Ni^{2+} cation proves to be a suitable probe.[37]

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[31] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.
[32] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, 1966, **44**, 3567.
[33] S. Meiboom, *J. Chem. Phys.*, 1967, **46**, 410.
[34] T. J. Swift and W. G. Sayre, *J. Chem. Phys.*, 1967, **46**, 411.
[35] D. S. Allam and W. H. Lee, *J. Chem. Soc.* (*A*), 1966, 5; 1966, 426.
[36] J. W. Akitt and A. J. Downs, *Chem. Comm.*, 1966, 222.
[37] T. J. Swift and H. H. Lo, *J. Amer. Chem. Soc.*, 1966, **88**, 2994.

(ii) *Solute nuclei.* The discussion so far has covered n.m.r. spectra of solvent nuclei. The study of line-widths for solute nuclei has been less widely employed, but can give pertinent information about solvation.

Close approach of cation to anion, as in ion-association, or complex formation, reduces the symmetry of the environments of the ions and thereby modifies relaxation times and line-widths. Much information on ion–solvent and ion–ion interactions in aqueous solution of alkali halides has been obtained from n.m.r. resonances of alkali metal and halogen nuclei.[38] Ion-pairing and complex formation in systems as diverse as Na^+ with keto- and hydroxy-acids,[39] In^{3+} and simple oxyanions,[40] and Zn^{2+}, Cd^{2+}, or Hg^{2+} with bromide or iodide,[41] have been monitored from line-width variations. From extensive studies of solutions of $R_4M\pm$ (M = B, N, As, etc.) salts we shall mention for illustration the cases of Et_4As^+ and Et_3MeAs^+ salts in water and chloroform.[42] The unsymmetrical Et_3MeAs^+ cation gives sharp proton resonances in water and in chloroform, but symmetrical Et_4As^+ gives sharp lines in chloroform, broad in water. In chloroform ion-pairing is extensive, which results in an asymmetric environment of the Et_4As^+ cation, promoting relaxation and giving sharp lines. In water the symmetry of solvated Et_4As^+ is not disturbed by ion-pairing, relaxation is slow, and proton n.m.r. lines are broad.

A more indirect approach to ion-association has been to study the effect of gegen-ions on rates of ferrocyanide–ferricyanide electron exchange, determined by ^{14}N line-widths, and to correlate rate variations with changes in concentrations and reactivities of ion-pairs.[43]

A link between n.m.r. and e.s.r. studies (p. 298) is provided by a ^7Li n.m.r. study of the paramagnetic lithium salt of fluorenone dissolved in tetrahydrofuran.[44] Line-broadening with increasing temperature and increasing anion concentration can be correlated with increasing rate of exchange of Li^+ between the Knight-shifted ion-pair and the free (solvated) cation.

C. Spin–Spin Coupling.—Spin–spin interaction between two magnetic nuclei occurs in many polyatomic ions, for example in BF_4^-, BH_4^-, $AsEt_4^+$, and should in principle be affected by the environment. However, variation in spin–spin coupling constants has been very little used as a probe for ion–ion or ion–solvent interactions. The tetrafluoroborate anion has been the most studied, but even here it has proved difficult to explain the differences in behaviour observed for the sodium, ammonium, and silver salts in a variety of solvents.[45] It is noteworthy that spin–spin coupling constants correlate linearly with ^{19}F chemical shifts.

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[38] *E.g.*, C. Deverell, D. J. Frost, and R. E. Richards, *Mol. Phys.*, 1965, **9**, 565.

[39] O. Jardetzky and J. E. Wertz, *J. Amer. Chem. Soc.*, 1960, **82**, 318.

[40] T. H. Cannon and R. E. Richards, *Trans. Faraday Soc.*, 1966, **62**, 1378.

[41] H. G. Hertz, *Z. Elektrochem.*, 1961, **65**, 36.

[42] A. G. Massey, E. W. Randall, and D. Shaw, *Spectrochim. Acta*, 1964, **20**, 379.

[43] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, 1965, **4**, 361; A. Loewenstein and G. Ron, *Inorg. Chem.*, 1967, **6**, 1604.

[44] G. W. Canters, H. van Willigen, and E. de Boer, *Chem. Comm.*, 1967, 566.

[45] R. Haque and L. W. Reeves, *J. Phys. Chem.*, 1966, **70**, 2753.

2 Electron Spin Resonance

Perhaps the major chemical difference between the techniques of n.m.r. and e.s.r. as applied to the study of ionic solvation is that, in the latter, at least one component must be specifically paramagnetic. Apart from the transition-metal ions, these are few and often very unstable. Nevertheless, some of the most informative spectra have come from solutions of very unstable species such as the alkali-metal salts of *m*-dinitrobenzene.

In general, e.s.r. cannot be used to 'look at' solvent molecules, although a solvent molecule bonded strongly to a paramagnetic ion can contribute a hyperfine splitting to the spectrum. In practice such couplings are not generally resolved because of rapid exchange, and n.m.r. studies of solvent nuclei then give more information.

We start by discussing briefly the information that can be derived from studying *g*-shifts. These may be compared with the chemical shifts of n.m.r. but are in general less useful for solvation studies. It is the hyperfine coupling to paramagnetic nuclei, discussed on p. 289, which is most informative, in complete contrast with n.m.r., where spin–spin multiplets have been of relatively little direct use.

