A MAGNETIC RESONANCE STUDY
OF SOLVENT INTERACTIONS

by

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To my parents

Without whose constant help and encouragement
this thesis would never have been written.

"A research worker in pure science who does not have at all times more problems he would like to solve than he has time and means to investigate them probably is in the wrong business."

E. Bright Wilson, Jr., An Introduction to Scientific Research (McGraw-Hill, New York, 1952).

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ABSTRACT

Solvent effects on the e.s.r. spectra of over forty semiquinones are reported and related to solvent basicity and radical structure. In many instances quantitative studies have been possible, based on a model due to Gendell, Freed and Fraenkel. Results obtained in H_2O-HMPA, H_2O-DMSO, H_2O-DMF, H_2O-EtOH and EtOH-HMPA comply with this simple exchange model. A treatment of results is presented which enables equilibrium constants to be determined readily, and it is demonstrated that true thermodynamic equilibria are being studied.

Studies on trihydroxybenzenes reveal a change in solvent structure in the region $[H_2O]/[HMPA] \approx 2$ such that dianions of hydroxysemiquinones cannot persist at higher HMPA concentrations. N.m.r. confirms this change and indicates that a relatively stable complex, HMPA.$2H_2O$, is formed. Extensive solvent-solvent interactions are also found in H_2O-DMSO, H_2O-DMF, EtOH-HMPA, EtOH-DMSO and EtOH-DMF.

The significance of the measured equilibrium constants is discussed. An interpretation in terms of preferential solvation by the aprotic solvent is rejected in favour of one in which solvent-solvent and radical-solvent interactions operate simultaneously. In H_2O-HMPA mixtures, for instance, competition between the radical and HMPA for water molecules is envisaged, the overall result being measured by e.s.r. Exchange occurs between hydrogen bonded and non-hydrogen bonded radicals, where bonding can be either to a water molecule or to the HMPA.$2H_2O$ moiety. This suggestion is compatible with the observed linear dependence of the e.s.r. parameters on $[H_2O]/[HMPA$ and on measures of solvent polarity such as ε and Z.

PUBLICATIONS

The following publications have drawn (in part) on data presented in this thesis:

1. Quantitative Aspects of the Solvation of Semiquinones in Water+HMPA Mixtures. J.C.S. Faraday II, 1978, 74, 541.

2. Electron Spin Resonance Spectra of Tri-, Tetra- and Penta-alkoxybenzene Radical Cations. J.C.S. Faraday II, 1979, 75, 1185.

3. An E.s.r. Study of Radicals Obtained by the Oxidation of 3,6-Dihydroxypyridazines. Tetrahedron Letters, 1979, 2821.

4. Determination of Acid Dissociation Constants of some Phenol Radical Cations. Part 2. J.C.S. Faraday II, 1979, 75, 1637.

5. The Electron Spin Resonance Spectra of Semiquinones obtained from Some Naturally Occurring Methoxybenzoquinones. J.C.S. Perkin II, in the press.

6. Effects of Near Degeneracy in the Frontier Orbitals on the Electron Spin Resonance Spectra of Radicals Related to 1,2,3-Trihydroxybenzene (Pyrogallol). J.C.S. Faraday II, in the press.

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CHAPTER 1

INTRODUCTION

1. Starting Point

In many instances, e.s.r. spectra of radicals obtained in aprotic solvents are markedly different in appearance from those in aqueous or alcoholic solution. This is true of many semiquinone radicals, the variation with solvent being apparently unsystematic. The largest deviations from values detected in protic systems are detected when the aprotic solvent employed is hexamethylphosphoramide (HMPA).

It was desirable, therefore, to undertake a more systematic investigation in an attempt to quantify, and hence predict, the manner in which the interaction between free radicals and the particular solvent in which they are generated affects the resulting e.s.r. spectrum. It was proposed to monitor changes in the spectra of semiquinone radicals in the solvent mixture water - HMPA, a system in which the magnitude of the variations in the e.s.r. parameters is sufficiently large for a study of the thermodynamic aspects of solvent - radical interactions to be feasible. In particular, such interactions could be treated in terms of a simple theoretical model proposed by Gendell, Freed and Fraenkel,[1] perhaps yielding meaningful equilibrium constants and free energy changes for these systems; thermodynamic parameters were not, in fact, measured in the original work.

Secondly, by variation of the substituents in the radicals and by extending the range of solvents studied, it was hoped, using semiquinones as sensitive probes of their environment, to deduce something of the nature of radical - solvent and solvent - solvent interactions in the mixtures.

2. Application of Magnetic Resonance Spectroscopy to the Study of Solvation

In recent years electron spin resonance (e.s.r.) and nuclear magnetic resonance (n.m.r.) have taken their place amongst other forms of spectroscopy as useful tools for obtaining structural and dynamic information about solvation.[2,3,4] In particular, the standard techniques for studying ions in solution have been supplemented by magnetic resonance methods which provide valuable information concerning the problems of ionic solvation and interactions between ions in solution. Information is obtained from changes in n.m.r. chemical shifts and spin-spin coupling constants, from e.s.r. hyperfine coupling constants and g-value variations, from the appearance of new resonance lines and from line widths and shapes.

Electron spin resonance is limited to the study of dilute paramagnetic solutes, as it applies specifically to molecules or ions possessing one or more electrons with unpaired spin. This endows the system with a net angular momentum, which may arise from net spin or net orbital angular momentum, or from some combination of the two. For organic radicals the orbital contribution is largely quenched. The possession of both spin and charge confers on the electrons a magnetic moment, μ, which is proportional to the magnitude of the spin:

$$\mu = -g\beta S \qquad \text{...Eq. 1}$$

$\hbar S$ is the spin angular momentum vector; S is the spin of the electron; β is the electronic Bohr magneton,[5] defined by the equation:

$$\beta = \frac{eh}{4\pi m_e c} \qquad \text{...Eq. 2}$$

where $-e$ and m_e are the charge and mass of the electron, respectively; g is a proportionality constant known as the g-value which takes the value 2.00232 for a free electron, small deviations from this value occurring in organic radicals attributable to spin - orbit coupling.[6]

Quantum mechanics demands that the allowable electron spin states are quantized; the component m_s of the electron spin vector in any specified direction can only take up one of a set of discrete values:

$$m_s = -S, -S+1, -S+2, \cdots, S-1, S \qquad \text{...Eq. 3}$$

m_s is the spin quantum number. For an electron with $S=\frac{1}{2}$, the allowed m_s values are $+\frac{1}{2}$ or $-\frac{1}{2}$, giving two degenerate energy levels called Zeeman levels. If a steady magnetic field, B_z, is applied to the electron, a strong interaction occurs between the field and the magnetic moment of the electron, which may be expressed as:

$$E = -\mu_z B_z = g\beta B_z m_s \qquad \text{...Eq. 4}$$

The degeneracy of the Zeeman levels is,,therefore, lifted, each orientation of the electron spin now corresponding to a distinct energy level.

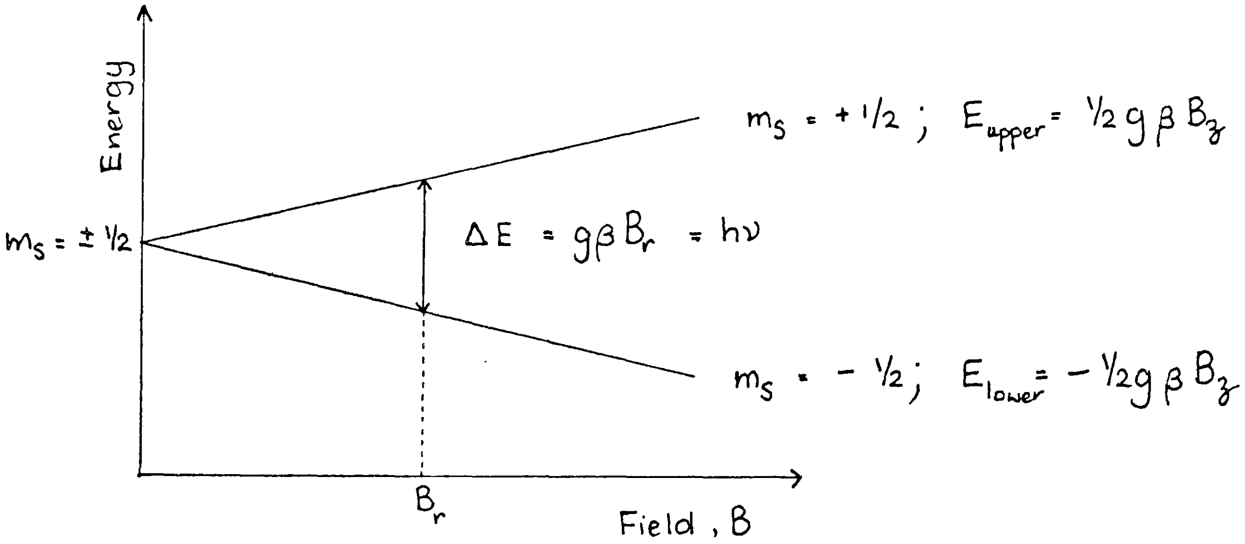
Energy
$m_s = \pm 1/2$
$m_s = +1/2$; $E_{upper} = 1/2\, g\beta B_z$
$\Delta E = g\beta B_r = h\nu$
$m_s = -1/2$; $E_{lower} = -1/2\, g\beta B_z$
B_r
Field, B

Figure 1. Electron spin levels in a variable magnetic field and at a fixed frequency.

As a consequence of the negative charge of the electron, and having defined the Bohr magneton as positive, the lower energy state corresponds to the situation in which $m_s=-\frac{1}{2}$ (or β - spin),* the spin magnetic moment being aligned with the field. The higher energy orientation corresponds to an antiparallel arrangement (α - spin, $m_s=+\frac{1}{2}$), and the separation between the two states, ΔE, is given by:

$$\Delta E = g\beta B_r = h\nu \qquad \text{...Eq. 5}$$

Transitions between the two levels may be induced by operating at a fixed microwave frequency, ν, and linearly varying the strength of the applied magnetic field until resonance occurs (at the field value B_r). The population over the two states is a Boltzmann distribution, so that at ordinary temperatures net absorption occurs. The population difference is maintained by spin-lattice relaxation processes[7] which prevent the onset of saturation.

Transitions between the Zeeman levels produce a single line e.s.r. spectrum; the only parameter obtainable from such a spectrum is the g-value of the radical, which determines the field strength at which the signal is observed (Eq. 5). The difference in g-factor for a free radical and that for a

---

[*] Here β- refers to a spin state and is not to be confused with the Bohr magneton (Eq. 2).

free electron is analogous to the chemical shift in n.m.r., but studies of *g* shifts have proved less useful[2] than their n.m.r. counterparts for solvation studies.

In n.m.r. experiments, nuclei with magnetic moments are effectively used as probes to measure the magnetic field B_{local} at the nucleus,[8]

$$B_{local} = (1 - \sigma) B \qquad \text{...Eq. 6}$$

B is the applied field strength and σ is the screening constant. The separation of resonance frequencies of nuclei in different structural environments from some arbitrarily chosen line position is generally termed the chemical shift.[9] The sensitivity of the chemical shift to the particular environment of the proton makes n.m.r. an extremely useful technique for the study of solvent -solute and solvent - solvent interactions, as molecular association will alter the proton chemical shift relative to its value in the isolated molecule.

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, whicn is the weighted mean of the individual resonances will be detected:[10]

$$\delta_{obs} = \sum_i \delta_i P_i \qquad \text{...Eq. 7}$$

P_i is the population fraction of species i of chemical shift δ_i. For example, in an electrolyte solution solvent molecules will be in a variety of environments. If exchange of solvent molecules between these various environments is slow ($\tau_{1/2} > \underline{ca}\ 10^{-4}$S) relative to the chemical shift differences between the various structures a number of peaks are expected in the n.m.r. spectrum of a solvent nucleus. Generally, however, the process is fast, Eq. 7 holds and the various resonances are time - averaged to a single peak whose shift from the pure solvent resonance reflects the mean effect of the different environments.[2]

In certain cases, however, especially at low temperatures a separate resonance due to solvent bonded, say, to cations may be resolved[11] and, then, from the relative peak areas the cation solvation number can be determined.

The changes in chemical shift for protons which can take part in hydrogen bonding can be very pronounced.[12] It is a general observation[13] that a hydrogen bonded proton resonates at a lower applied magnetic field than one which is not. Assuming the hydrogen bond to be primarily electrostatic in character[14,15] the proton involved is drawn slightly from its bonding electrons. The shielding experienced by the proton is thereby reduced and resonance occurs at a lower field.

This empirical observation has been so extensively reported that n.m.r. is now widely employed as a criterion for the establishment of co-ordination, the change in chemical shift observed being taken as evidence for "co-ordination" of the proton.[16] Thus, the proton resonance signal of an associated hydroxy proton is shifted to a lower magnetic field relative to its position in the unassociated molecule. Shifts are normally to lower field except when aromatic donor sites are involved in hydrogen bonding.

Protons which can form hydrogen bonds usually have chemical shifts which depend upon the strength and concentration of the hydrogen bonded complex, and on the nature of the donor.[9] This is useful in a diagnostic sense.

The analogous e.s.r. parameter, the g-value, is by contrast of very limited potential as a parameter on which to base solvation studies.[2] For the majority of organic radicals g deviates from the "free-spin" value by ±1% at most[17] so that great experimental precision is required if this parameter is to be used to characterise species. The g-factor has been shown to be solvent dependent[18-23] but the perturbation induced by changing the solvent for p-benzosemiquinone from water (g=2.00469) to DMSO (g=2.00541)[18] is too small to be used as a quantitative measure of solvent interactions. The accuracy with which g-values can be measured may only be of the order ±.001, which is greater than the observed variation. The most informative solvation studies[2] employing e.s.r. have been those concerned with changes in the hyperfine coupling to paramagnetic nuclei present in a particular radical. This is in contrast to n.m.r., where the corresponding spin - spin multiplets have been of little direct use.[24]

Hyperfine structure occurs in the e.s.r. spectra of radicals containing nuclei whose spin quantum number, I , is non-zero. Such nuclei provide additional "local" magnetic fields which modify the effects of the external field on the unpaired electron. In a hydrogen atom the proton spin may be aligned with the field ($m_I = +\frac{1}{2}$), thus reinforcing its effects, so that the electron resonates at a lower applied field than B_r (Fig. 2) by an amount equal to a/2, where a is known as

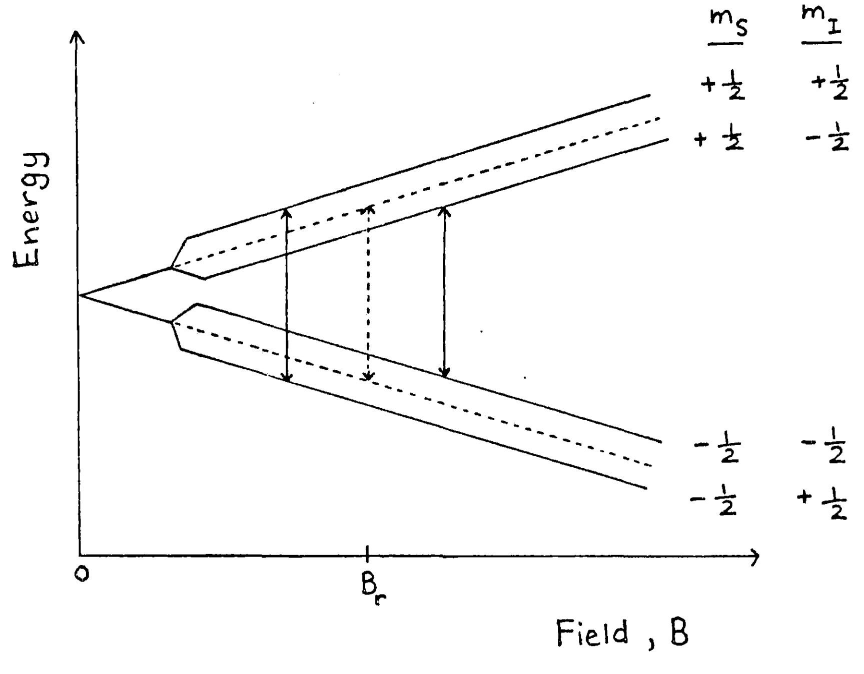

Fig. 2(a) Energy levels for an electron in an applied magnetic field together with that produced by a single proton (ν constant).

<---> Transition which would occur in absence of proton

<——> Observed transition

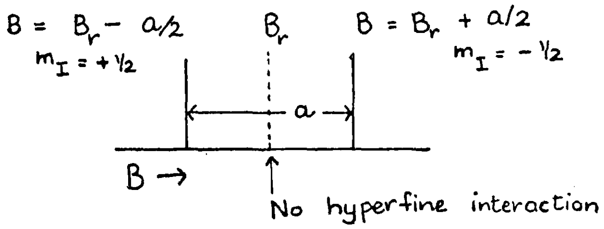

Fig. 2(b) E.s.r. spectrum observed for system 2(a).
(a = hyperfine coupling constant/G)

the hyperfine splitting constant or coupling constant. Alternatively, the proton spin may be aligned against the field direction, resonance now occurring at a correspondingly higher field value than B_r. Both situations are equally probable under the conditions of the experiment so that interaction with the proton splits each electronic energy level into two, resulting in four energy levels, each characterised by the quantum numbers $m_s=\pm\frac{1}{2}$, $m_I=\pm\frac{1}{2}$. The selection rules governing the two allowed e.s.r. transitions are $\Delta m_s=\pm1$, $\Delta m_I=0$. The observed spectrum (Fig. 2) then consists of two hyperfine components.