One reason for this is that the isotropic hyperfine coupling constants derived from solution spectra are strongly dependent upon the spin-density on the nucleus concerned or on adjacent nuclei. Strong interaction can alter this spin-density, and this is directly reflected in the hyperfine splitting.

A result of outstanding significance in the field of ion-pairing was the detection of hyperfine multiplets derived from coupling to the nuclei of diamagnetic cations in solutions of paramagnetic anions.[46] This is elaborated in section 2B, which is based, in part, upon a recent more extensive review of this aspect of the problem.[47]

As with n.m.r., there is a lot of useful kinetic information hidden within the widths of lines and again, although special saturation techniques can be used,[48] most work has been carried out on slow-passage spectra. As with n.m.r., we distinguish two major sources of line broadening, one involving only the tumbling motion of the ion and its neighbouring solvent molecules, and the other involving chemical reactions.

In many instances, especially when there are large anisotropies of the magnetic parameters, or when the spin-state of the ion is greater than $\frac{1}{2}$, line-widths may be so great that no e.s.r. spectrum can be detected. It is just this situation that gives rise to a Knight-shifted n.m.r. line, and hence the two techniques are complementary to each other in this sense. Indeed, if e.s.r. lines are narrow, it may be useful to broaden them deliberately in order to obtain n.m.r. information. Concentrated solutions where spin-exchange is rapid are often suitable for this purpose.

[46] F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.
[47] M. C. R. Symons, *J. Phys. Chem.*, 1967, **71**, 172.
[48] D. C. McCain and R. J. Myers, *J. Phys. Chem.*, 1967, **71**, 192.

A. Shifts in g-Values.—Since the *g*-values for organic radicals are close to 2·0023 solvent shifts have rarely been detected. One example for which small *g*-shifts were found on ion-pairing is that of the anion of benzophenone.[49] The effect of the cation close to the oxygen is to reduce the spin-density thereon. Since the small positive deviation from the free-spin value is primarily caused by spin on oxygen this has the effect of reducing the *g*-value. Other examples of small *g*-shifts of this sort are given in Table 2 of ref. 47.

A similar qualitative argument can be used to explain the shift from 2·00469 to 2·00541 on going from water to dimethyl sulphoxide observed by Zandstra.[50] Alternatively, one can say that hydrogen-bonding stabilises the non-bonding electrons relative to the π electrons, thus increasing the $n \rightarrow \pi^*$ energy gap.

The presence of low-lying excited states causes the range of *g*-values for transition-metal complexes to be far more extensive, and if one or more of the ligands is labile then varying the solvent will often result in ligand replacement and a consequent shift in the average *g*-value. In such a case either a set of lines from the individual complexes, or a single averaged line will be detected. The widths of such lines will give information about the rates of ligand replacement in exactly the way obtained for chemically shifted n.m.r. lines. However, the actual *g*-values are a rather complex property of the nature of the bonding to the transition-metal ion, and are not of direct significance to the problem of solvation as discussed here.

B. Changes in Hyperfine Coupling Constants.—(i) *Nuclei within the paramagnetic ion.* These can arise from changes in the spin-density distribution induced by changes in solvation, or from changes in the shape of the ion. For transition-metal complexes, the complex itself is changed when one ligand displaces another and hence there can be quite drastic changes in the magnetic parameters.

The first effect is generally quite small, but can become dramatically large when the symmetry of the molecule is changed by the interaction. This occurs frequently on ion-pair formation when there is more than one site of high charge-density in the paramagnetic ion. Thus *p*-benzosemiquinones tend to hold a cation close to one oxygen at a time and this causes a drift in the charge and spin densities. The effect is very much more marked for *m*-dinitrobenzene anions. Examples of these phenomena are now discussed in more detail.

Semiquinones. Three different nuclei can be monitored, ^{1}H, ^{13}C, or ^{17}O, and in the case of the parent ion, benzosemiquinone, all have been investigated in a range of solvents.[51–53] The protons are remarkable for their relative insensitivity, which is apparently carried right through to the diprotonated cation in sulphuric acid.[54] This is neither true of the carbonyl-carbon isotropic

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[49] A. M. Reddoch, *J. Chem. Phys.*, 1965, **43**, 3411.
[50] P. J. Zandstra, *J. Chem. Phys.*, 1964, **41**, 3655.
[51] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **36**, 1944.
[52] E. W. Stone and A. H. Maki, *J. Amer. Chem. Soc.*, 1965, **87**, 454.
[53] W. M. Gulick and D. H. Geska, *J. Amer. Chem. Soc.*, 1966, **88**, 4119.
[54] J. R. Bolton and A. Carrington, *Proc. Chem. Soc.*, 1961, 385.

coupling nor of the ^{17}O coupling which change in a complementary fashion.

These changes[55] summarised in Figure 6 are qualitatively in good accord with expectation. Small, strongly interacting solvent molecules tend to pull negative charge on to the oxygen atoms, thus lowering the spin-density on oxygen and increasing it on carbonyl carbon. Since the isotropic coupling to oxygen may be thought of as being made up from a positive contribution from spin on oxygen and a negative one from spin on carbon, a shift in the spin-density from oxygen to carbon is additive in the overall changes in the hyperfine coupling constants.

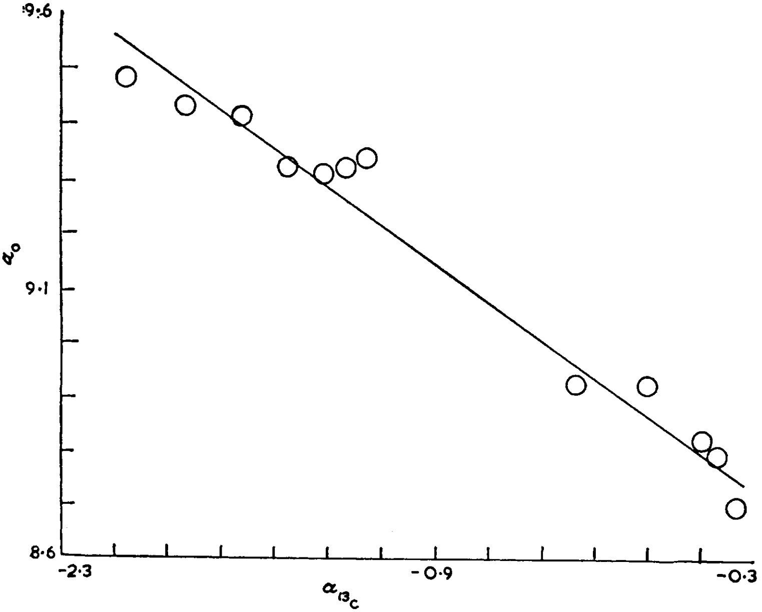

Figure 6 ^{17}O *Coupling constant of* p*-benzosemiquinone plotted against the corresponding carbonyl–*^{13}C *coupling constant in various solvent mixtures*

When a proton is attached to one of the oxygen atoms, the pattern of hyperfine lines changes from a group of five to two groups of three lines, as is to be expected from the change in symmetry. These monoprotonated neutral species have e.s.r. spectra which are quite sensitive to the nature of the solvent.[56–58]

More pertinent to this Review is the fact that lithium salts in 'poor' solvents induce a similar asymmetry, although differentiation between the two halves of the molecule is much less marked.[59] This observation enables us to say

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[55] J. Oakes and M. C. R. Symons, *Trans. Faraday Soc.*, in the press.
[56] T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 279.
[57] T. E. Gough, *Trans. Faraday Soc.*, 1966, **62**, 2321.
[58] T. A. Claxton, J. Oakes, and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 2125.
[59] T. A. Claxton, J. Oakes, and M. C. R. Symons, *Trans. Faraday Soc.*, 1968, **64**, 596.

conclusively not only that ion-pairs are formed, but that the cation is held closely to one oxygen at a time. The situation for larger cations is even more intriguing. At low temperatures similar asymmetric species are detected, but as the temperature is raised, lines broaden and merge to give spectra with alternating line-widths. This alternation is ascribed to a migration of the cation between the two equivalent sites, and is discussed in detail on p. 298.

A similar asymmetry induced by solvent molecules has not been detected in pure or mixed solvents, despite the expectation that, especially in mixed solvents, there will be momentary asymmetry. Evidently it is normally too imprecise and the fluctuations are too rapid to be 'seen' in the e.s.r. specta. This is probably not the case for *m*-dinitrobenzene anions, as we shall see later.

In order to gauge the influence of different solvents, it is helpful to use some device for linking the diverse results from a wide range of techniques. This can be done by utilising the *Z*-value or E_T scales which are based on shifts in ultraviolet spectra.[60] Once again [cf. section IA (iv)] there is often a fairly good linear correlation despite the widely different factors involved. For example, Rassar found a fair correlation between *Z* and the ^{14}N hyperfine coupling constant of $(Ph)_2NO$ in a range of solvents.[61] Results for the hyperfine coupling to ^{17}O in benzosemiquinone anions[55] correlated even better with *Z* as is shown in Figure 7.

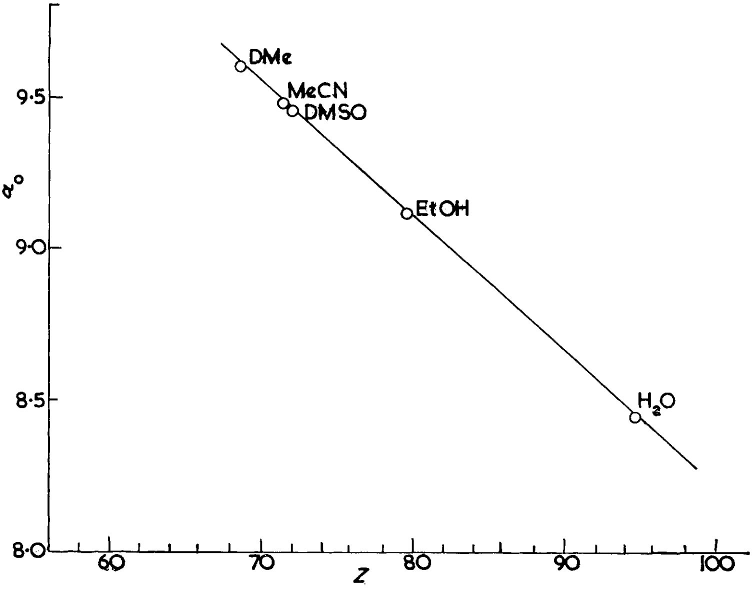

Figure 7 *Dependence of the* ^{17}O *coupling constant of* p-*benzosemiquinone upon the Z value of the solvent*

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[60] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.
[61] R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.