In general, the expected single absorption line is split into a number of hyperfine components depending on the number of allowed nuclear spin states. For nuclear spin I, the number of observed components (all of the same intensity) is $(2I+1)$. When there are n nuclei of the same spin which couple equally to the proton (i.e. n equivalent nuclei) the number of spectral lines produced is $(2nI+1)$. In this case there will be some degeneracy of the energy levels and this will be reflected in the relative intensities of the spectral lines. When there is a coincidence of two levels, transitions involving these levels produce a spectral line which is twice as intense as that expected from transitions between non-degenerate states. For n equivalent protons the relative intensities of the hyperfine lines are given by the coefficients of the binomial expansion $(1+x)^n$. Where there are n equivalent nuclei of spin I and a further set of m equivalent nuclei, also of spin I, each group interacts independently and unequally with the electron to give $(2nI+1)(2mI+1)$ components with the intensity distribution appropriate to each group (except in the case of accidental overlap of lines). The total width of an e.s.r. spectrum is given by $2\sum_i I_i a_i$, where a_i is the coupling constant of nucleus i with spin I_i, the summation being carried out over all nuclei contributing to the hyperfine pattern.

It has been proposed[1] that strong interactions with the solvent can alter the spin density distribution within a radical, causing a critical dependence of the coupling constants derived from solution spectra on the nature of the medium. The mechanisms of hyperfine interaction operative in organic radicals in the liquid phase[6] ensure that the hyperfine splitting constant determined for a particular nucleus is directly proportional to the spin density on the nucleus concerned or on adjacent nuclei. Changes in spin density, therefore, are directly reflected in the observed hyperfine splittings, which provide a most useful parameter by which the strength of solvent interactions may be monitored, and give some idea of the environment of the radical.

In liquid samples of low viscosity a radical is continually and randomly changing its orientation with respect to the external field via Brownian motion. As a consequence the anisotropic dipole-dipole interaction between the electronic and nuclear magnetic moments is averaged to zero[25] and makes no contribution to the observed hyperfine splitting. The g-value recorded for a radical in solution is also an average isotropic result in contrast to the anisotropy exhibited by the g-values of solid samples. The isotropic mechanism which gives rise to hyperfine structure in liquid phase e.s.r. spectra is the Fermi contact interaction.[26]

This mechanism requires a finite unpaired electron density at the nucleus involved in the hyperfine interaction, i.e. the unpaired electron must have some s-orbital character . Hyperfine structure would not, therefore, be predicted in the spectra of benzosemiquinone radicals. The existence of hyperfine structure is explained by the phenomenon of "spin polarisation" which results from a mixing of the π- and σ-systems, otherwise known as configuration interaction.[27,28] In an isolated $>\dot{C}-H$ fragment of a conjugated system (Fig. 3), a C—H σ-bond is formed by overlap of the carbon sp^2 hybrid orbital with the hydrogen 1s orbital and the unpaired electron resides in a carbon $2p_\pi$ orbital whose axis is perpendicular to the C—H bond.

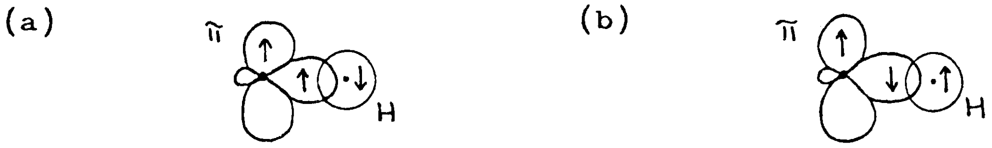

Fig. 3 Possible electronic configurations for a $>\dot{C}-H$ fragment in an aromatic molecule.

The two possible arrangements of the electron spin orientation are normally equally important: the electron in the $2p_\gamma$ orbital has undetermined spin since it is involved in a further bond in which the electrons, being paired, are mutually indistinguishable. However, for a free radical the spin of the odd electron is specifically either α- or β-, and structure (a) is more stable due to the favourable exchange interaction between the π-electron and the carbon σ-electron whose spins are parallel (modification of Hund's rule). The spins of the electrons in the C—H σ-bond are, therefore, polarized slightly: if the odd electron has α-spin there is a slight excess α-spin in the carbon σ-orbital, and corresponding excess β-spin in the hydrogen 1s orbital. It is this β-spin which is responsible for the isotropic splitting, negative due to the net negative spin density (i.e. an excess of β- over α-spin) at the proton.

The sign of the proton hyperfine splitting is not obtainable from solution e.s.r. spectra but has been confirmed by single crystal[29] and n.m.r. studies.[30]

The polarisation effect is rather small: for unit unpaired-electron density on the carbon atom the proton hyperfine splitting is of the order of 23G (i.e. 23×10^{-4}T) compared to a splitting of 508G for the hydrogen atom. This corresponds to ca 4% spin polarisation induced coupling. In aromatic radicals delocalization of the odd electron means that the average unpaired electron density on a particular carbon $2p_\gamma$ orbital is considerably smaller than unity. The McConnell equation:[27]

$$a_H = Q\,\rho_\pi \qquad \text{...Eq. 8}$$

relates the unpaired-electron density at a given carbon atom, ρ_π, to the hyperfine splitting, a_H, due to an adjacent ring proton. Q is a negative constant, numerically lying between 22.5 and 30G, and sometimes known as the sigma-pi parameter.[27] Coupling to nuclei which are even further away from the "site" of the odd electron (e.g. the methyl group in methylsemiquinones) has been attributed to hyperconjugation.[31] Radical-solvent interactions which result in a polarization of the π-electron charge and spin-density distributions, therefore, cause a variation in the hyperfine splittings of that radical (Eq. 8), which ought to give some indication of the strength of this interaction.[1]

Despite the limited number of systems to which, by definition, e.s.r. is applicable it is currently the most powerful technique available in the field of ion-pair formation.[3,4] A wealth of information has been obtained concerning the presence, structure (e.g. whether solvent-shared or solvent-separated) and energetics of ion-pairs using e.s.r. spectroscopy. This is due mainly to the fact that alkali-metal gegen-ions in ion-pairs often give rise to extra hyperfine coupling,[3,32] as well as modifying the couplings exhibited by the anion nuclei. Useful information concerning solvent interactions is provided even in the absence of ion-pairing. Transfer from an aprotic solvent has been shown to induce similar modifications of spin-density and g-factor; perturbation caused by transfer can be greater than that induced by cations in ion pairs.[33]

In general, e.s.r. cannot be used to "look at" solvent molecules. A solvent molecule bonded strongly to a radical ion could contribute a hyperfine splitting to the spectrum, but such splittings are, in practice, not normally resolved as a consequence of rapid exchange. In such cases n.m.r. studies provide more information than e.s.r.

As with n.m.r. much useful kinetic information may be concealed within the widths of e.s.r. lines.[2] Generally both a and the g-value 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.[2] The important parameter which can be extracted then, at least in principle, from the pattern of line broadening that results is the tumbling correlation time of the radical or complex.[34] Solvation studies utilising line-broadening effects are, however, complicated in that several other relaxation mechanisms may also contribute to the line-width.[2]

Dynamic processes in which the components have lifetimes in the region 10^{-6}-10^{-9}S (for example, equilibria between different types of ion pair) are readily probed using e.s.r.[3] This is a range not readily accessible by other techniques and is the chief reason why dialkyl nitroxides have been so extensively used as 'spin-labels' in biological studies.[35] A major strength of e.s.r. is its sensitivity in detecting solvent effects which might not show up in other types of investigation. In addition, with the particular exception of m-dinitrobenzene anions,[36] the spectra obtained from organic radicals in solution are averaged spectra resulting from fast exchange between all possible radical species present in the solution. Therefore, e.s.r. is complementary to i.r. and Raman studies of solvation[3] in that averaging processes are generally "slow" on the i.r. timescale, and the possibility of observing features due to more than one species exists.

3. Magnetic Resonance Studies of Solvent Interactions.

A. E.S.R. Studies

Numerous investigations[1,18-22,37-52,55-69,72-78] have indicated that the hyperfine splitting constants of radicals depend critically on the medium in which the spectra are determined. Such qualitative studies of solvent effects have generally focused on the sensitivity of the observed coupling constants to changes of environment, whereas corresponding variations in the g-factor and in the widths of the various spectral lines have been less frequently employed.

Solvent effects on e.s.r. spectra were first recognised by Geske and Maki[37] in 1960. The nitrogen splitting, a_N, in the nitrobenzene anion radical was found to be 10.32 G in acetonitrile and 9.70 G in DMF. Similarly the ^{14}N coupling constants for the negative ions of aromatic nitro-compounds were some 3-4 G larger in water than in acetonitrile,[38] whereas the spectra of aliphatic anions[39] and non-polar radicals,[40] by contrast, were insensitive to the nature of the solvent.

Environmental effects on a_N for diphenylnitroxide[41] were accompanied by much smaller variations in the proton splittings, the total change in a_H being of the order 1-2%. Indeed, the first significant changes in proton splittings with solvent were reported by Stone and Maki,[42] who demonstrated that the proton splittings of semiquinones generated in DMSO were markedly different from values previously determined in aqueous and/or alcoholic solutions. Replacement of an aqueous solvent by an aprotic one resulted in variations in a_H of up to 45%. The magnitude of the change in any particular case appeared to be governed by the nature of the radical and by the site of the proton in the radical, apparently in an unsystematic manner. The ^{13}C splitting from the carbonyl carbon atom was also observed[42] to alter under these conditions.

Dissimilarities in the spectra of the thio-indigo radical obtained in actone and ethanol[43] were attributed to variations in the electric dipole interaction of the ion with the two liquids. Further solvent influences on e.s.r. spectra were reported[44] for nitroxides observed in toluene and in aqueous alcohol. Changes in both ring proton and ^{31}P coupling constants in a number of phosphobetaine radicals (phosphonium-substituted p-benzosemiquinones) were found [45] when the solvent was altered. In apolar solvents such as benzene the radicals were considered to be self-associated, whereas in hydrogen bonding solvents such pairs were broken down. Similarly, a_N and a_H (ring) for mono- and diphenylnitroxide were found [46] to increase as the polarity of the solvent was raised. For a variety of semiquinones in H_2O-DMF ring proton splittings approached[47] those of unsubstituted 1,4-benzosemiquinone as the concentration of DMF was increased. Also, those semiquinones exhibiting the largest substituent effects in aqueous media underwent the greatest changes in hyperfine splitting constants when the solvent was changed to the aprotic DMF.

The addition of small amounts of water to an acetonitrile or DMF solution of the nitrobenzene anion[48,49] caused a rapid increase in both a_N and the p-proton coupling constant (a_H), followed by an asymptotic approach to a limiting value at appreciable water concentrations. A 1:1 correlation was found between a_N and a_H for all solvent systems studied. The degree of variation of a_N for aromatic nitro- compounds was qualitatively related[48] to the dissociation constant of the protic solvent in the mixtures investigated, and to steric hindrance of, and intramolecular hydrogen bonding to, the nitro-group. It was concluded[48] that the interaction between the radical ions and the solvent was closely related to the possibility of hydrogen bond formation, a hypothesis supported by the negligible shifts observed for o-substituted nitrobenzene anions in which intra-molecular hydrogen bonding is possible. However, this does not imply that the radical is unsolvated in DMF, merely that solvation through hydrogen bonding is much stronger. Large variations in a_N occurred only when the solvent was capable of acting as a proton donor and when the radical could act as an acceptor: compare, for example, the effect of adding water to acetonitrile solutions of the anthracene and nitrobenzene anions.[48]

Attempts have been made to correlate observed changes in hyperfine splitting constants with various parameters measuring solvent polarity. (Here solvent polarity is taken as the sum of all molecular properties responsible for all the interaction forces between solvent and solute molecules).[24] The dielectric constant or relative permittivity, ε , has frequently been employed in this respect. The ascendency of ε over other criteria is due to the simplicity of electrostatic models of solvation. However, ε is a macroscopic property of the bulk solvent, representing the ability of a solvent to separate charge and to orient its dipoles. The dielectric constant has been demonstrated experimentally[24] to be an unsuitable measure of molecular-microscopic interactions. It is for this reason that attempted correlations of e.s.r. parameters with ε have been of very limited success.[21,50-52]

The failure of the solvent dielectric constant to represent most solute-solvent interactions has led to the definition of polarity in terms of empirical parameters.[24] One commonly employed is the Kosower Z-value.[53] Kosower used the longest wavelength intermolecular charge-transfer transition of 1-ethyl-4-methoxycarbonyl-pyridinium iodide as a model process to establish a comprehensive scale of solvent polarity. This transition gives rise to a uv/visible absorption band which exhibits a pronounced change in position with a change in the polarity of the medium. The Z-value is defined as the molar transition energy,[*] E_T, expressed in kcal mol^{-1}, for the charge transfer absorption band in this compound in the appropriate solvent according to the equation:

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[*] The choice of kcal mol^{-1} as the unit for the Z scale is due to the usefulness of Z for comparison with chemical reactions and their activation energies. It has been widely reported in the literature and therefore conversion into kJ mol^{-1} has not been carried out to avoid confusion.

$$E_T\,(\mathrm{kcal\ mol^{-1}}) = h\,c\,\bar{\nu}\,N = 2.859 \times 10^{-3}\,\bar{\nu}\,(\mathrm{cm^{-1}}) = Z \qquad \text{...Eq. 9}$$

$\bar{\nu}$ is the wavenumber of the photon producing the electronic excitation.

A Z-value of 83.6, for example, for methanol means that a transition energy of 83.6 kcal is necessary to bring one mole of the standard dye, dissolved in methanol, from the electronic ground state (which is an ion-pair) to the first excited state (which is a radical pair). The stronger the stabilising effect of the solvent on the ground state ion-pair as compared with the less dipolar radical pair in the excited state, the higher is the transition energy and, therefore, the Z-value. A high Z-value corresponds to high solvent polarity.

The Dimroth Reichardt polarity parameter[54] $E_T(30)$ is based on the transition energy for the longest-wavelength solvatochromic* absorption band of a pyridinium N-phenoxide betaine dye. The $E_T(30)$-value for a solvent is the transition energy of the dissolved betaine dye, measured in kcal mol^{-1}. The extraordinarily large solvent-induced shift of the solvatochromic absorption band makes this parameter a particularly sensitive characterization of solvent polarity, the most comprehensive empirical scale yet developed.

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* The term solvatochromism is used to describe the pronounced change in position (and sometimes intensity) of a uv/visible absorption band accompanying a change in the polarity of the medium.

It has been found[21,50] that a_N for a series of pyrrolidinyl and piperidinyl radicals is linearly related to the Z-value, but not to the dielectric constant of the medium. In N-t-butyl-N-phenyl nitroxide[50] a_N is a linear function of the same parameter. An e.s.r. investigation of alkylnitroxides[55] explained the solvent dependence of the ratio of the nitrogen and proton splitting constants in t-butyl nitroxide on the basis of mesomeric contributions to the structure of the radical, and demonstrated that the variation of a_N/a_{NH} is a linear function of the E_T value. Studies of the same radical in mixed aqueous solvents[51] revealed a linear correlation of both a_N and a_{NH} with the dielectric constant, ε , provided that ε was not too low.

No satisfactory correlation of the coupling constants with the Z-factor of the solvent was detected[56] for monoprotonated durosemiquinone. By contrast, correlations have been found[56,57] for $a(^{13}C)$ and $a(^{17}O)$, even in p-benzosemiquinone; in this radical a_H is invariant[58] as the solvent is changed, a change of spin density at one carbonyl group being exactly balanced by a change in the second. For 2,6-di-substituted benzosemiquinones,[58,59] on the other hand, a plot of the change in coupling against Z is only poorly correlated, the scatter with other solvent polarity parameters being greater. The poor correlation indicates that opposing factors are involved. For these radicals monoprotonation and cation binding occur almost exclusively at the oxygen remote from the substituents.[58-60] It is likely, therefore, that solvation is also asymmetric, making the ring protons far more sensitive to change. A more theoretical treatment of this problem[61] has shown that the sensitivity results from a combination of the molecular asymmetry and an asymmetric solvation. The major additional factor for 2,6-disubstituted radicals compared with other semiquinones is considered to be steric,[58] bulky solvent molecules giving a greater differential solvation than smaller ones. Alternatively, it is possible that ion-pairing with the alkylammonium salts used as supporting electrolytes in the generation of the radicals is responsible for the scatter in the observed plot.[60]

The effect of the ion-pairing of nitrobenzene anions to tetra-n-butylammonium ions[33] resembles that of added DMF, and is primarily a consequence of the gradual displacement of protic molecules by the cation. Solvent induced perturbations of anions may be as great, or greater, than those induced in ion-pairs by cations.[33] This appears to be a general conclusion: the local effects of hydrogen bonding are capable of outweighing the coulombic effects of a partially-solvated cation.