The low sensitivity for a_H in both benzosemiquinone and durosemiquinone anions on diprotonation fits in with the very minor changes induced in these parameters on changing the solvent. In marked contrast, diprotonation of 2,6-dimethylbenzosemiquinone results in a major change in both $a_{H(methyl)}$ and $a_{H(ring)}$, which suggests that the proton couplings for this anion might be strongly dependent upon the solvent. Further, it has been found[58] that monoprotonation occurs only at the unhindered oxygen, and when ion-pairs are formed with alkali-metal cations, these spend most of their time at the unhindered end of the anion.[59] This suggests that interaction with solvent molecules might be somewhat stronger at the unhindered end, although since both ends must interact such differentiation will be relatively small. Both such trends will operate in the sense of increasing $a_{H(methyl)}$ and decreasing $a_{H(ring)}$ on increasing the solvating power of the solvent, and in fact quite large changes are detected.[55] That more than one factor is involved is suggested by the plot of $[a_{H(methyl)} - a_{H(ring)}]$ against Z (Figure 8) which is a very poor correlation in comparison with the trends in the ^{17}O hyperfine coupling for benzosemiquinone.

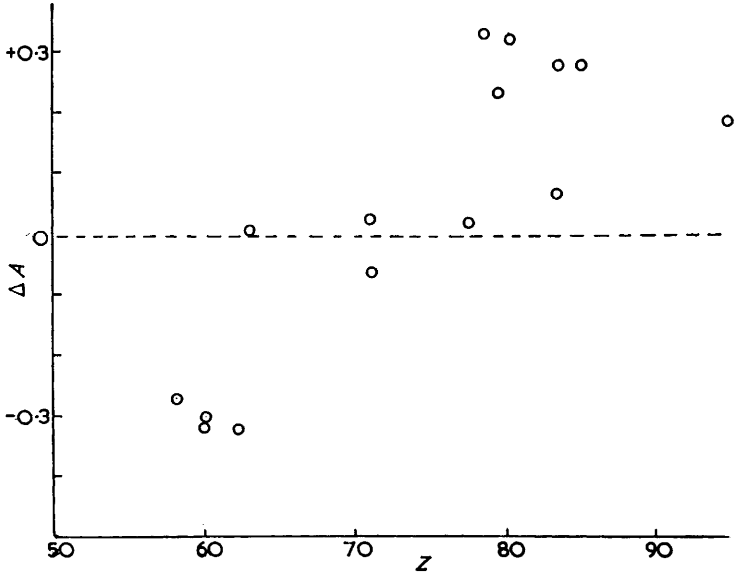

Figure 8 *Dependence of ΔA $[a_{H(Me)} - a_{H(ring)}]$ of 2, 6-dimethyl-benzosemiquinone on solvent Z value*

Aromatic nitro-anions. The hyperfine coupling to ^{14}N in nitrobenzene anions is extremely sensitive to the nature of the environment, and again there is a rough correlation with the Z-value of the solvent. Solid-state studies strongly suggest that, in contrast with the neutral molecule, the nitro-group in the anion is slightly pyramidal, the more so the greater the spin-density on the group.[62] There are, indeed, good theoretical reasons for this, and any shift of spin density into the group will result in a greatly magnified increase in the ^{14}N coupling because, on bonding, there is a direct admixture of 2*s*-character into the orbital of the unpaired electron which will add to the normal spin-polarisation term.[63] It is interesting that in the limiting case of nitroalkane anions there is practically no solvent effect. This implies that the ^{14}N coupling in the pyramidal RNO_2^- group is not very sensitive to small changes in spin-density *within* the NO_2 group itself.

Both the *m*- and *p*-dinitrobenzene anions have provided a wealth of information with respect both to solvation and to ion-pair formation. A key factor seems to be that their structures, especially that of the *meta*-anion, are very readily distortable, in a sense that may be described as 'all or nothing'. Thus, if a cation, say, becomes associated with one of the nitro-groups the ^{14}N coupling involving this group becomes double the original value, whilst that of the latter tends to zero. One possible explanation would be that the unpaired electron in the unperturbed ion is in a degenerate orbital and that the asymmetric perturbation lifts the degeneracy; but whatever may be the reason for the phenomenon, the *meta*-anion is certainly a very useful 'probe' for studying solvation.

The situation is then comparable with that for the semiquinones; strongly held cations such as Li^+ remain at one end long enough for the asymmetric species to be detected (the 'static' case), but most other cations jump from one nitro-group to the other, and this gives rise to a line-width alternation. However, on cooling, the 'static' situation can again be detected.[64]

In addition, the normal gain or loss of spin-density shows up as trends in a_N, and plots of their shifts against the solvent *Z*-values give a fair correlation. One very important factor has emerged, however, which did not show up in the study of semiquinones.