The nitrogen hyperfine splitting constant of the nitroxide functional group has recently been proposed[52] as a solvent polarity parameter. Parameters currently employed may be divided into two classes: (a) those not involving a model reaction and which do not probe the solvent at a molecular level (i.e. in the cybotactic region, the volume around a solute molecule in which the order of the solvent molecules has been affected by the solute), and (b) those involving a model reaction and probing the solvent at the molecular level. The dielectric constant and dipole moment are parameters of type (a), while class (b) is typified by the Z-value[53] or $E_T(30)$[54] parameter. The nitrogen hyperfine splitting constants of di-t-butyl nitroxide, 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy represent a solvent polarity parameter in which the nitroxide functional group is used as a non-model, cybotactic probe. The correlation between a_N and parameters of type (b) is good, whereas that with type (a) is generally poor. As a_N is easily determined in more than thirty solvents it may prove a useful empirical measure of polarity, particularly in cases where the other parameters are difficult to determine.

The largest variations in hyperfine splitting constants with solvent yet detected occur in the neutral 4-acetyl-1-methyldihydropyridyl radical.[62] Changes are of the order 300-400%, compared with approximately 50% for some nitroxides.[20,52] These results have been explained in terms of the relative contributions of the various nonpolar and dipolar mesomeric structures which can be written down for this species.

The solvent dependence of the g-value was first reported in 1964 when Zandstra[18] observed the change in this parameter for p-benzosemiquinone in DMSO from its value in water. For pyrrolidinyl and piperidinyl radicals,[21] also, the g-factors vary with the solvent polarity. Relative to its value in carbon tetrachloride the g-factor of 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO) decreases[22] in hydrogen bonding solvents, and the hyperfine structure of the radical is also altered. For 2,2,6,6-tetramethyl-4-piperidone-N-oxide (OTEMPO) the isotropic ^{17}O and ^{14}N hyperfine splittings are solvent dependent,[23] as is the g-value.

Linewidth studies have been used to investigate solvent effects on a new series of cyclic nitroxides: imino, amidino and carbamoyl nitroxides.[63] Halogen nuclear quadrupole coupling in the e.s.r. spectra of imino nitroxides enabled the effects of solvent on rotational correlation times to be determined. In cases where coupling to the halogen was observed the linewidth was proportional to the rotational correlation time, and an empirical dependence of the rotational correlation time on the solvent was found. In 2-Br-4,4,5,5-tetramethylimidazoline-1-oxyl and the corresponding iodo- compound, a_N exhibits a small solvent dependence while coupling to the halogen nuclei is solvent independent.[63]

Linewidth measurements were also used in considering solvent effects on the spectra of the two nitroxides TEMPO and OTEMPO.[23] A distinction was made between a uniform broadening induced by spin-rotation relaxation and an asymmetric broadening due to modulation of the $\underline{g}$ and $\underline{a}$ tensor components by the rotational motion. Similar studies were carried out on di-t-butylnitroxide,[64] but for this radical it was more useful to concentrate on changes in a_N.

E.s.r. has been used to measure the enthalpy of hydrogen bonding. Stevenson and co-workers generated the nitrobenzene anion by lithium reduction in HMPA,[65-68] a method which ensures that the radical is obtained essentially free from solvation and counter-ion interactions. Addition of proton donors such as water, ethanol or t-butanol to this system sets up an equilibrium between hydrogen bonded HMPA plus the free nitrobenzene and free HMPA plus hydrogen bonded nitrobenzene. The equilibrium constant for this reaction is algebraically related to the nitrogen hyperfine coupling constant of the radical. The observed value of a_N increases smoothly upon addition of the proton donor, indicating that a_N is a time-average between the values in the free and hydrogen bonded ion. As more proton donor is added to the solution the concentration of the time-averaged species increases at the expense of the ion pair. Clearly, then, hydrogen bonding stabilises the formally free ion relative to the ion-pair. The results demonstrate that the concentration of hydrogen bonded HMPA is much greater than that of the hydrogen bonded ions.[68] Similarly, the enthalpy of hydrogen bonding was estimated using methylacetylene[65] and methanol[69] as donors for several p-substituted nitrobenzene anions. In the latter case, when the data was subjected to a Hammett[70] type correlation, a linear relationship was found between the equilibrium constant and the Brown[71] σ^+ substituent constant.

Previous Magnetic Resonance Studies of Solvent Interactions

B. N.M.R.

Broadly speaking, solvent effects on n.m.r. spectra may be divided[10,24] into two classes: specific and non-specific. The general equation[79,80] for the shielding, σ, of a nucleus in some medium is:

$$\sigma = \sigma_g + \sigma_b + \sigma_a + \sigma_w + \sigma_E + \sigma_c \qquad \text{...Eq. 10}$$

The term σ_g is the gas-phase shielding. The bulk susceptibility shift, σ_b, arises when an external standard is used. It is due to bulk susceptibility differences of the solution and reference samples. Its magnitude depends on the shape of the sample, and it is zero for a spherical sample or by use of an internal reference. σ_a is derived from any non-zero averaging of magnetic anisotropies of the solvent molecules, and is significant, say, for disc-shaped molecules of aromatic solvents. The van der Waals term, σ_w , is always present in the liquid phase, while σ_E is the so-called reaction field term,,sometimes considered with σ_c. It is extremely difficult to distinguish between these non-specific effects, but numerous attempts have been made at calculating and describing these five quantities.[8,81-3]

In Eq.10 σ_c accounts for specific solute-solvent interactions and is the only structurally significant shift. It is the only term of real chemical significance. The most important specific solvent effects on the resonance positions of the nuclei of dissolved compounds give rise to hydrogen bonding shifts or aromatic solvent-induced shifts (ASIS effects).[8,81,84] In these cases the interactions between the solute and the surrounding solvent molecules lead to molecular species which are more or less definable entities.

Since the discovery, in 1951, that protons involved in hydrogen bonds experience large shifts in their resonance signals[85] the behaviour of proton chemical shifts, as affected by hydrogen bond interactions, has been widely studied and thoroughly reviewed.[8,10,81,82,84,86] There is a general observation that the magnitude of the change in the proton chemical shift which occurs when a hydrogen bond is formed is related to its strength. However, in view of the various non-specific effects which can occur care must be taken in attributing all shifts to structural effects. It has been suggested[3] that for medium shift studies it may be wiser simply to use the shift to provide empirical information about the system, rather than attempting a detailed explanation of the physical sources of the shift.

N.m.r. has frequently been employed in the study of ion-solvent interactions,[2,3,10,87] and has yielded information concerning the nature of the bonding involved,[88] association constants and chemical shifts for 1:1 ion-solvent complexes,[89,90] and ionic solvation numbers.[2,3,87]

Just as with e.s.r. studies, correlations of chemical shifts with mole fraction (MF) composition of one solvent in mixed aqueous solution have been observed: for example, a linear correlation of caesium fluoride ^{19}F shifts has been detected[91] in aqueous methanol and in aqueous DMF. This behaviour implies a smoothly changing statistically controlled variation of the solvation shell with solvent composition. Correlations with the Z-value[53] of the solvent have also been observed, as in the case of ^{7}Li shifts in binary solvent mixtures.[92]

There have been relatively few studies in which n.m.r. has been applied specifically to the study of binary solvent mixtures. One study[93] of ternary aqueous solutions employed bis(methylsulphonyl) methane, $(CH_3SO_2)_2CH_2$, as a probe for solute-solvent interactions in the H_2O-DMSO system. For each ternary mixture the behaviour of the water resonance was given as a function of solvent composition, and it was shown that the trends were not affected by the presence of the probe. The position of the water resonance at various mole fractions of water is linearly correlated with data[94] for the free enthalpies of transfer of a series of solutes (such as acetone) from water to the corresponding H_2O-DMSO mixtures. In a study of the solvation of Ag(I) in binary solvent mixtures[95] the influence of solvent-solvent interactions on solvation processes is demonstrated, and evidence presented which may be interpreted in terms of the formation of a complex between methanol and DMSO.

In a study[96] of the pure solvents, the position of the

-OH resonance in DMSO was found to be almost independent of concentration below 25 mole% for ethanol, methanol, 2-propanol and *t*-butanol. Aqueous alcoholic solutions have received much attention.[97-100] Alcohols cause an initial downfield shift in the hydroxyl proton resonance, whereas most organic compounds induce an upfield shift. Various explanations have been offered, but the shift is a combined one[101] since exchange between water and alcohol is fast in the water-rich region. Separate -OH resonances have been resolved for *t*-butanol in water[102] at low temperatures and this has confirmed the occurrence of initial downfield shifts. A fairly extensive study of the behaviour of the hydroxyl proton resonance in mixtures of ethanol and water[103] concentrated on the chemical shift and linewidth over the entire mole fraction range. No single molecular mechanism could be invoked to encompass the whole range of observations. At $MF_{EtOH} < 0.08$ there is a "structure making" effect, leading to increased water self-association. As the amount of ethanol increases, the alkyl groups seem to hinder the ability of the water to form three-dimensional associated structures, and at higher concentrations still it appears that the water molecules co-ordinate to, or are incorporated into, the linear ethanol hydrogen bonded aggregates.

Small downfield shifts in the water proton resonance on adding basic aprotic solvents such as acetone or tetrahydrofuran(THF)[98,104] were interpreted in terms of "structure making".[104] Shifts for aprotic solutes were divided into "polar" and "non-polar" effects,[98] but the structures envisaged in the polar effect were not detailed and the way in which the proton shielding was affected was not specified. Aqueous solutions of ammonia[105] and amines[106] exhibit shifts in ^{1}H, ^{15}N and ^{13}C resonances which are largely controlled by hydrogen bonding to the nitrogen lone pairs. The ^{1}H and ^{13}C signals observed in aqueous solutions of amides[107] exhibit very complex concentration shifts for which no clear explanation has yet been advanced.

An n.m.r. investigation[13] of aqueous mixtures of formamide, N-methylformamide and N,N-dimethylformamide (DMF) over the entire concentration range revealed the existence of extensive solvent interactions. In each case, the water resonance signal was displaced to a higher frequency upon dilution with an amide, due to a decrease in the hydrogen bonding known to exist in pure water. The upfield shift is most noticeable with DMF, in which only the carbonyl oxygen and the nitrogen free electron pairs are available as sites for possible interaction with water, whereas the other solvents have protons bonded to nitrogen. The methyl resonance signals of DMF shift equally in water and carbon tetrachloride, indicating that no appreciable interaction occurs at nitrogen; the predominant site for hydrogen bonding between the substituted amides and water, therefore, appears to be the carbonyl oxygen.

On adding basic aprotic solvents such as DMSO or DMF,[108] little change or a small downfield shift of the water signal occurs in the water-rich region ($MF_{H_2O} \geqslant 0.95$). As more DMF or DMSO is added an upfield shift is observed, which is a function of the basicity of the solvent. This study concentrated chiefly on the $MF_{H_2O} \geqslant 0.95$ range as specific water structure effects are expected only in the water-rich region, when the medium still resembles bulk water. The region of insensitivity is explained in terms of the scavenging of the free OH groups (detected by overtone infra-red spectroscopy) which results when hydrogen bonding to the base occurs. (By a free OH group is meant[109] the unbound -OH group which remains when water molecules form only three hydrogen bonds). On the basis of both n.m.r. and infra-red experiments it has been concluded that free -OH groups play an important rôle in the dissolution of aprotic solvents in water, and that the presence of these groups is largely responsible for the high solubility of weakly basic species.

Proton spin-lattice times (T_1) of water and DMSO in H_2O-DMSO mixtures at 9.8-41.4 °C exhibit minima near MF_{H_2O} =0.65.[110] The depth of the minimum increases as the temperature is lowered. Over the range -60-45 °C the proton chemical shifts of water with reference to DMSO move to higher field as the temperature is raised. This temperature dependence is considerably affected by changes in the composition, as when the concentration of DMSO is increased, the signal moves to higher field. The experimental evidence is consistent with the presence of strong intermolecular interactions.

The intra- and inter-molecular contributions to the proton spin-lattice relaxation rate ($1/T_1$) for the methyl and -OH groups of methanol as well as for DMSO in MeOH-DMSO mixtures were determined[111] as a function of composition at 0-41.4 °C. From the intermolecular contributions to $1/T_1$ the distances of closest approach between two groups for various intermolecular interactions were evaluated. The order of magnitude in the interactions were evaluated. The order of magnitude in the equimolar and methanol-rich mixtures is OH-OH > OH-DMSO > Me-DMSO ≈ Me-Me. In the DMSO-rich mixtures the order changes to: OH-DMSO ⪆ OH-OH > Me-DMSO > Me-Me, implying a distinct change in liquid structure with composition.

4. The Gendell-Freed-Fraenkel Model:[1] The Effects of Solvent Interactions on E.S.R. Spectra

A. Qualitative Treatment of Solvent Effects

Gendell, Freed and Fraenkel[1] have proposed a simple theory to account, both qualitatively and quantitatively, for the solvent dependence of the hyperfine splittings of organic free radicals such as those presented in a previous section, (Section 3.A). In this model it is assumed that the most important radical-solvent interactions occur at substituents such as a nitro-group, a carbonyl oxygen or at hetero atoms. Experimentally, by far the most significant changes in e.s.r. spectra occur when the solvent can form hydrogen bonds to some specific site in the radical. This theory (G.F.F. theory) is based on the fact that radical-solvent interactions induce a polarization of the π-electron charge and spin density distributions and, consequently, the hyperfine splittings vary to an extent which is governed by the strength and nature of the radical-solvent complex formed. For a particular nucleus, the solvent variation of the coupling constant will depend on the location of the nucleus in the radical, and on the relationship between spin density and the hyperfine splitting for that nucleus.

For π-electron radicals, the isotropic hyperfine splittings for protons bonded directly to a carbon atom in the π-system are linearly related to the π-electron spin density on that carbon atom (Eq. 8). When primary solvent interactions result in the formation of a localised complex with a polar substituent or heteroatom, the influence of this substituent is modified by the solvent, and the modification transmitted through the π-system, leading to a change in proton splittings. Most solvent interactions do not cause a great alteration of the substituent effects, except in the case of strong specific interactions such as the conversion of $-O$ to $-OH$ or $-NH_2$ to $-NH_3$ on increasing the acidity of the solvent. Therefore, only small changes in the magnitudes of proton splittings are anticipated under normal conditions. Some positions of small spin density can, however, demonstrate large fractional changes in coupling constant with solvent.

For nuclei such as ^{14}N or ^{13}C the prediction of the isotropic hyperfine splitting is more difficult.[5] Experimental ^{13}C splittings, for example, are not simply proportional to the π-spin density on the same carbon atom: it is necessary to consider contributions from the π-spin densities on neighbouring atoms. The splitting arising from a ^{13}C nucleus at the carbonyl position is given[112] by the equation:

$$a_1^C = S^{C_1} + (2Q^{C_1}_{C_1C_2} + Q^{C_1}_{C_1O})\rho_1^\pi + Q^{C_1}_{C_2C_1}(\rho_2^\pi + \rho_{2'}^\pi) + Q^{C_1}_{OC_1}\rho_O^\pi \qquad \text{...Eq. 11}$$

where 1 is the carbonyl carbon atom, 2 and 2' are the two carbon atoms to which it is bonded and O is the oxygen atom; ρ_1^π and ρ_2^π are the π-electron spin densities on atoms 1 and 2 respectively; S^{C_1} gives the contribution to the splitting from the 1s electrons of atom C_1, the Q values give the contribution of the 2s electrons, where, for example, $Q^{C_1}_{OC_1}$ is the parameter for the nucleus of atom C_1 resulting from the interaction between the bond C_1O and the π-electron density on atom O. The analogous equation for the nitrogen splitting in a nitro-group is,

$$a_N = (S^N + 2Q^N_{NO} + Q^N_{NC})\rho_N^\pi + 2Q^N_{ON}\rho_O^\pi + Q^N_{CN}\rho_C^\pi \qquad \text{...Eq. 12}$$

where N and O are the nitrogen and oxygen atoms of the nitro-group and C is the carbon atom to which the nitro-group is bonded.

By analogy with the $>\dot{C}H$ fragment (Fig. 3), some of the Q values in Eqs. 11 and 12 are expected to be positive and others negative. The presence of large terms, opposite in sign, but of comparable magnitude in these equations is significant in determining the degree of solvent effects, as small variations in spin densities can cause appreciable changes in the splittings. There is a large solvent variation in the ^{14}N splitting in an $-NO_2$ group, or of the ^{13}C splitting of a carbonyl group, because the oxygen atoms are probably the most directly affected by solvent interactions. Bonding of cations or protic solvent molecules to the oxygen atoms pulls negative charge from the oxygen, increasing the spin density on the nitrogen or carbon atom. Therefore, although the alteration of the π-electron density of the oxygen atom may be large, this change may be compensated by large changes in the spin density of the nitrogen or carbon atom bonded to the oxygen, so that only small changes in spin density occur throughout the rest of the molecule.