As we have stressed, absence of hyperfine coupling to the cations cannot be correlated with absence of ion-pairs. Since, at best, this coupling is very small (Table 1 of ref. 47), we expect that only contact ion-pairs will show up in this way, and that any form of solvent-separated ion-pair will not give a detectable coupling. In many cases, especially when 'good' solvents are used, the radical-anions under consideration are generated electrolytically by use of a large excess (*ca.* 0·1M) of a tetra-alkylammonium salt. It has been widely accepted that these large cations have little or no tendency to form ion-pairs and this has received support from the observation that a_N for *p*-chloronitrobenzene anions was independent of the concentration of R_4N^+, although it changed markedly when other electrolytes were added.[65]

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[62] W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 448.
[63] P. W. Atkins and M. C. R. Symons, 'Structure of Inorganic Radicals', Elsevier, Amsterdam, 1967.
[64] T. A. Claxton, W. M. Fox, and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 2570.
[65] T. Kitagawa, T. Layoff, and R. N. Adams, *Analyt. Chem.*, 1964, **36**, 925.

However, a_N for *p*-dinitrobenzene anions in alcoholic solutions is very dependent upon the concentration of alkylammonium salts,[55, 66] although it is independent of the concentration of sodium salts except in the very dilute region (Figure 9). This means that R_4N^+ readily forms ion-pairs even in 'good' solvents such as methanol. The reason for the marked shift can be thought of as a loss of hydrogen-bonded solvent rather than as a perturbation by R_4N^+, and the lack of shift in such solvents as dimethylformamide arises because the two environments are now quite similar.

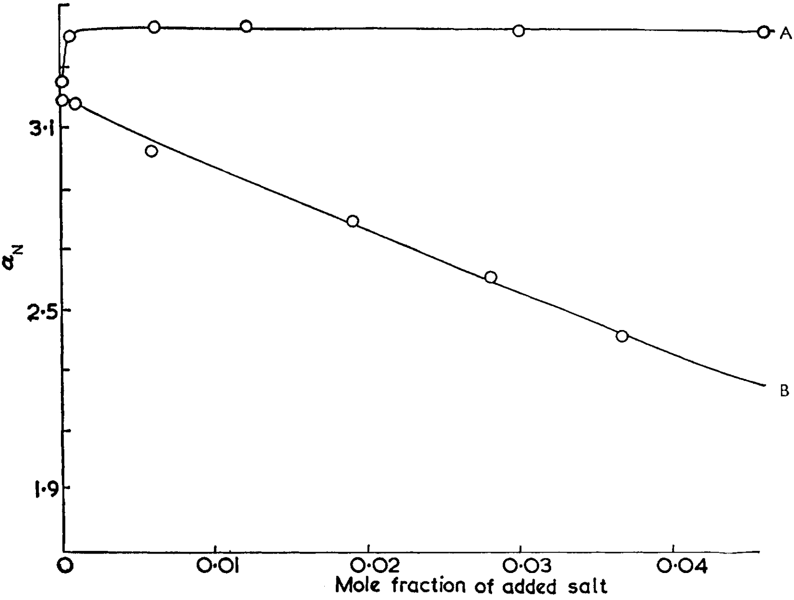

Figure 9 *Dependence of* a_N *for* p-*dinitrobenzene on the concentration of added salt*
A : NaOEt; B : Bu^n_4NBr

Mixed solvents. A considerable effort has been directed towards the interpretation of trends in hyperfine coupling constants on changing from one solvent to another. A typical shift is given in Figure 10 for nitrobenzene anions,[67] and the marked curvature indicating preferential solvation by water is typical of such plots. It can be compared with very similar trends observed for the maximum of the first absorption band of iodide ion in this solvent mixture.[67]

Sometimes a reasonable fit for such curves can be obtained from simplified models involving equilibria such as:

$$A^- S_1 + S_2 \rightleftharpoons A^- S_2 + S_1$$

[66] J. Oakes and M. C. R. Symons, *Chem. Comm.*, 1968, 294.

[67] M. J. Blandamer and M. C. R. Symons, *Internat. Symp. Solvation Phenomena*, Calgary, 1963.

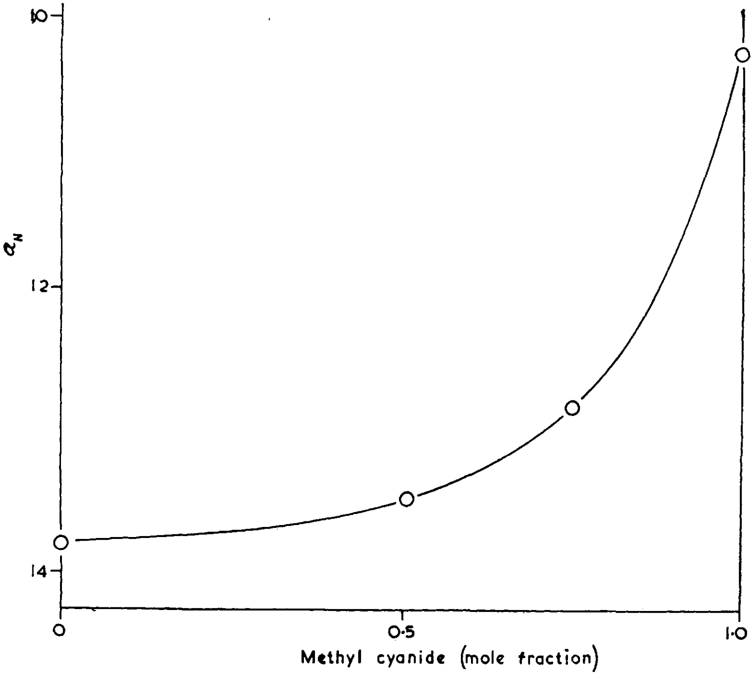

Figure 10 *Dependence of the nitrogen coupling constant,* a_N, *for nitrobenzene anion on solvent composition for mixtures of methyl cyanide and water*

or more complex versions which take the presence of two solvation sites into account.[52, 68] However, the agreement is often very poor, and since alkylammonium ions are usually present in high concentration, the shifts observed must often be a rather complex mixture of solvation and ion-pairing effects.