This is precisely the situation for semiquinone anions: the ring protons are effectively "buffered" against solvent effects.[113] In an isolated anionic carbonyl group, $R_2C \doteq O^-$, hydrogen bonding to oxygen tends to stabilise the form $R_2\dot{C}\text{-}O^- \cdots HA$, thereby forcing the unpaired electron more on to carbon. This produces an increase in $a(^{13}C)$ and a corresponding decrease in a(^{17}O).[42,56,57] For most semiquinones the solvent interacts to stabilise the negative charge equally on both carbonyl groups. Therefore, the ring proton hyperfine coupling is effectively "buffered" and normally relatively insensitive to changes of solvent, except in the case of the asymmetrically-solvated 2,6-disubstituted benzosemiquinones.[58-61]

B. Quantitative Treatment of Solvent Effects

Consider a radical, R, such as the nitrobenzene anion radical, with a single functional group. It is assumed that the radical forms relatively stable 1:1 complexes with each of two pure solvents, S_1 and S_2; the structures of the complexes are represented as RS_1 and RS_2, and these are the predominant species in mixtures of the two solvents, having assumed that the only significant solvent interactions take place in the vicinity of the functional group. The radical species will exchange solvent molecules according to Eq. 13.

$$RS_2 + S_1 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} RS_1 + S_2 \qquad \text{...Eq. 13}$$

Generally, the hyperfine splitting caused by a particular nucleus in RS_2 (a_2) will differ form that due to the same nucleus in the complex RS_1 (a_1). For slow exchange the observed spectrum will contain both splittings a_1 and a_2. For fast exchange the lifetimes of the radical species, τ , are short compared to the differences in hyperfine splittings:

$$\tau \ll (\gamma\,|a_1 - a_2|)^{-1} \qquad \text{...Eq. 14}$$

where γ is the magnetogyric ratio of the electron, and only a single averaged splitting, $\bar{a}$, of the appropriate value is observed:

$$\bar{a} = P_1 a_1 + P_2 a_2 \qquad \text{...Eq. 15}$$

P_1 and P_2 are fractions of the total amount of radical in the forms RS_1 and RS_2, respectively, and may be expressed in terms of the lifetimes of RS_1 (τ_1) and RS_2 (τ_2):

$$\tau_1 = \frac{1}{k_1[S_2]} \qquad \text{...Eq. 16}$$

$$\tau_2 = \frac{1}{k_2[S_1]} \qquad \text{...Eq. 17}$$

P_1 and P_2 are, in turn, related to the equilibrium constant, K, for the exchange process (Eq. 13) by Eqs. 18 and 19.

$$P_1 = \frac{\tau_1}{\tau_1 + \tau_2} = \frac{Kx}{1 + Kx} \quad \text{...Eq. 18}$$

$$P_2 = \frac{\tau_2}{\tau_1 + \tau_2} = \frac{1}{1 + Kx} \quad \text{...Eq. 19}$$

The equilibrium constant is given by the expression:

$$K = \frac{k_2}{k_1} = \frac{[RS_1][S_2]}{[RS_2][S_1]} = \frac{[RS_1]}{x[RS_2]} \quad \text{...Eq.20}$$

where the ratio of solvent concentrations, $\frac{[S_1]}{[S_2]}$, is denoted x. Eq. 15 gives an adequate description in the limit of small concentrations of one solvent, say S_1, even though τ_2 becomes large, because the relative amount of RS_1 then becomes too small to make a measurable contribution to the spectrum.

Substituting for P_1 and P_2 (Eqs. 18 and 19) in Eq. 15 yields Eqs. 21 and 22:

$$\bar{a} = \frac{(a_1 + a_2)}{2} + \frac{(Kx-1)(a_1 - a_2)}{2(Kx+1)} \quad \text{...Eq. 21}$$

$$K = \left(\frac{a_2 - \bar{a}}{\bar{a} - a_1}\right)\frac{}{x} = \left(\frac{a_2 - \bar{a}}{\bar{a} - a_1}\right)\frac{[S_2]}{[S_1]} \qquad \text{...Eq. 22}$$

A plot of Eq. 21 (as $2\delta\bar{a} = \dfrac{2[\bar{a}-(\frac{1}{2})(a_1+a_2)]}{(a_1-a_2)}$ against x) is of the same form as that noted, for example, in studies of the nitrobenzene anion.[38,39] There is a rapid increase in the splitting $\bar{a}$ from the value a_2 in pure solvent S_2 ($x=0$) as small amounts of S_1 are added and, at larger concentrations of S_1, the splitting approaches the limiting value a_1 asymptotically. Large values of K correspond to the situation in which the complex with S_1 is considerably stronger than that with S_2.

Eq. 15 may be generalised if all the species RS_1, RS_2 and R, or even other species involving more than one solvent molecule, are important. In the limit of fast exchange, the general equation is:

$$\bar{a} = \sum_i P_i a_i \quad , \quad \sum_i P_i = 1 \qquad \text{...Eq. 23}$$

Radicals such as benzosemiquinones or dinitrobenzene anions have two functional groups capable of complex-formation with the solvent. In a pure solvent the singly solvated species has a lower symmetry than the doubly or unsolvated radical.

Also, the two possible forms of singly solvated species are not equivalent. If exchange rates are slow, therefore, two different splittings are expected from a particular nucleus, corresponding to each of the two singly solvated complexes. However, this inequivalence is averaged out in the fast exchange region; this follows from Eq. 23 and the fact that the concentrations of asymmetric species are always equal.

The averaging effects of fast exchange also explain why hyperfine splittings are not normally observed from solvent nuclei, even though strong solvent-radical complexes may be formed. If the lifetime of the complex, τ, is short, such that $\tau(\gamma a_S^H) << 1$, where a_S^H is a splitting from the solvent proton, the environment of the unpaired electron changes rapidly from one in which solvent protons are of spin $+\frac{1}{2}$ to one in which they are of spin $-\frac{1}{2}$, and hence the splitting is averaged to zero. Conversely, the observation of alkali-metal hyperfine splittings implies that ion-pairs are relatively long-lived. The lifetime of the complex must be greater than or comparable to the reciprocal of the splitting (expressed as a frequency), i.e. $\tau \gg (\gamma a_H^S)^{-1}$, and the splitting must be greater than or comparable to the linewidth.

Data for the ^{13}C splitting from the carbon atom at the carbonyl position in p-benzosemiquinone[1,42] does not comply with Eq. 21, and this has been attributed[1] to the presence in this radical of two functional groups which can complex with the solvent. However, $a(^{13}C)$ does vary monotonically with the solvent ratio, and the data is consistent with the appropriate form of Eq. 23 for the case of a radical with two functional groups. This study did not represent an adequate test of Eq. 22, though, as the limiting values of a(^{13}C) for pure water or pure ethanol was not known.

C. Quantitative Studies Employing the G.F.F. Model

The G.F.F. model was not applied by the authors to their own experimental data due to the small changes observed: the largest variation in a_H was ±0.247 G. A further difficulty was created as the protic hyperfine splittings were, in fact, determined in water-ethanol mixtures rather than in either of the pure solvents; thus three-solvent systems were considered rather than binary mixtures. Since the appearance of this model it has largely been neglected. Little quantitative work on the competition between solvents for a radical has been reported, despite the numerous qualitative studies (Section 3A) on which the model might have been tested.

The first detailed quantitative test of the G.F.F. theory was made on fluorenone ketyl.[72] When generated in binary mixtures of ethanol or methanol with DMF the spectrum of the fluorenone anion depended critically on solution composition. The addition of small amounts of methanol to a DMF solution of the radical produced relatively large initial increases in three of the four coupling constants. Changes were more gradual at $MF_{\text{alcohol}} \geqslant 0.1$.

In mixed solvents the existing equilibrium involves solvated ketyl molecules and hydrogen bonded ketyl-alcohol adducts. To account for variations in the range $MF_{alcohol} = 0-0.1$, it was proposed that the two species had different hyperfine coupling constants, and that exchange of the alcohol was sufficiently rapid to produce an averaged spectrum. The variation of the spectrum at $MF_{alcohol} > 0.2$ could only be understood if splittings in the ketyl-alcohol adduct were solvent dependent, either on account of the formation of a 1:2 adduct or due to some more general solvent effect. It was this possible further generalised solvent effect which prompted the recent comment[24] that whereas the G.F.F. theory is qualitatively informative, its quantitative validity is somewhat limited.

The G.F.F. treatment was extended to two-centre solvation, specifically the dependence of the ^{13}C coupling constant, a_1^C, of p-benzosemiquinone-1-^{13}C on the composition of DMSO-H_2O and acetonitrile-water mixtures.[42] The ^{13}C splitting changed by a much larger amount than the proton coupling constant when water was added to DMSO ($\Delta a_H = 0.06$ G, $\Delta a_1^C = 2.37$ G). Three radical-solvent complexes were assumed to be in equilibrium :

$$S_2RS_2 + S_1 \overset{K}{\rightleftharpoons} S_2RS_1 \text{ (and } S_1RS_2\text{)} + S_2 \qquad \text{...Eq. 24}$$

$$S_2RS_1 \overset{K''}{\rightleftharpoons} S_1RS_2 \qquad \text{...Eq. 25}$$

$$S_1 + S_2RS_1 \ (\text{and } S_1RS_2) \overset{K'}{\rightleftharpoons} S_1RS_1 + S_2 \qquad \text{...Eq. 26}$$

S_1RS_2 and S_2RS_1 refer to complexes in which the solvent molecule S_1 is complexed with the labelled carbonyl and non-labelled carbonyl, respectively. It was assumed that K"=1 and that all equilibria were rapid, the single ^{13}C coupling constant then being given by,

$$\bar{a} = \frac{a_1 + Ka_2S + KK'a_3S^2}{1 + KS + KK'S^2} \qquad \text{...Eq. 27}$$

where $S=a_{S1}/a_{S2}$, the ratio of solvent activities; a_1, a_2 and a_3 are the coupling constants of S_2RS_2, the average of S_2RS_1 and S_1RS_2, and S_1RS_1, respectively. Eq. 27 may be simplified to:

$$\bar{a} = \frac{a_1(2+KS) + a_3(KS + 2KK'S^2)}{2(1 + KS + KK'S^2)} \qquad \text{...Eq. 28}$$

The possibility that the ion did not complex with the non-aqueous solvent was at first considered, since a_1^C in DMSO and acetonitrile are equal. However, quantitative agreement could not be obtained for either system if radical-aprotic solvent complexing was neglected.

Eq. 28 applied to all data obtained for p-benzosemiquinone-1-^{13}C in the H_2O-DMSO system, lending support to the G.F.F. theory and to the specific solvation model employed by Stone and Maki.[42] However, the model was unsuccessful in the treatment of results from the water-acetonitrile system; it is unclear whether this failure is due to an over simplification of the solvation model, or to uncertainties in activity measurements for these two solvents.

Pannell[77] successfully applied the G.F.F. model to the variation of the ^{14}N hyperfine splitting constants of diphenyl and p,p'-dianisyl nitroxide with solvent composition in mixtures of di-t-butylperoxide with t-butylperoxide. Despite this success, Gross and Symons[114] found that data for a number of p-substituted nitrobenzene anions[39,48] in H_2O-DMF mixtures were not well represented by Eq. 13, assuming as it does that a given radical forms a complex with just one solvent molecule and that there is simple exchange between the two possible solvated-radical structures in a mixed solution. The calculated equilibrium constants varied with solvent composition, leading to the conclusion that the model was applicable only when the two solvents had similar characteristics, and in the absence of complicating factors such as ion-pairing.

In a less simplistic approach, Gross and Symons[114] treated their results for these radicals in methanol mixtures in terms of a modified model. Since the nitro-anions should be preferentially solvated by methanol over the range studied ($MF_{MeOH} > 0.1$), the anion, complexed with one methanol molecule, was considered as a single unit; this model is mathematically equivalent to that of G.F.F. The actual number of methanol molecules retained by the anions in the mole fraction range covered is not, however, revealed by these experiments. For simplicity, one strongly bonded molecule has been considered but two or even more may be involved. The data suggest that the equilibrium shown in Eq. 29 is the only one figuring significantly.

$$K = \frac{(\bar{a} - a_{ab})}{(a_a - \bar{a})x} \qquad \text{...Eq. 29}$$

(Compare with Eq. 22 for G.F.F. model). The hyperfine splittings of the complexes R•MeOH and R•MeOH•S_b, where S_b is the non-hydroxylic solvent, are denoted a_a and a_{ab}, respectively. The average values of the equilibrium constants are all close to unity, indicating that, following the initial strong interaction further solvation is almost non-selective.

CHAPTER 2

EXPERIMENTAL

1. Generation of Radicals

Semiquinone radical anions were generated by autoxidation in alkaline media. High concentrations of p-semiquinones can be obtained from both the quinones or the hydroquinones under these conditions.[115] This apparent paradox results from the formation of secondary radical intermediates capable of reducing the quinones. In the present work, best e.s.r. spectra were obtained using the hydroquinones as precursors. When the quinones were used lines were less sharp due to exchange broadening.

In a typical experiment approximately 0.05 millimoles of a dihydroxy-compound were dissolved in 5 cm^3 of solvent of the required composition. The solution was then made alkaline by the addition of sodium methoxide, a base sufficiently soluble in pure aprotic solvents such as HMPA to provide a suitable concentration of semiquinone. In the case of o-semiquinones the base used was potassium t-butoxide, to ensure that the spectral lines were not further split by coupling with a sodium counter-ion. The resulting solution was shaken well in the air and transferred immediately to an aqueous cell in the cavity of an e.s.r. spectrometer.

The radicals were found to be most stable in HMPA and least stable in pure ethanol, in which the semiquinones are highly susceptible to attack by alkoxy ions.[116] In all cases, however, the lifetimes were such that a static, rather than a flow system, could be employed. In some instances an induction period elapsed before a sufficient concentration of radical was built up. Spectra determined in the pure aprotic solvents DMSO, DMF and HMPA generally exhibited broader lines than their aqueous counterparts; the increased viscosity of these solutions broadens the lines *via* anisotropy effects caused by a reduced tumbling rate.

To study the effects of solvation on the e.s.r. spectrum of a particular radical an experimental run was carried out as follows. Solvents were dried as detailed in Table 2, and used immediately in the preparation of binary solvent mixtures. The solvent systems investigated were: H_2O-HMPA; H_2O-DMF; H_2O-DMSO; H_2O-EtOH; EtOH-HMPA; EtOH-DMF and EtOH-DMSO. For a given system, H_2O-HMPA, for example, a series of mixtures were made up by weight fraction. These mixtures, usually about thirty in number, covered the complete range pure water to pure HMPA. The radical concerned was then generated, by the usual autoxidation method, in each solution in turn. Thus at least thirty different spectra were obtained for the radical in each solvent system. To minimise random errors spectra, including those in the pure solvents, were recorded in a single run. For radicals selected for detailed study (Ch. 4) at least three runs were carried out to ensure reproducibility.

2. Materials

Most of the required dihydroxy-compounds were commercially

Table 1: Commercial Materials Used Without Further Purification

1,2,4-benzenetriol
catechol (1,2-dihydroxybenzene)
2,5-di-t-butylhydroquinone
2,3-dichloro-5,6-dicyano-1,4-benzoquinone
2,3-dicyanohydroquinone
2,6-dihydroxynaphthalene dihydrate
2,3-dimethoxyhydroquinone
2,3-dimethoxy-5-methylhydroquinone
hydroquinone (1,4-dihydroxybenzene)
3-isopropylcatechol
3-methoxycatechol
2-methoxyhydroquinone
3-methylcatechol
4-methylcatechol
tetrafluoro-1,4-benzoquinone
thymohydroquinone (2-methyl-5-isopropylhydroquinone)
toluhydroquinone (2-methylhydroquinone)
1,2,3-trihydroxybenzene (pyrogallol)
1,4,5-trihydroxynaphthalene (juglone)
trimethylhydroquinone

potassium t-butoxide
sodium dithionite
sodium methoxide

acetone
1-butanol
t-butanol
ethanediol
formamide
methanol
1-propanol
2-propanol
sulpholane (tetrahydrothiophen-1,1-dioxide)

Table 2: Purification of Commercial Materials

Compound	Method	Physical Data
t-Butylhydroquinone	Recrystallised from aqueous ethanol	Colourless needles, m.p. 127-129°
Hexamethylphosphoramide (HMPA)	Final traces of water removed by type 13X molecular sieve. Dried solvent stored over sieve.	b.p. 125-127/20 mm Hg (lit.[117] 127°/20 mm Hg, 233°/760 mm Hg)
Dimethylformamide (DMF)	Azeotropic distillation with benzene. Fraction boiling between 70-75° collected. Fractional distillation of residual solvent under reduced pressure.	b.p. of water-benzene azeotrope 68-74° (lit.[118] 69.4°) b.p. DMF 72-75° /38 mm Hg (lit.[119] 70°/30 mm Hg 76°/39 mm Hg)
Dimethylsulphoxide (DMSO)	Fractional freezing Liquid cooled to 5° and crystals filtered	f.p. 18-19° (lit.[118] 18.45°)
Ethanol	Treatment with magnesium[118] followed by distillation. Stored over type 4A molecular sieve.	b.p. 78.2-78.5° (lit.[118] 78.5°)

Table 3: Synthesis of Materials

Precursor	Method	Product and Physical Data
1. 9,10-Anthraquinone	Reduction of quinone by treatment with sodium dithionite ($S_2O_4^{2-}$ reduction)	9,10-Dihydroxyanthracene. Yellow-green needles, m.p.178° (lit.[119] 180°). Readily oxidised in moist air.
2. 2,6-Di-*t*-butyl 1,4-benzoquinone	$S_2O_4^{2-}$ reduction	2,6-Di-*t*-butylhydroquinone. White solid, slowly oxidised in air.
3. 4,5-Dimethoxy-1,2-benzoquinone	$S_2O_4^{2-}$ reduction	4,5-Dimethoxycatechol. White solid.
4. 2,6-Dimethoxy-1,4-benzoquinone, prepared as in Ref. 121; m.p. of unpurified material $234-240^{\circ}$ (lit.[122] 255°)	$S_2O_4^{2-}$ reduction	2,6-Dimethoxyhydroquinone. White crystals m.p. $146-151^{\circ}$ (lit.[122] 160°). Rapid darkening in moist air due to decomposition.
5. 2,3-Dimethoxy-5,6-dimethyl-1,4-benzoquinone (Aurantiogliocladin)	$S_2O_4^{2-}$ reduction	2,3-Dimethoxy-5,6-dimethylhydroquinone. White solid, m.p. 84° (lit.[119] 84°)

Cont.

Table 3 Continued:

Precursor	Method	Product and Physical Data
6. 2,6-Dimethoxyhydroquinone	As in Ref. 121, via intermediacy of 1,2,3,5-tetramethoxybenzene and 2-hydroxy-3,4,6-trimethoxyacetophenone	3,4,6-Trimethoxycatechol. Light brown solid from benzene, m.p. 78-80° (lit.[121] 82°).
7. 2,6-Dimethyl-1,4-benzoquinone, m.p. 70-71°(lit.[120] 72-3°) prepared by oxidation of 2,6-dimethylphenol[120]	$S_2O_4^{2-}$ reduction	2,6-Dimethylhydroquinone. White crystals from water. Readily oxidised in air. m.p. 149-151° (lit.[118] 153-4°)
8. 2-Hydroxy-3,4-dimethoxyacetophenone	Alkaline peroxide oxidation[121]	3,4-Dimethoxycatechol. Pale yellow oil, lit. b.p. 160-170°/20 mm Hg[121]
9. 2-Hydroxy-3,4-dimethoxy-6-methyl-acetophenone, m.p. 90-91°(lit.[121] 92°), prepared from 3,4,5-trimethoxytoluene.[121]	Alkaline peroxide oxidation[121]	3,4-Dimethoxy-6-methylcatechol. Pale orange crystals from light petroleum, m.p. 98-100° (lit.[121] 101°)

Cont.

Table 3 Continued:

Precursor	Method	Product and Physical Data
10. 6-Hydroxy-2,3,4-trimethoxyacetophenone	Alkaline peroxide oxidation[121]	3,4,5-Trimethoxycatechol. Red-brown oil.
11. 4,5-Methylenedioxy-1,2-benzoquinone, prepared by oxidation of 3,4-methylene -dioxyphenol	$S_2O_4^{2-}$ reduction	1,2-Dihydroxy-4,5-methylenedioxybenzene. Grey-brown solid, m.p.159-160° (lit.[123] 159°)
12. 1,4-Naphthoquinone	$S_2O_4^{2-}$ reduction	1,4-Dihydroxynaphthalene. White solid,m.p. 194° (lit.[118] 192°)
13. Tetramethyl-1,4-benzoquinone (Duroquinone)	$S_2O_4^{2-}$ reduction	Tetramethylhydroquinone. Colourless needles, m.p. 226° (lit[119] 233°, sintering at 220°)
14. 2,3,4-Trimethoxybenzaldehyde.	Hydrazine hydrate-potassium hydroxide reduction, followed by treatment with HBr.[117]	2,3,4-Trihydroxytoluene. Yellow solid, m.p. 142-3° (lit.[119] 140-141°)

Cont.

Table 3 Continued:

Precursor	Method	Product and Physical Data
15. 3,4,5-Trimethoxybenzaldehyde	As for 14	3,4,5-Trihydroxytoluene. Yellow solid, m.p. 119^{o} (lit.[119] 120^{o})
16. Tropolone (2-hydroxycycloheptatrienone)	Elbs persulphate oxidation[124]	5-Hydroxytropolone. Yellow solid, m.p. 245^{o} (lit.[124] 245^{o})

available and were used without further purification (Table 1). Materials listed in Table 2 were purified prior to use; no water signals were detected in the n.m.r. spectra of the dried solvents. Other compounds were synthesised by methods given in Table 3 and, where it was possible to ascertain, had physical constants in good agreement with those of the cited literature. Physical constants are not quoted for products 2,3,8 and 10, which were used immediately due to their considerable instability.

3. Instrumentation

E.s.r. spectra were recorded on a Varian E4 spectrometer, employing 100 kHz modulation, and operating at a fixed microwave frequency ca. 9.5 GHz with a linearly varied static magnetic field strength in the region of 3400 G (0.34 T).

N.m.r. spectra were obtained using a Perkin Elmer Model R12 60MHz spectrometer with tetramethylsilane (TMS) as an external standard. By adopting such a procedure the line positions depend on the volume susceptibility of the sample and are not a true measure of intramolecular shielding. This difficulty would have been eliminated had it been possible to find a suitable internal reference for the aqueous solutions under investigation. However, the magnitude of such a solvent effect as measured, for example, by the change in chemical shift of the methyl signal for HMPA with increasing water concentration (Ch. 5) is small in comparison with the shift of the water signal; for the purposes of this investigation it was considered negligible.

Spectra were recorded at sweep ranges of both 10 p.p.m. and 50 Hz, the proton chemical shift of water in aqueous mixtures being determined with greater accuracy by monitoring this resonance at a field sweep of 50 Hz. The water signal was offset downfield to appear between 550 and 600 Hz, thus expanding the scale in the region of interest.

CHAPTER 3

TREATMENT OF RESULTS

The results presented in this thesis have been analysed using a treatment adapted from the G.F.F. model[1] (Ch.1-4), and outlined below using data for 1,2-benzosemiquinone (radical II, Ch. 4) in the H_2O-HMPA system. This radical represents an adequate test of the validity of the method: o-semiquinones, while undergoing larger solvent-induced variations in hyperfine splittings, were less stable, in general, than the p-analogues. One of the most unstable radicals investigated was o-benzosemiquinone and this is reflected in the quality of the spectra (Fig. 4). The instability of the radical is demonstrated, moreover, by the presence of extra lines in the spectrum of II in pure DMF or DMSO; this triplet (1:2:1, a_H=0.64 G) has been attributed [125] to an o-semiquinone resulting from dimerisation. As a consequence, the error inherent in the measurement of the coupling constants of II is greater than in more favourable cases, and K known with correspondingly less accuracy.

Table 4 details the variation in the two e.s.r. parameters $2a_{3,6}$ and $2a_{4,5}$; twice the coupling constant has been measured in each case so that the maximum possible change has been recorded. The data from Table 4 is represented graphically in Fig. 5, a straightforward plot of the spectral parameters (p) against the molar ratio of solvents. Errors in the solvent composition function, x, are not represented on the figure, as these are not expected to be constant over the range pure water to pure HMPA: errors will be greatest when x is very

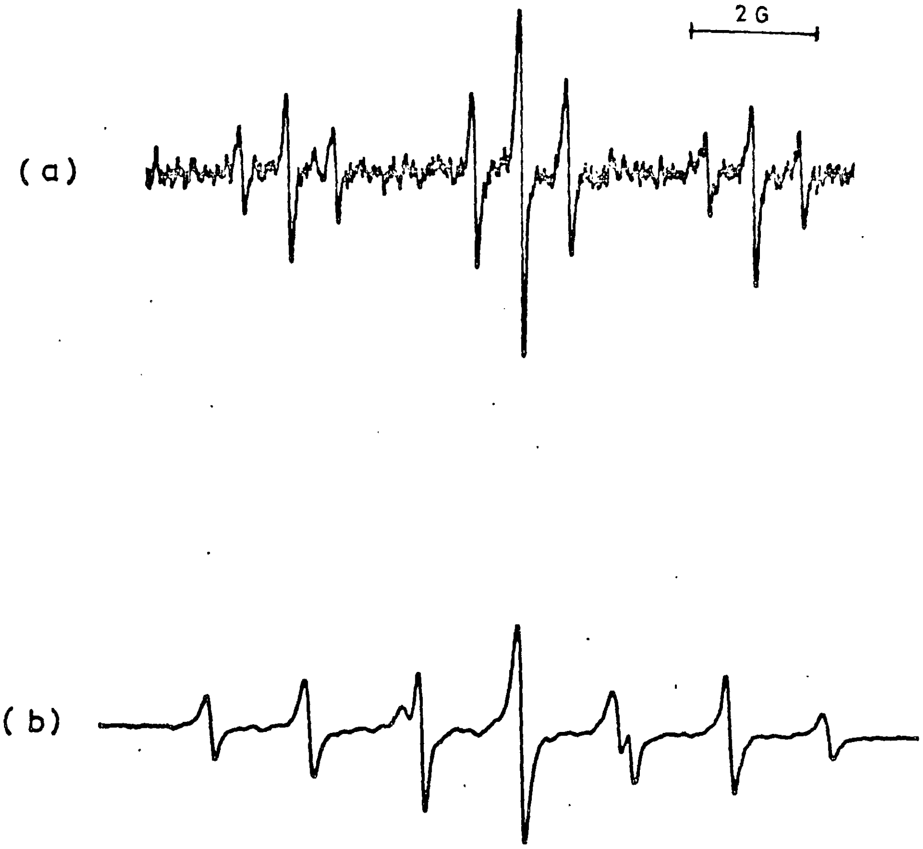


Fig. 4: E.s.r. spectra of 1,2-benzosemiquinone (radical II). (a) In water and (b) in HMPA.

Table 4: Variation of E.s.r. Parameters of 1,2-Benzosemiquinone in H_2O-HMPA Mixtures

$x=\frac{[H_2O]}{[HMPA]}$ ($x\pm0.01$)	$2a_{4,5}/G$ (±0.03)	$2a_{3,6}/G$ (±0.03)	log x	$\left\lvert\frac{1}{(\rho-\rho_1)}\right\rvert$	x^{-1}	$\left\lvert\frac{1}{(\rho-\rho_2)}\right\rvert$
H_2O	7.38	$\rho_1=1.50$				0.62
104.10	7.38	1.55	2.02		0.01	0.64
28.47	7.28	1.65	1.45		0.04	0.68
9.68	7.10	1.95	0.99		0.10	0.85
7.96	7.07	2.02	0.90		0.13	0.91
6.97	7.03	2.05	0.84		0.14	0.93
6.51	7.03	2.09	0.81		0.15	0.97
5.87	7.05	2.13	0.77		0.17	1.01
3.31	6.96	2.33	0.52		0.30	1.27
1.98	6.83	2.48	0.30	1.02	0.51	1.56
1.41	6.83	2.59	0.15	0.92	0.71	1.89
1.10	6.76	2.67	0.04	0.85	0.91	2.22
0.90	6.81	2.71	-0.05	0.83	1.11	2.44
0.58	6.75	2.85	-0.24	0.74	1.72	3.70
0.43	6.73	2.91	-0.37	0.71		
0.20	6.73	3.03	-0.70	0.65		
0.002	6.68	3.11	-2.70	0.62		
HMPA	6.68	$\rho_2=3.12$		0.62		

small (i.e. at the HMPA end) and when x^{-1} is very small (i.e. at the water end), so that less reliance may be placed on data obtained in these solutions. Graphical procedures are, therefore, generally less successful in the treatment of e.s.r. results from solutions at either extremity. However, over the range $0.01 \leqslant x \leqslant 10.00$ it is estimated that the total experimental error associated with x is ± 0.01, compared with ± 0.03 G for p.

Figure 5 is analogous to that presented with the G.F.F. model originally,[1] although in that work p was not plotted directly. This type of variation is predicted by the more general form of Eq. 22 (Ch.1-4,p.49) in which $\bar{a}$ has been replaced by p:

$$\left(\frac{p_2 - p}{p - p_1}\right)\frac{[S_2]}{[S_1]} = K \qquad \text{...Eq. 30}$$

For some radicals the greatest change with solvent composition is not that observed for a single coupling constant, but perhaps the sum of two or more individual coupling constants or even the total width of the spectrum. In such situations, Eq.30 may be applied, providing the most accurate determination of K possible.

From Eq.30, the equilibrium constant is given by the value of $[S_2]/[S_1]$ at which p is the mean of the two extreme values, p_1 and p_2. Fig. 5 shows this to occur at x=3.30, so that K is 0.30 for II in H_2O-HMPA ($S_1=H_2O$, S_2=HMPA, so that p_1 and p_2

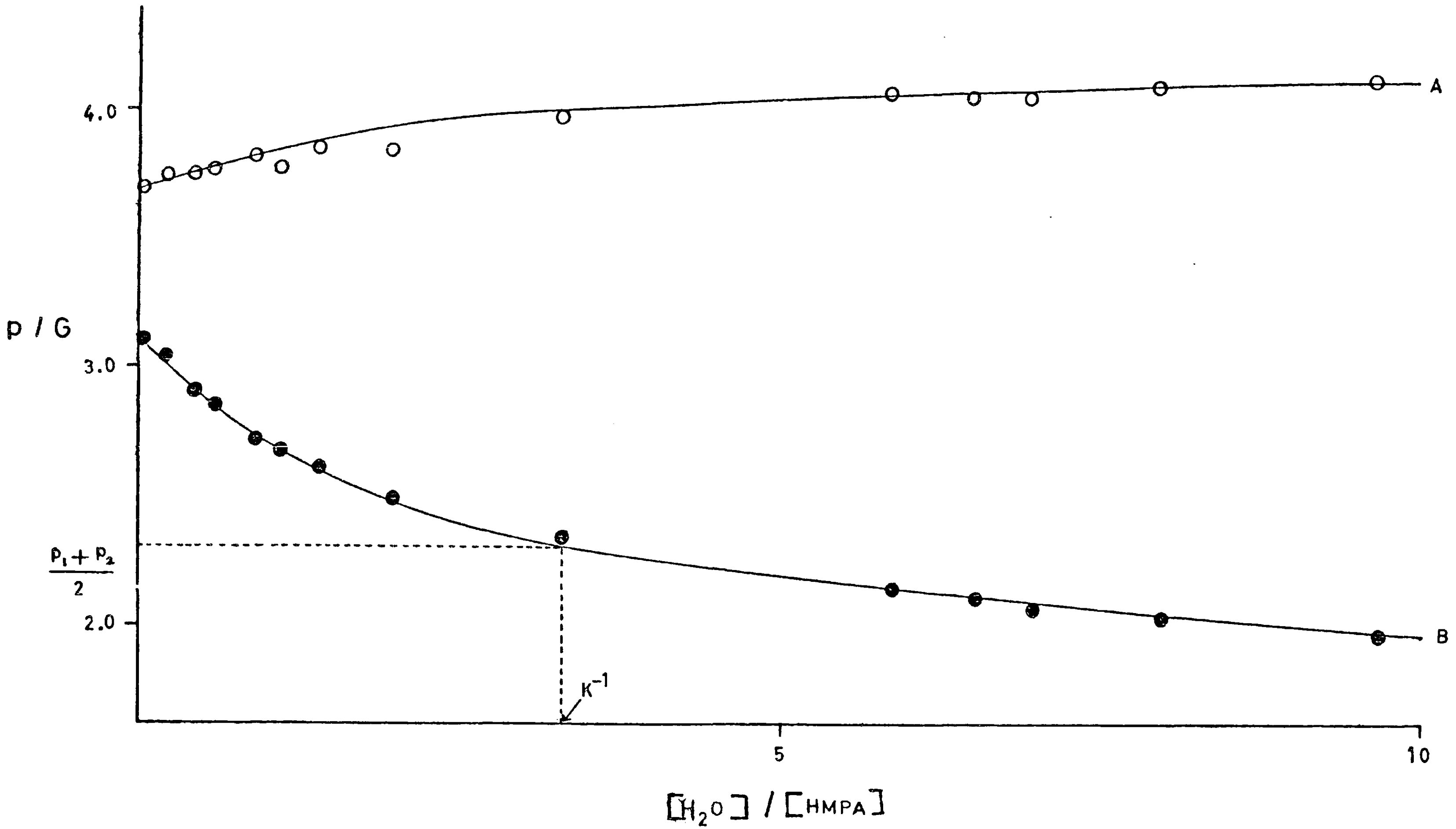


Fig. 5: Parameter p as a function of the molar ratio of solvents for radical II in H_2O-HMPA. A, $p=2a_{4,5}-3.0$; B, $p=2a_{3,6}$.

are the values of p in water and HMPA, respectively). Such a method is obviously unsatisfactory for determining K, relying as it does on the absolute magnitudes of p_1 and p_2, which may be uncertain. It was desirable, therefore, to develop a method capable of assessing the applicability of Eq.30 to the spectra of semiquinones obtained in mixed solvents, and enabling equilibrium constants to be calculated conveniently, even in cases where the experimental data was incomplete.