One result of interest to those concerned with the special behaviour of water is the rather complex shift behaviour of $a_{H(ring)}$ and $a_{H(methyl)}$ for 2,6-dimethylsemiquinone ions in water, on the addition of t-butyl alcohol.[69]

(ii) *To solvent nuclei.* As we have stressed, this is inevitably a minor section, but we wish to mention two phenomena which may point the way to future work. One is that when hydrogen atoms are trapped in a matrix of xenon, strong hyperfine coupling to six of the surrounding xenon nuclei was detected.[67] The other is that the e.s.r. spectra of frozen solutions of cobalt phthalocyanine in various amine solvents gives clear indication of ^{14}N hyperfine coupling involving two co-ordinated solvent molecules.[70]. These well-defined results show that detailed structural information can be obtained in favourable circumstances. It seems likely that solid-state studies will help, because the

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[68] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, 37, 2832.

[69] M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wootten, *Chem. Comm.*, 1967, 273.

[70] J. M. Assour, *J. Amer. Chem. Soc.*, 1965, **87**, 4701.

rapid exchange of solvent molecules that normally results in an exchange-narrowed single line can be eliminated. The chance of actually resolving hyperfine coupling to neighbouring nuclei will be small, but under favourable circumstances it seems that E.N.D.O.R. techniques will provide considerable information about solvent molecules in contact with paramagnetic ions, which will complement n.m.r. results from the liquid phase.

However, great care has to be observed when trying to obtain frozen solutions because of the dangers of phase-separation or clustering which are both hard to detect and to avoid, and which can seriously modify spectra. Further, hyperfine parameters are frequently temperature-sensitive[71] and so extrapolation has many pitfalls.

C. Relaxation Studies.—Factors governing line-widths of e.s.r. spectra are quite comparable with those discussed above for n.m.r. We need a time-dependent process to cause a modulation; some of these are briefly outlined below, particular attention being given to chemical processes.

(i) *Relaxation associated with tumbling.* Generally both A and g are strongly anisotropic and hence, even though the tumbling motion in solution is fast enough to cause complete averaging, the resulting modulation can cause a relaxation and consequently broaden the line by a factor which will depend upon the magnitude of the original anisotropy. This is one of the most important sources of line-broadening for dilute solutions of $S = \frac{1}{2}$ radicals. The situation is illustrated in Figure 11.

From the viewpoint of solvation, the important parameter that can be extracted, at least in principle, from the pattern of line-broadening that results is the tumbling correlation time of the radical or complex. The factors involved have been extensively studied.[72, 73] However, care must be exercised in deriving such parameters because several other relaxation mechanisms may also contribute to the line-width.

These include spin–rotational relaxation of the type discussed for n.m.r. above, in which the rotating motion of the radical itself generates an indirect magnetic field due to the electrons, whose rotation fails to keep up with the molecular framework. The effect will only be important when interactions with the solvent are weak, and rotation can begin to approach the gas-phase situation. It is not easy to extract contributions made by this mechanism to the overall relaxation of a radical, but it seems to be the major source of line-broadening for small neutral molecules such as NO_2.[74, 75]

The isoelectronic radicals SO_2^- and ClO_2 make an interesting contrast in this respect since the former gives very narrow ^{33}S hyperfine lines in aqueous solution under which conditions the individual components of the ^{35}Cl and

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[71] W. M. Walsh, J. Jeener, and N. Bloembergen, *Phys. Rev.*, 1965, **139, A,** 1338.

[72] D. Kivelson, *J. Chem. Phys.*, 1964, **41,** 1904.

[73] C. P. Slichter, 'Principles of Magnetic Resonance', Harper and Row, New York, 1963.

[74] P. W. Atkins, *Mol. Phys.*, 1967, **12,** 133.

[75] G. Nyberg, *Mol. Phys.*, 1967, **12,** 69.

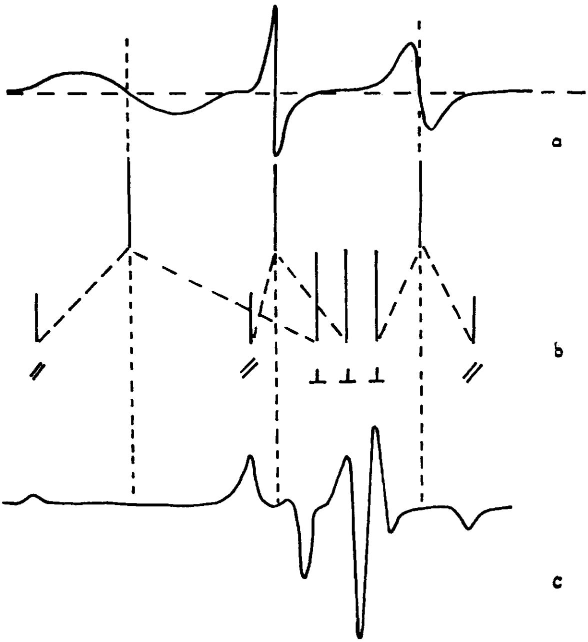

Figure 11 *Diagrammatic representation of the connection between* g- *and A-anisotropy and the line-widths of liquid-phase e.s.r. spectra.*
(a) Typical liquid-phase spectrum for a radical with hyperfine coupling to a single nucleus with $I = 1$.
(b) Shows how these spectra are linked.
(c) Envelope spectrum for stationary radicals.