In accordance with this principle, Eq.30 was converted into more useful forms as follows. When the substitution $z=\ln\{[S_2]/[S_1]\}$ is made and the equation differentiated with respect to z, a plot of p against $\log\{[S_1]/[S_2]\}$ is shown to be sigmoid in character. The point of inflection ($d^2p/dz^2=0$) occurs when $p=(p_1+p_2)/2$, so that the value of $\log\{[S_2]/[S_1]\}$ at this point is simply log K. This is illustrated in Fig. 6 for 1,2-benzosemiquinone. When $2a_{3,6}$ takes its mean value, 2.31 G, the corresponding value of $\log\{[H_2O]/[HMPA]\}$ is 0.55. Having defined S_1 as water, $\log K^{-1}$ is, therefore, equal to 0.55 and K is 0.29. Note that the parameter exhibiting the largest solvent variation in this radical was the one chosen for Fig. 6, rather than $2a_{4,5}$; this precedent was followed in studies on all later compounds.

Despite the ease with which K may be obtained using this method, some unsatisfactory features remain. Not least of these is the degree to which the method relies on the absolute magnitudes of the two extreme values, i.e. the coupling constants in the pure solvents. Due to difficulties associated

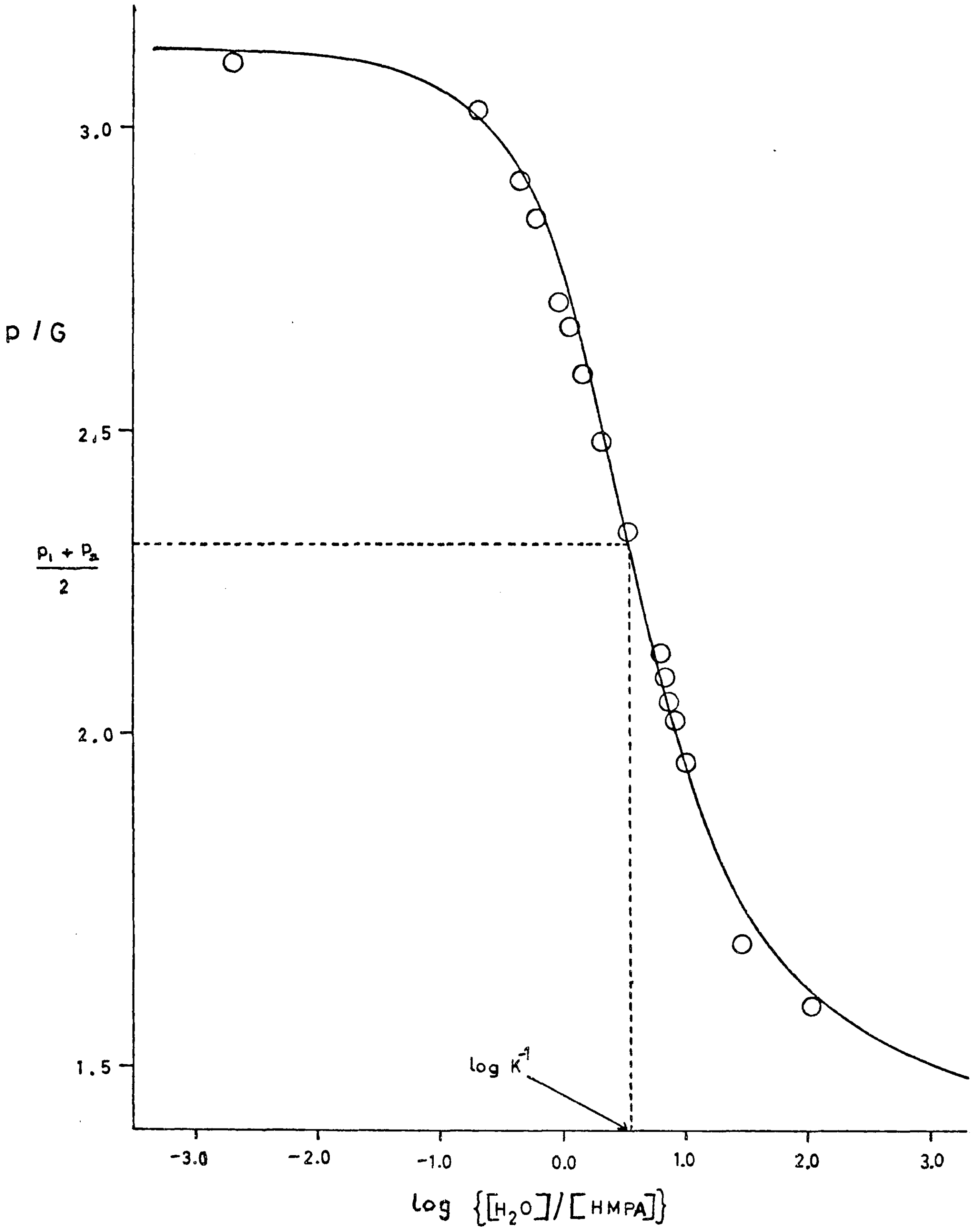


Fig. 6: Plot of p against log x for II in H_2O-HMPA, where $p=2a_{3,6}$ and $x=[H_2O]/[HMPA]$.

with the purification of solvents and the generally broader hyperfine lines obtained for radicals in aprotic solution, inaccuracies in individual measurements are liable to be significant and larger in the region of the aprotic component than in any other part of the solvent range. Also, there are many types of relationship which can give rise to sigmoid curves, of which the equilibrium given in Eq.13 (Ch.1-4, p.46) is only one.

A more rigorous test of the model is given by Eqs.31 and 33, derived from Eq.30. Eq.31 may also be written as in Eq.32:

$$1 + \frac{[S_1]}{[S_2]}K = \left(\frac{p_2 - p_1}{p - p_1}\right) \qquad \ldots\text{Eq.31}$$

$$\frac{1}{(p - p_1)} = \frac{1}{(p_2 - p_1)} + \frac{K}{(p_2 - p_1)}\frac{[S_1]}{[S_2]} \qquad \ldots\text{Eq.32}$$

Thus, a plot of $\left|1/(p-p_1)\right|$ against $[S_1]/[S_2]$ is expected to be linear (provided p is not too close to the value p_1), with intercept $\left|1/(p_2-p_1)\right|$ and slope $\left|K/(p_2-p_1)\right|$. Fig. 7 shows that such a plot for 1,2-benzosemiquinone in H_2O-HMPA is linear over the range $0 \leqslant x \leqslant 2.0$. (The best straight line was calculated by linear regression; the correlation coefficient,

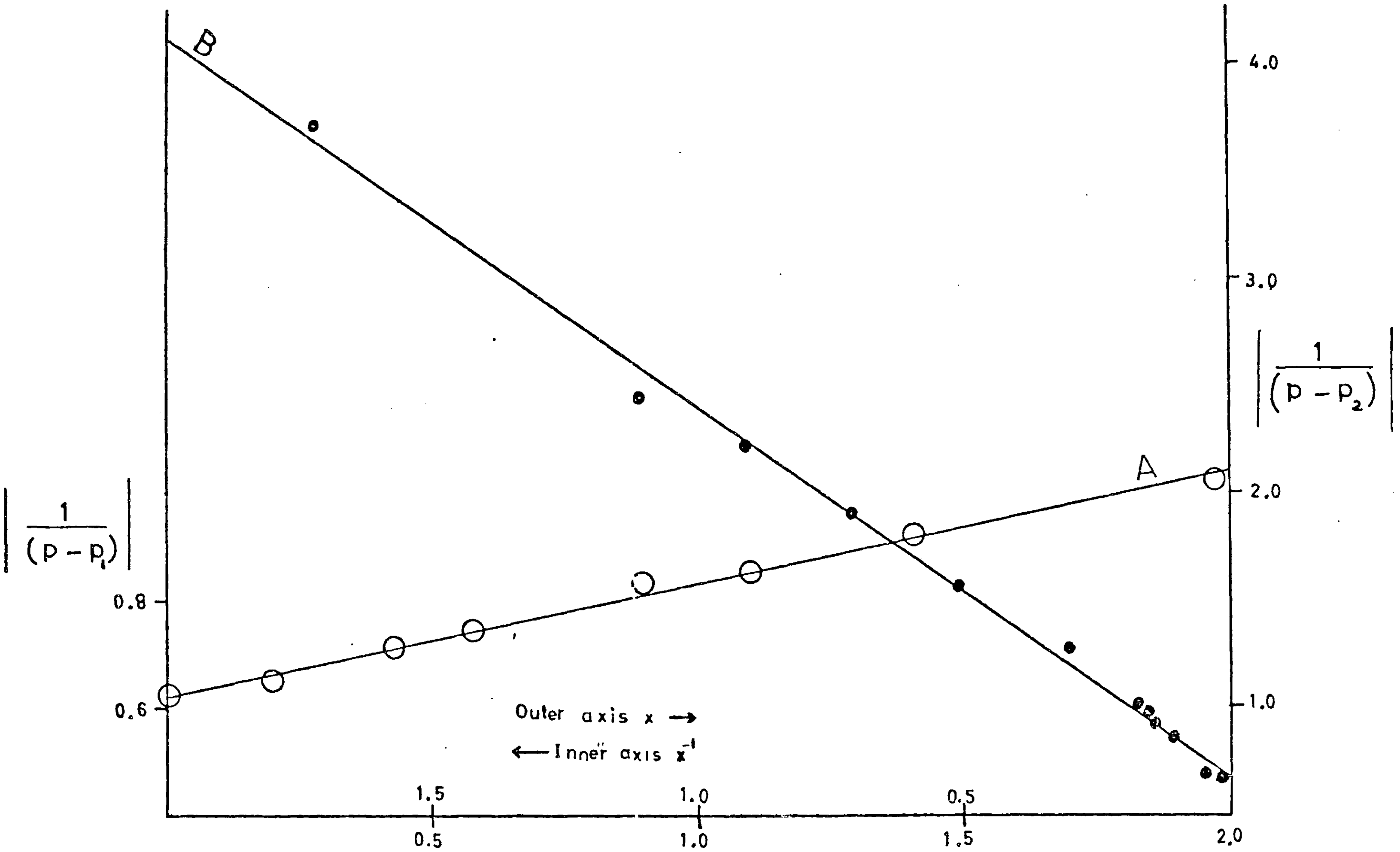


Fig. 7: Plots suggested by Eqs. 31 and 33 for II in H_2O-HMPA.
A, $x \longrightarrow |1/(p-p_1)|$; B, $x^{-1} \longrightarrow |1/(p-p_2)|$, where $p=2a_{3,6}$

r, is 0.997, indicating that the data fits the linear regression extremely well). Values of 0.208 and 0.621 for the slope and intercept, respectively, yield a value of 0.33±0.02 for the equilibrium constant.

Similarly, Eq.33 is also obtained from Eq.30:

$$\left(\frac{p_2 - p_1}{p_2 - p}\right) = 1 + \frac{[S_2]}{K[S_1]} \qquad \ldots\text{Eq.33}$$

A plot of $\left|1/(p_2-p)\right|$ against $[S_2]/[S_1]$ is, therefore, linear and of slope $\left|1/K(p_2-p_1)\right|$ and intercept $\left|1/(p_2-p_1)\right|$. The observed straight line for 1,2-benzosemiquinone in H_2O-HMPA (Fig. 7, plot B) has a correlation coefficient of 0.998; the intercept (0.675) and slope (1.715) yield an equilibrium constant of 0.39±0.02. The agreement with the value obtained from plot A is encouraging, particularly as this system was chosen specifically for its practical difficulties as a test of this method of treating results.

The linear plots also reveal (from the intercepts) a value for the parameter $2a_{3,6}$ of 3.05 G in pure HMPA. The difference between this value and that determined experimentally (Table 4) may be linked to the nature of the base used (MeO^- or EtO^-), and shows the unreliability of measurements in the pure aprotic solvents. It also accounts for the discrepancies in equilibrium constants determined by different methods: those relying on the absolute values of p_1 and p_2 (Figs. 5 and 6) give K as 0.29, whereas the linear plots yield a value of 0.36.

The treatment of results presented here has several distinct advantages. Equilibrium constants are readily accessible from straight line graphs, i.e. from a series rather than a lone measurement, and therefore the values obtained are less susceptible to inaccuracy. Two independent estimates of K are available, one from the aprotic solvent end (Eq.31) and the other from solutions in which the concentration of protic solvent is high (Eq.33). In addition, the method allows K to be determined (from slope and intercept values) even when p_1 and/or p_2 are not available, a factor which has hampered previous quantitative studies of solvation.[1]

Table 5, Figs. 8 and 9, and Table 6, Figs. 10 and 11 indicate that the H_2O-DMSO and H_2O-DMF systems, respectively, may be treated in an analogous manner. The sigmoid curves are included for comparison with that given earlier for the same radical in H_2O-HMPA (Fig. 6), and provide useful estimates of K. The linear plots were used to give more reliable values of the equilibrium constants. (Correlation coefficients for these lines are given in Tables 11 and 12, Ch. 4). The values of K for 1,2-benzosemiquinone in H_2O-DMSO and H_2O-DMF are, respectively, 0.57 and 0.51, averaging the values obtained from the individual linear plots.

Table 5: Variation of E.s.r. Parameters of 1,2-Benzosemiquinone in H_2O-DMSO Mixtures

$x=\frac{[H_2O]}{[DMSO]}$ ($x\pm0.01$)	$a_{4,5}/G$ (±0.03)	$2a_{3,6}/G$ (±0.03)	log x	$\left\lvert\frac{1}{(\rho-\rho_1)}\right\rvert$	x^{-1}	$\left\lvert\frac{1}{(\rho-\rho_2)}\right\rvert$
H_2O	3.69	$\rho_1=1.50$				0.79
366.30	3.69	1.49	2.56		0.003	0.78
107.29	3.68	1.50	2.03		0.009	0.79
30.44	3.69	1.56	1.48		0.03	0.83
17.51	3.67	1.60	1.24		0.06	0.85
9.97	3.65	1.66	1.00		0.10	0.89
5.60	3.63	1.76	0.75		0.18	1.00
3.16	3.58	1.93	0.50		0.32	1.18
1.79	3.54	2.11	0.25	1.64	0.56	1.52
0.98	3.52	2.29	-0.01	1.27	1.02	2.08
0.62	3.48	2.44	-0.21	1.08	1.61	2.94
0.57	3.46	2.45	-0.24	1.06	1.75	3.13
0.32	3.48	2.54	-0.50	0.97		
0.11	3.46	2.65	-0.98	0.87		
0.03	3.44	2.80	-1.57	0.76		
0.01	3.46	2.73	-2.00	0.82		
DMSO	3.45	$\rho_2=2.77$		0.79		

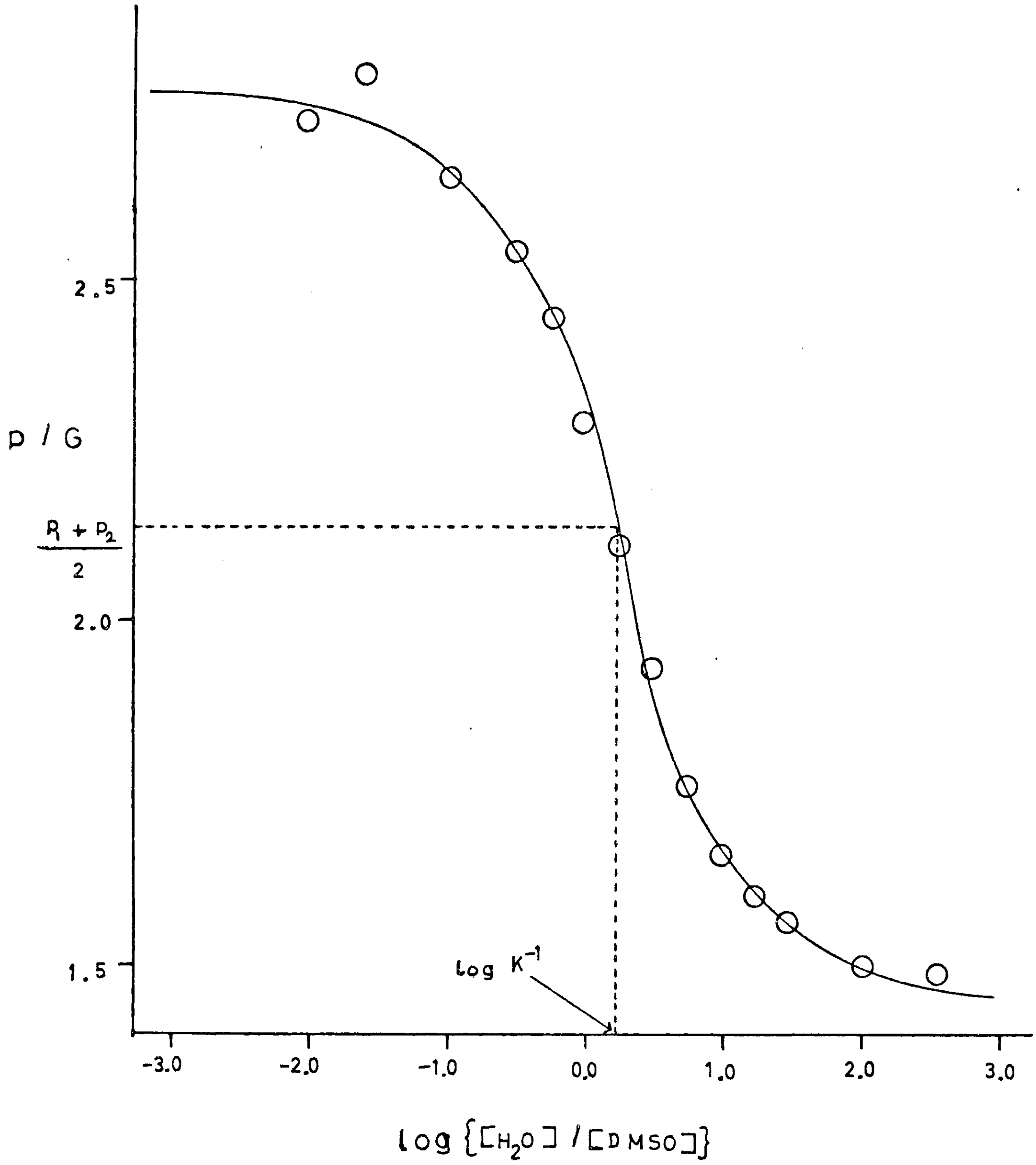


Fig. 8: Plot of p against log x for II in H_2O-DMSO.