^{37}Cl hyperfine lines from the latter are so broad that they are only just resolved. The reason for this remarkable contrast is almost certainly the fact that SO_2^- interacts very much more powerfully with the solvent because of its charge.[76] Perhaps the most important aspect of this mechanism is that such broadening should increase with temperature, in contrast with that due to the anisotropy of the *g*- and hyperfine-tensors.

Yet another important source of broadening is commonly called the Orbach process which especially applies to radicals in near-degenerate states which are not coupled directly by spin–orbit coupling.[77] Another is the dynamic Jahn–Teller effect, in which a Jahn–Teller distortion migrates so rapidly between equivalent distortions that an isotropic spectrum results.[78] At very low temperatures in crystalline solids, these distortions may be 'static' and as the temperature is raised lines are broadened before merging according to expectation. A typical example is the ion $Cu(H_2O)_6^{2+}$, the distortion being an elongation along any one of the three ligand axes.[78] To what extent this dynamic

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[76] P. W. Atkins, A. Horsfield, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 5220.
[77] R. Orbach, *Proc. Phys. Soc.*, 1961, **A**, **77**, 821.
[78] M. C. M. O'Brien, 'Low Symposium on Paramagnetic Resonance', Academic Press, New York, 1967, p. 323.

distortion contributes to the line-widths of such complexes in fluid solution at room temperature is not really established. Tetragonal distortion of $Cu(H_2O)_6^{2+}$ in aqueous solution has been studied by ^1H and ^{17}O n.m.r.[79]

Yet another factor of this general type that needs to be considered for radicals which deviate considerably from a spherical shape is restricted rotation. Again, in crystal or glassy lattices such rotations can be detected readily, a good example being NO_2 trapped in rare-gas matrices, in which rotation about the long axis of the molecule remains free so that two of the principal values of the ^{14}N hyperfine tensors are effectively averaged, leaving the third unchanged.[80] If rotation in one sense can occur far more effectively than in another, this can clearly modify the extent of broadening of particular lines in an average spectrum. This has been discussed theoretically by Freed.[81]

We now turn to somewhat more tractable problems which have direct bearing upon chemical rections. The first involves the transfer of nuclei, such as protons in acid–base reactions or alkali-metal cations in ion-pair equilibria. The second involves transfer of electrons between molecules, and this is used as a link to a final brief consideration of spin exchange and triplet states.

(ii) *Equilibria involving ion-pairs.* To illustrate the way in which line-widths can be used to obtain kinetic information relating to ion-pairing we consider the equilibria (1)—(4). Equilibrium (1) will be characterised by the separate weighted spectra of A^- and M^+A^- if the rates are slow, but as the life-times of these species are reduced (on warming, for example) each component line will broaden until ultimately a spectrum comparable with that of the solvated ion A^- is obtained. This is because any given A^- will combine with different M^+ ions having arbitrary nuclear spin states.

$$M^+A^- \rightleftharpoons M^+ + A^- \quad (1)$$

$$M^+ + A^-M^+ \rightleftharpoons M^+A^- + M^+ \quad (2)$$

$$A^-M^+ \rightleftharpoons M^+A^- \quad (3)$$

$$(M^+A^-)_1 \rightleftharpoons (M^+A^-)_2 \quad (4)$$

Then (2) is simply the bimolecular equivalent of (1) and again loss of metal hyperfine coupling will be the main result as the lifetime of any one M^+A^- unit is reduced. This situation can readily be achieved by adding a diamagnetic salt, M^+B^-, and rates can be calculated from the excess of broadening.[82] These rates do not directly relate to (2), however, since competing ion-pair equilibria with B^- will play an important rôle. In addition to giving kinetic information this reaction has important practical aspects in that it can be used to simplify a complex spectrum. However, if it is unplanned, one can be misled into concluding that ion-pairs are absent or that the metal hyperfine coupling is too small to detect.

Reactions (3) and (4) are closely related and give rise, when the rates are appropriate, to specific line-broadening. In (3), an intramolecular jump of the

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[79] W. B. Lewis, M. Alei, and L. O. Morgan, *J. Chem. Phys.*, 1966, **44**, 2409.
[80] P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2873.
[81] J. H. Freed, *J. Chem. Phys.*, 1964, **41**, 2077.
[82] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, 1964, **86**, 2537.

cation between equivalent sites of the anion is envisaged, as for example between the oxygens of *p*-benzosemiquinone or the nitro-groups of *p*-dinitrobenzene anions. As already described, for slow exchange, spectra characteristic of the asymmetric ion-pairs are obtained whilst for fast exchange spectra similar to those of the symmetrical anions result, except that hyperfine coupling to the metal remains sharp since the same cation is involved in many migrations. For intermediate exchange rates, some lines of the averaged spectrum will be broadened, possibly beyond detection, whilst others will have narrow and sharp components, and the outermost lines remain sharp. The situation both for the initial broadening of the lines of the 'static' ion-pair and for the final narrowing of the merged lines for a radical having two normally equivalent nuclei with unit spin is fully described and illustrated in ref. 47. In the limit of extreme broadening the spectrum appears to be a 1 : 1 : 1 triplet having twice the normal hyperfine coupling.