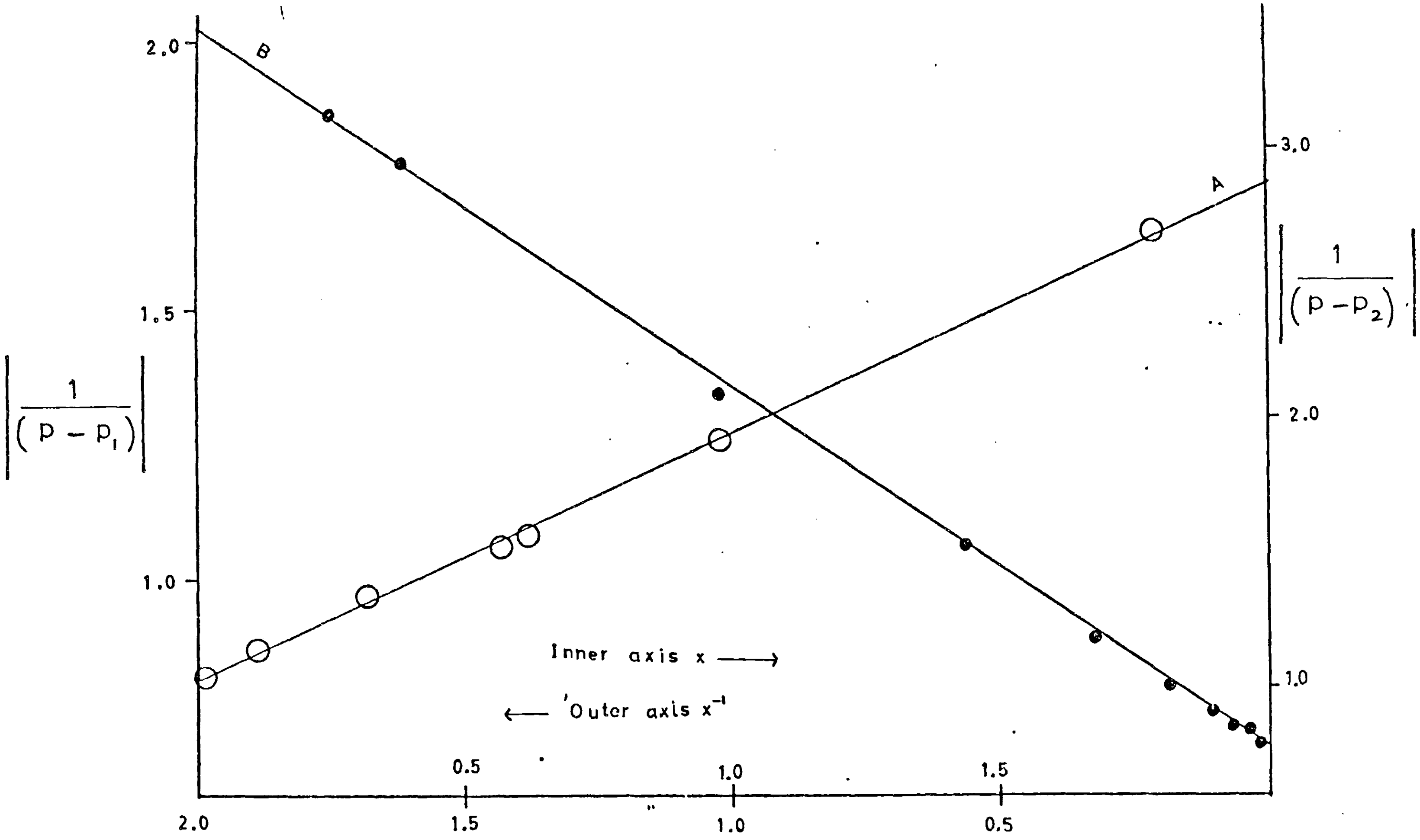


Fig. 9: Linear plots for II in H_2O-DMSO.

A, $x \longrightarrow |1/(p-p_1)|$; B, $x^{-1} \longrightarrow |1/(p-p_2)|$.

Table 6: Variation of E.s.r. Parameters of 1,2-Benzosemiquinone in H_2O-DMF Mixtures

$x=\frac{[H_2O]}{[DMF]}$ ($x\pm0.01$)	$a_{4,5}/G$ (±0.03)	$2a_{3,6}/G$ (±0.03)	log x	$\left\lvert\frac{1}{(\rho-\rho_1)}\right\rvert$	x^{-1}	$\left\lvert\frac{1}{(\rho-\rho_2)}\right\rvert$
H_2O	3.75	$\rho_1=1.50$				0.94
362.10	3.74	1.50	2.56		0.003	0.94
94.27	3.73	1.54	1.97		0.01	0.98
32.05	3.67	1.56	1.51		0.03	1.00
16.65	3.68	1.61	1.22		0.06	1.05
9.99	3.66	1.67	1.00		0.10	1.12
6.92	3.64	1.72	0.84		0.14	1.19
4.88	3.61	1.80	0.69		0.20	1.30
4.31	3.60	1.80	0.63		0.23	1.32
3.16	3.65	1.92	0.50		0.32	1.56
2.01	3.58	1.96	0.30	1.96	0.50	1.79
1.51	3.58	2.10	0.18	1.67	0.66	2.17
1.33	3.54	2.13	0.12	1.59	0.75	2.33
1.10	3.53	2.19	0.04	1.44	0.91	2.78
0.92	3.52	2.23	-0.04	1.37	1.09	3.03
0.72	3.51	2.29	-0.14	1.27	1.39	3.70
0.51	3.48	2.39	-0.29	1.12	1.96	5.88
0.43	3.51	2.34	-0.37	1.19		
0.29	3.45	2.44	-0.54	1.06		
0.19	3.49	2.50	-0.72	1.00		
0.13	3.46	2.49	-0.89	1.01		
DMF	3.48	$\rho_2=2.56$		0.94		

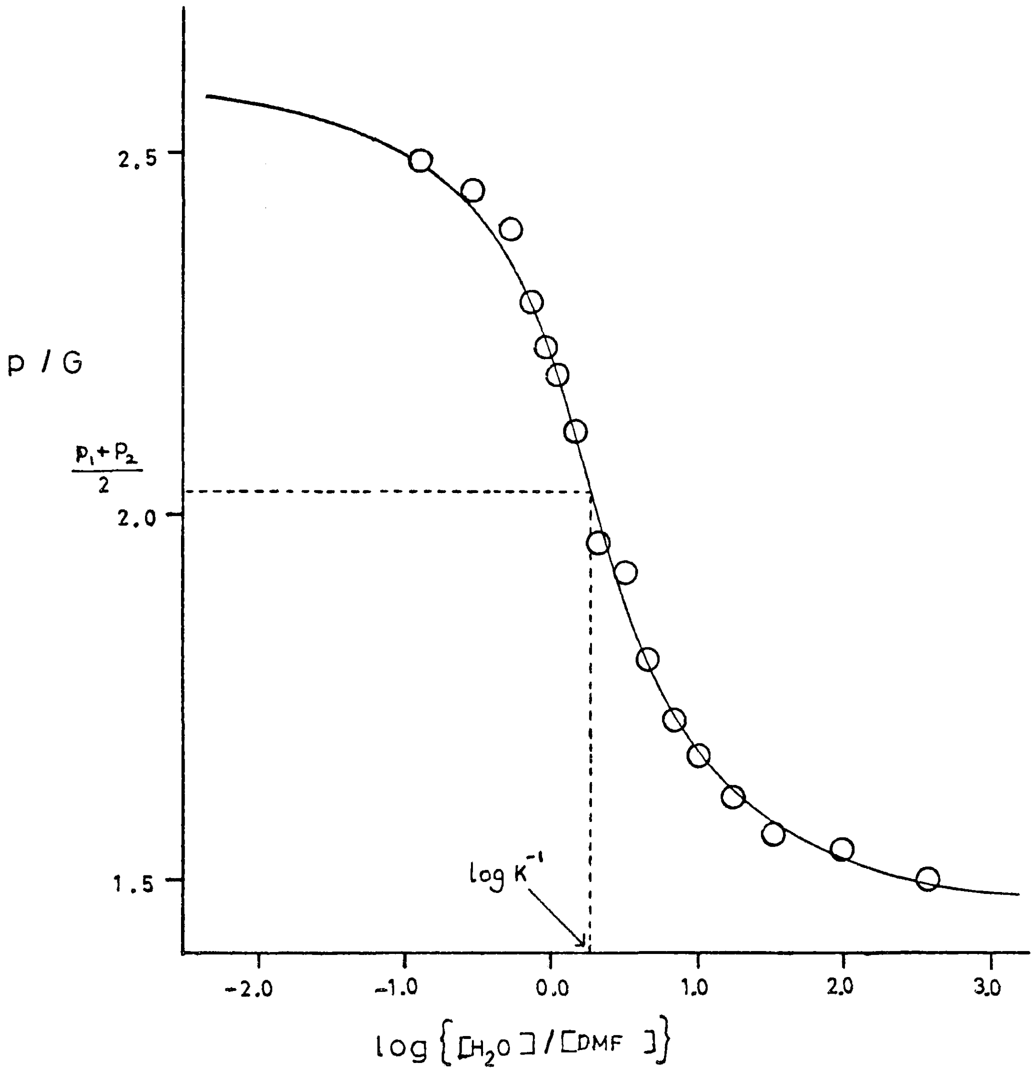


Fig. 10: Plot of p against log x for II in H_2O-DMF.

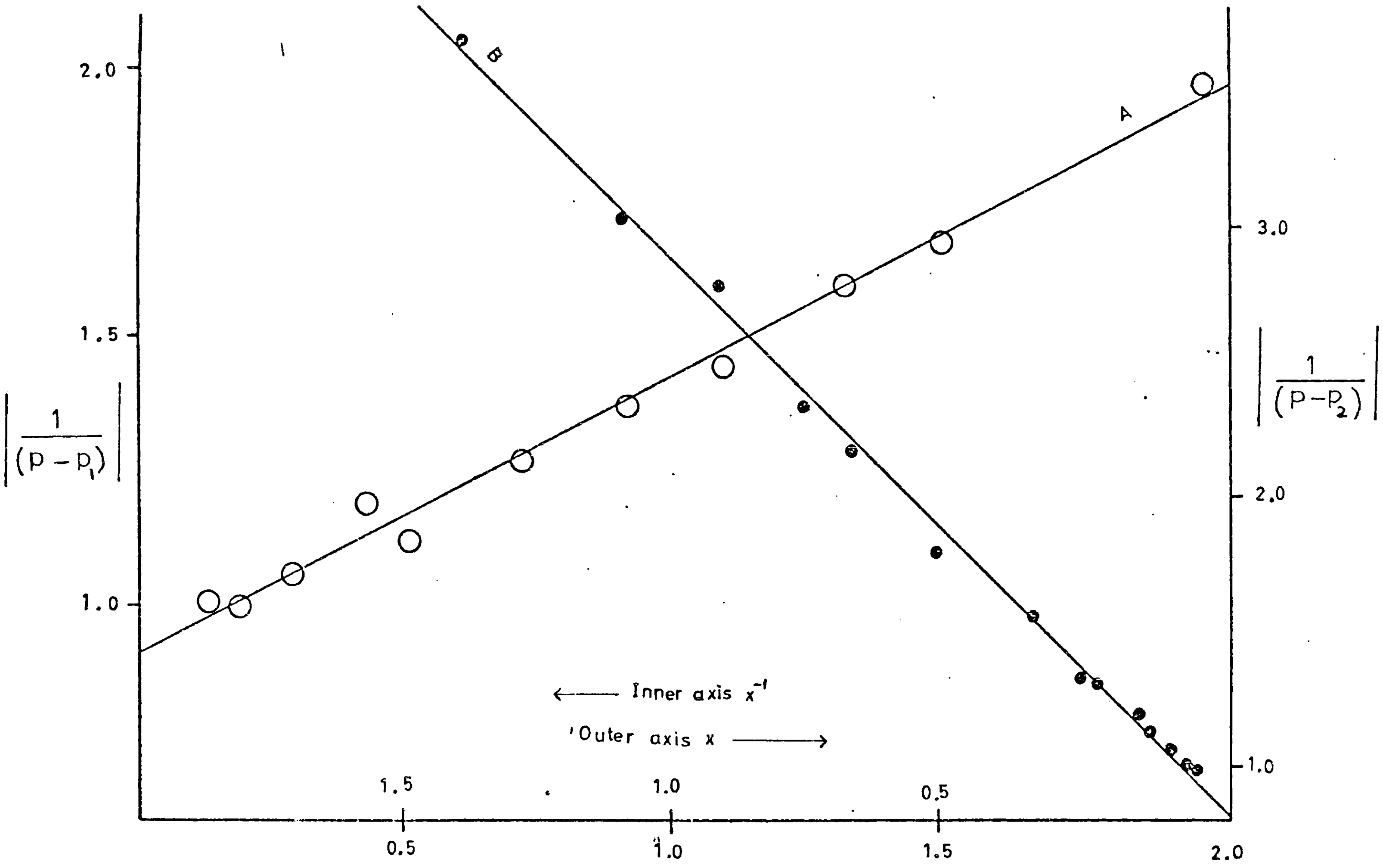


Fig. 11: Linear plots for II in H_2O-DMF. A, x $\longrightarrow$ $|1/(p-p_1)|$,
B, $x^{-1} \longrightarrow$ $|1/(p-p_2)|$.

CHAPTER 4

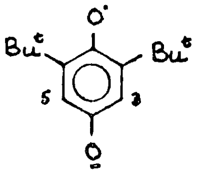
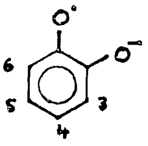
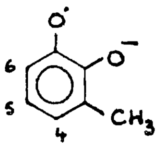
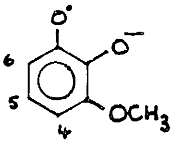
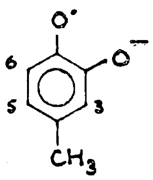
E.S.R. RESULTS

1. Choice of Radicals for Quantitative Study

The hyperfine splitting constants obtained for some semiquinones in the solvents H_2O, EtOH, DMSO, DMF and HMPA are given in Table 7. It is clear that differences are at a maximum when the radicals are generated in water and HMPA; it was in this system, therefore, that trials were carried out to find radicals whose spectra altered sufficiently for quantitative studies to be undertaken. For such studies to be feasible Tables 9-13 reveal that there are two requirements to be met: firstly, there must be a change in one of the e.s.r. parameters of at least 0.5 G and, secondly, the measurement of this parameter must be unhampered by factors such as unresolved splittings, so that the observed spectral lines are sharp. Only when both these conditions are fulfilled can accurate hyperfine splittings be obtained and K determined with reasonable certainty.

The results of the H_2O-HMPA trials (Table 8) indicate that the first criterion is not fulfilled by VIII, X, XI, XIII-XVI, and XXII-XXIV; for these radicals only qualitative studies were possible. For the remainder of the species in Table 8, although in theory at least one e.s.r. parameter (whether the total spectral width or some combination of the individual hyperfine splittings) was changing by more than 0.5 G, practical difficulties specific to that system meant that the second requirement was absent, and that equilibrium constants could not be obtained. In the case of radical VII, unresolved *t*-butyl splittings served to broaden the spectral lines,

Table 7: Comparison of Coupling Constants for Some Semiquinones in Various Solvents

Radical	Solvent	a_3	a_4 (/G±0.03)	a_5	a_6
 I	H_2O	1.31		1.31	
	EtOH	1.21		1.21	
	DMSO	2.01		2.01	
	DMF	2.12		2.12	
	HMPA	2.25		2.25	
 II	H_2O	0.75	3.69	3.69	0.75
	EtOH	0.93	3.59	3.59	0.93
	DMSO	1.39	3.45	3.45	1.39
	DMF	1.28	3.48	3.48	1.28
	HMPA	1.56	3.34	3.34	1.56
 III	H_2O	$a_{Me}=0.63$	2.85	4.13	0.28
	EtOH	$a_{Me}=0.80$	2.80	4.07	0.44
	DMSO	$a_{Me}=1.00$	2.80	3.70	1.00
	DMF	$a_{Me}=1.06$	2.90	3.66	0.98
	HMPA	$a_{Me}=1.06$	2.83	3.54	1.06
 IV	H_2O	$a_{OMe}=0.65$	1.25	4.76	-0.59
	EtOH	$a_{OMe}=0.65$	1.30	4.59	-0.40
	DMSO	$a_{OMe}=0.60$	1.60	4.00	0.18
	DMF	$a_{OMe}=0.60$	1.75	4.00	0.20
	HMPA	$a_{OMe}=0.47$	1.90	3.78	0.46
 V	H_2O	0.07	$a_{Me}=4.89$	3.89	0.98
	EtOH	0.33	$a_{Me}=4.47$	3.70	1.10
	DMSO	0.80	$a_{Me}=4.08$	3.62	1.51
	DMF	0.89	$a_{Me}=4.01$	3.65	1.60
	HMPA	1.00	$a_{Me}=3.85$	3.55	1.69

cont.