If no cation hyperfine lines are detected, then the alternation may be caused either by migration of a cation, possibly strongly solvated, or by concerted redisposition of solvent molecules such that the negative charge is 'trapped' at one end of the anion or the other depending upon the orientation of the adjacent solvent molecules. We have been unable to detect such asymmetric solvation for *p*-duroquinone or *p*-benzosemiquinone anions even using mixed solvents with the strongly interacting component in low concentration, but it probably does occur for solutions of *m*-dinitrobenzene anions.[83, 84] (W. E. Griffiths, C. J. W. Gutch, G. F. Longster, J. Myatt, and P. F. Todd have recently detected a large and a small ^{14}N isotropic hyperfine coupling for aqueous solutions of *m*-dinitrobenzene anions, showing that, in water, asymmetric solvation is long-lived.) Specific examples of cation migrations are reviewed in greater depth elsewhere.[47]

Equation (4) also represents a cation migration, but between different sites. One example is that of the 2,6-dimethyl-*p*-benzosemiquinone anion.[59] Migration should now modulate all but part of the central hyperfine component. Also, the outer lines of the quartet from a cation with spin $^3/_2$ should broaden more than the inner pair.

Because the populations of the two states now differ, the unhindered site being greatly favoured by the cation, interpretation of the different spectra is far more complicated. Important features are (i) that for slow exchange two species should be detected, but the one in low concentration may be masked by the other; (ii) the lines for the unfavoured species will broaden first; (iii) when only one species is detected, slow exchange broadening can be distinguished from fast exchange in that for the former all exchanging components are equally broadened.

These considerations apply equally well to equilibria of type (4) in which contact and solvent-separated ion-pairs are involved. The interesting results

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[83] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **41**, 699.
[84] C. J. W. Gutch and W. A. Waters, *Chem. Comm.*, 1966, 39.

of Hirota for alkali-metal anthracene salts may be illustrative of such reactions.[85] (iii) *Electron-transfer processes.* We now consider yet another equilibrium (5) involving M^+A^- ion-pairs. As the rate of such a process increases, so the individual hyperfine components of A^- broaden and merge to a single line which ultimately can become very narrow. If the reaction involves M^+A^- rather than just A^-, and if hyperfine multiplets from M^+ are detected, then the exchange-averaged feature will also be such a multiplet. This was observed by Ward and Weissman[86] for such systems as sodium naphthalenide and naphthalene.

$$^*A + M^+A^- \rightleftharpoons {}^*A^-M^+ + A \qquad (5)$$

These reactions are of significance to solvation studies in that the major barrier to electron-transfer is usually the fact that solvent molecules are in quite different states in the vicinity of the reactants. To some extent it may be possible for suitably polarised solvent molecules to be 'transferred' rather as the cation is, but otherwise reactions must await fortuitous arrangements when the solvent favours equally the electron on either site. Hence reaction energies and entropies have a direct bearing on solvent organisation.

This is in marked contrast with the situation for spin exchange. A fair model would now be to consider the approach of two A^- radicals, with or without their gegen-ions. When there is effective overlap between the orbitals of the two anions, the electrons will exchange, but now there is no solvation barrier and hence rates are very much greater, being in general diffusion controlled.

Generally the broadening of hyperfine lines and ultimate appearance of an exchange-narrowed single line, which follows exactly the pattern for single electron transfer, is simply a nuisance, and is avoided by spectroscopists by using very dilute solutions. If, however, gegen-ions do participate, the 'transition state' may be greatly stabilised and the resulting ion-cluster may have a life of sufficient length for direct detection.

The sort of problems that then arise have been briefly reviewed elsewhere.[47] Suffice it to say that generally two different units seem to occur commonly. In one the radicals are about 6—7 Å apart, and the fluid spectra are very broad singlets. The frozen solutions, however, give well resolved fine-structure features in the $g = 2$ region from which the effective spin-separation can be calculated.

In the weakly interacting species the spins are usually too distant for resolution of the fine-structure features in the solid state, but the fluid spectra are quite well resolved. The most significant result is then that two alkali-metal cations are involved, showing that neutral ion-tetramers are present.

The interaction in these 'triplet-state' species is almost entirely of a classical dipolar nature, and the line-broadening in solution follows from this. For transition-metal complexes having $S > \frac{1}{2}$, however, the coupling between electrons occurs largely by a spin-orbit coupling mechanism, which is far more

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[85] N. Hirota, *J. Phys. Chem.*, 1967, **71**, 127.

[86] R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, 1957, **79**, 2086.

effective. The result is that in the solid-state resonance features are spread over such a huge range of field that many are beyond the range of detection. Such complexes often cannot be detected at all in fluid solution. Factors controlling line-widths have been considered by Carrington and Luckhurst.[87]

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[87] A. Carrington and G. R. Luckhurst, *Mol. Phys.*, 1964, **8**, 125.