Table 7 continued.

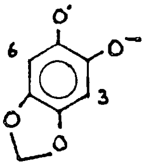
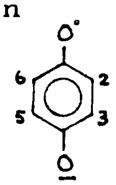
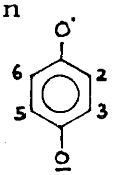
Radical	Solvent	a_3	a_4	a_5	a_6
			(/G±0.03)		
	H_2O	-0.33	a_{CH_2}=4.22	a_{CH_2}=4.22	-0.33
	EtOH	-0.08	a_{CH_2}=3.64	a_{CH_2}=3.64	-0.08
	DMF	0.43	a_{CH_2}=2.52	a_{CH_2}=2.52	0.43
VI	HMPA	0.50	a_{CH_2}=2.39	a_{CH_2}=2.39	0.50

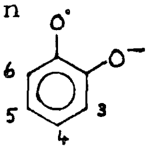
Table 8: Trial Compounds in H_2O-HMPA

(i) Substituents in 	Sol-vent	Coupling Constants* (/G±0.03)			
		a_2	a_3	a_5	a_6
2-Bu^t	H_2O^a		1.65	2.17	2.82
VII	HMPA		2.14	2.52	2.55
2,3-$(OCH_3)_2$	H_2O	a_{OMe}=0.0	a_{OMe}=0.0	2.64	2.64
VIII	HMPA	a_{OMe}=0.0	a_{OMe}=0.0	2.87	2.87
2-CH_3,5-$CH(CH_3)_2$	H_2O^b	a_{Me}=2.30	1.82	$a_H^{Pr^i}$=1.45	1.76
(Thymosemiquinone, IX)	HMPA	a_{Me}=2.08	2.05	$a_H^{Pr^i}$=1.28	2.05
2,3-$(CN)_2$	H_2O	a_N=0.60	a_N=0.60	1.15	1.15
X	HMPA	a_N=0.65	a_N=0.65	1.10	1.10
2,3-$(OCH_3)_2$,5-CH_3	H_2O	a_{OMe}=0.0	a_{OMe}=0.0	a_{Me}=2.45	1.95
XI	HMPA	a_{OMe}=0.0	a_{OMe}=0.0	a_{Me}=2.20	2.35
2,3,5-$(CH_3)_3$	H_2O^c	a_{Me}=2.00	a_{Me}=1.85	a_{Me}=2.45	1.90
XII	HMPA	a_{Me}=2.05	a_{Me}=1.75	a_{Me}=2.30	1.80
2,3,5,6-F_4	H_2O	a_F=3.99	a_F=3.99	a_F=3.99	a_F=3.99
XIII	HMPA	a_F=4.03	a_F=4.03	a_F=4.03	a_F=4.03
2,3,5,6-$(CH_3)_4$	H_2O	a_{Me}=1.97	a_{Me}=1.97	a_{Me}=1.97	a_{Me}=1.97
(Durosemiquinone, XIV)	HMPA	a_{Me}=1.97	a_{Me}=1.97	a_{Me}=1.97	a_{Me}=1.97

cont.

Table 8 continued:

(i) Substituents in 	Sol-vent	Coupling Constants* (/G±0.03)			
		a_2	a_3	a_5	a_6
2,3-$(OCH_3)_2$,	H_2O	$a_{OMe}=0.0$	$a_{OMe}=0.0$	$a_{Me}=2.03$	$a_{Me}=2.03$
5,6-$(CH_3)_2$ XV	HMPA	$a_{OMe}=0.0$	$a_{OMe}=0.0$	$a_{Me}=2.04$	$a_{Me}=2.04$
2,3-Cl_2,5,6-$(CN)_2$	H_2O			$a_N=0.55$	$a_N=0.55$
XVI	HMPA			$a_N=0.60$	$a_N=0.60$

(ii) Substituents in 	Sol-vent	Coupling Constants /G			
		a_3	a_4	a_5	a_6
3-$CH(CH_3)_2$	H_2O^d	$a_H^{Pr^i}=0.58$	2.83	4.22	0.25
XVII	HMPA	$a_H^{Pr^i}=1.18$	2.88	3.60	0.78
3,4,5-$(OCH_3)_3$	H_2O^e	$a_{OMe}=0.0$	$a_{OMe}=0.12$	$a_{OMe}=1.16$	-0.60
XVIII	HMPA	$a_{OMe}=0.0$	$a_{OMe}=0.0$	$a_{OMe}=0.91$	0.0
3,4-$(OCH_3)_2$,6-CH_3	H_2O	$a_{OMe}=0.0$	$a_{OMe}=0.53$	2.95	$a_{Me}=1.68$
XIX	HMPA	$a_{OMe}=0.0$	$a_{OMe}=0.20$	3.30	$a_{Me}=1.30$
3,4-$(OCH_3)_2$	H_2O^f	$a_{OMe}=0.0$	$a_{OMe}=0.45$	3.88	1.70
XX	HMPA	$a_{OMe}=0.0$	$a_{OMe}=0.0$	3.75	1.80

cont.

Table 8 continued:

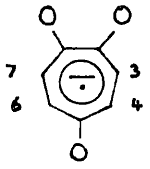
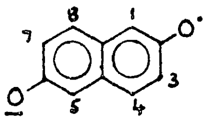
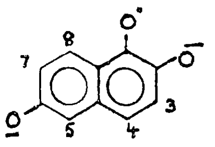
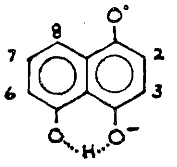
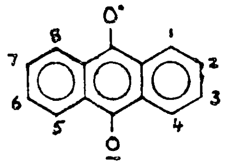
(iii)Radical	Solvent	Coupling Constants/G		
 XXI	H_2O^g	$a_{3,7}=0.80$	$a_{4,6}=2.10$	
	HMPA	$a_{3,7}=1.22$	$a_{4,6}=2.00$	
 XXII	H_2O^h	$a_{1,5}=4.25$	$a_{4,8}=0.68$	$a_{3,7}=1.33$
	HMPA	$a_{1,5}=4.18$	$a_{4,8}=0.60$	$a_{3,7}=1.43$
 XXIII	H_2O^i	$a_3=0.63$	$a_4=5.10$	$a_5=1.47$
	HMPA	$a_3=0.35$	$a_4=5.25$	$a_5=1.10$
	H_2O^i	$a_7=0.35$	$a_8=1.45$	
	HMPA	$a_7=0.10$	$a_8=1.90$	
 XXIV	H_2O^j	$a_2=3.90$	$a_3=2.70$	$a_6=0.80$
	HMPA	$a_2=4.13$	$a_3=2.45$	$a_6=0.85$
	H_2O^j	$a_7=0.30$	$a_8=1.12$	$a^H_{peri}=0.80$
	HMPA	$a_7=0.65$	$a_8=0.98$	$a^H_{peri}=0.35$
 XXV	H_2O^k	$a_{1,4,5,8}=0.63$	$a_{2,3,6,7}=0.95$	
	HMPA	$a_{1,4,5,8}=0.23$	$a_{2,3,6,7}=1.00$	

Table 8 continued:

* Coupling constants were assigned as follows:

a As in Ref. 47

b By analogy with 2,5-dimethyl[a]- and 2,5-di-t-butyl-1,4-benzosemiquinone (radical XXIII, Table 9).

c By McLachlan S.C.F. calculation.

d By comparison with 3-methyl-1,2-benzosemiquinone (radical III, Table 7): S.C.F. calculations indicate a_6 is small (0.14 G), but in the case of radical XVII values for a_6 and a_H^{Pri} are, of course, ambiguous.

e By McLachlan S.C.F. calculation, as in Ref. 126.

f Using graphical procedures, as in Ref. 126.

g On basis of McLachlan S.C.F. calculation.

h As in Ref. 127.

i Dianion obtained as secondary radical in the autoxidation of 2,6-dihydroxynaphthalene; assignments as in Refs. 127 and 128.

j Radical from juglone; assignments in water as in Ref. 128 and in HMPA as in Ref. 127 but, considering the magnitude of the changes in other coupling constants from water to HMPA, assignments for a_2 and a_3 are interchanged.

k As in Ref. 1.

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reducing the accuracy with which coupling constants could be measured. Broadening also occurred for XVIII-XX, as at least one of the coupling constants tended towards zero as the HMPA concentration was increased; XVIII is an extreme example as three splittings approach zero in pure HMPA. The consequent practical difficulties make a "run" on this radical impossible.

The overlapping of spectral lines made e.s.r. parameters less accessible and was the preventative factor for IX, XII and XXI. This was most troublesome at the HMPA end for IX (a_{Me} and a_3 becoming equal in HMPA) and XXI; for XII overlapping was serious throughout the range of solvent concentrations. Radical XXV was characterised by a small, partially resolved splitting in its spectrum in HMPA, which hindered the measurement of the total spectral width, the parameter undergoing the greatest variation with solvent. A quantitative study of XVII was not undertaken as its spectrum varied in a similar manner to that of 3-methyl-1,2-benzosemiquinone (III, Table 7). This suggests that the equilibrium constant would also be of comparable magnitude.

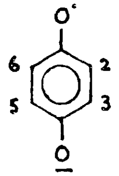
The results presented in Table 8 were, nevertheless, of intrinsic interest in establishing a more complete picture of solvent effects. With the exception of durosemiquinone (XIV)[60] and the radicals from juglone (XXIV) and 2,6-dihydroxynaphthalene (XXII, XXIII),[127] these radicals have not previously been observed in HMPA and provide useful comparisons with differently substituted semiquinones for which equilibrium constants can be determined.

Assignments of hyperfine splitting constants were based on McLachlan S.C.F. calculations, on empirical graphical procedures[126,129] or on comparisons with similar radicals of known spin distribution, as detailed in Table 8. Without following the smooth variation in a coupling constant over the range pure water to pure HMPA (as in Figs. 5 and 6, Ch. 3) it was not certain which value a particular coupling constant in water acquired in HMPA. For the majority of species in the table, however, generation of the radical in a 50:50 (volume: volume) mixture of water and HMPA enabled the splittings in HMPA to be assigned with some confidence.

2. Determination of Equilibrium Constants in the H_2O-HMPA System.

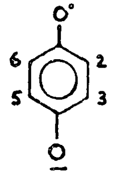
Table 9 contains equilibrium constants obtained for semiquinones in H_2O-HMPA. Using Eq.30 estimates of K were determined from p against log x plots, and more accurate figures were given by the linear plots: (i) $1/(p-p_1)$ against x (Eq.31), and (ii) $1/(p-p_2)$ against x^{-1} (Eq.33). The straight lines which best fitted the experimental data were found by linear regression. To establish how well the data fitted the linear regression the correlation coefficient, r, was calculated in each case. Where no value of r is given (Table 9), for example, for *p*-benzosemiquinone itself (XXVI), the magnitude of the

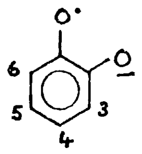
Table 9: Equilibrium Constants in the H_2O-HMPA System

(i) Substituents in 	Solvent	a_2	a_3 (/G±0.03)	a_5	a_6	$K^{\neq}$	r^*	Parameter used
Unsubstituted	H_2O	2.38	2.38	2.38	2.38	1.4		
XXVI	HMPA	2.45	2.45	2.45	2.45			T.W.** $=4a_H$
2-CH_3	H_2O	$a_{Me}=2.10$	1.73	2.60	2.39	(i) 0.35	0.929	$a_3+a_5+a_6=\Sigma a_H$
XXVII	HMPA	$a_{Me}=1.77$	2.05	2.73	2.43			
2-OCH_3	H_2O	$a_{OMe}=0.82$	0.52	3.60	1.94	(i) 0.67	0.993	a_3
XXVIII	HMPA	$a_{OMe}=0.47$	1.16	3.48	2.31	(ii) 0.68	0.993	
2,5-Bu^t_2	H_2O		2.08		2.08	0.07		T.W.$=a_3+a_6$
XXIX	HMPA		2.33		2.33			
2,6-Bu^t_2	H_2O		1.31	1.31		(i) 1.16	0.999	T.W.$=a_3+a_5$
I	HMPA		2.25	2.25		(ii) 0.80	0.996	

cont.

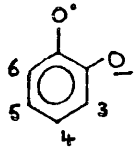
Table 9 continued:

(i)Substituents in 	Sol-vent	a_2	a_3 (/G±0.03)	a_5	a_6	$K^{\neq}$	r^*	Parameter used
2,6-$(OCH_3)_2$	H_2O	$a_{OMe}=0.80$	1.47	1.47	$a_{OMe}=0.80$	(i) 0.58	0.975	$6a_{OMe}$
XXX	HMPA	$a_{OMe}=0.50$	1.92	1.92	$a_{OMe}=0.50$	(ii) 0.68	0.995	
						(i) 0.38	0.986	$2a_H$
						(ii) 0.44	0.980	
2,6-$(CH_3)_2$	H_2O	$a_{Me}=2.10$	1.87	1.87	$a_{Me}=2.10$	(i) 0.64	0.989	$2a_H$
XXXI	HMPA	$a_{Me}=1.85$	2.22	2.22	$a_{Me}=1.85$			

(ii)Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	$K^{\neq}$	r^*	Parameter used
Unsubstituted	H_2O	0.75	3.69	3.69	0.75	(i) 0.33	0.997	$2a_{3,6}$
II	HMPA	1.56	3.34	3.34	1.56	(ii) 0.39	0.998	

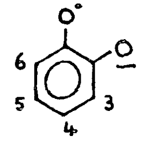
cont.

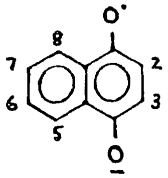
Table 9 continued:

(ii)Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	$K^{/}$	r^*	Parameter used
3-CH_3	H_2O	a_{Me}=0.63	2.85	4.13	0.28	(i) 0.42	0.990	T.W.
III	HMPA	a_{Me}=1.06	2.83	3.54	1.06	(ii) 0.46	0.989	
3-OCH_3	H_2O	a_{OMe}=0.65	1.25	4.76	-0.59	(i) 0.62	0.994	a_5
IV	HMPA	a_{OMe}=0.47	1.90	3,78	0.46	(ii) 0.61	0.994	
4-CH_3	H_2O	0.07	a_{Me}=4.89	3.89	0.98	(i) 0.34	0.993	a_3
V	HMPA	1.00	a_{Me}=3.85	3.55	1.69	(i) 0.23	0.983	a_{Me}
						(i) 0.09	0.942	T.W.
4,5-$(OCH_3)_2$	H_2O	-0.32	a_{OMe}=1.05	a_{OMe}=1.05	-0.32	(i) 0.80	0.990	$2a_{3,6}$
XXXII	HMPA	0.33	a_{OMe}=0.85	a_{OMe}=0.85	0.33			
4,5-OCH_2O	H_2O	-0.33	a_{CH_2}=4.22	a_{CH_2}=4.22	-0.33	(i) 0.22	0.997	a_{CH_2}
VI	HMPA	0.50	a_{CH_2}=2.39	a_{CH_2}=2.39	0.50	(ii) 0.23	0.996	
						(i) 0.30	0.972	$2a_{3,6}$

Cont.

Table 9 continued:

(ii) Substituents in 	Sol- vent	a_3	a_4	a_5	a_6	K[≠]	r[*]	Parameter used
3,4,6-$(OCH_3)_3$ XXXIII	H_2O HMPA	$a_{OMe}=0.0$ $a_{OMe}=0.0$	$a_{OMe}=0.90$ $a_{OMe}=0.50$	1.15 2.13	$a_{OMe}=0.66$ $a_{OMe}=0.25$	(ii) 0.87	0.995	T.W.

(iii) Radical	Sol- vent	Coupling Constants	K[≠]	r[*]	Parameter used
 XXXIV	H_2O HMPA	$a_2=a_3=3.20$ $a_5=a_6=a_7=a_8=0.66$ $a_2=a_3=3.33$ $a_5=a_8=0.24$ $a_7=a_8=0.65$	(i) 0.13	0.965	$2a_{5,8}$

≠ Values of equilibrium constants:
(i) From $|p-p_1|^{-1}$ against x plot (ii) From $|p-p_2|^{-1}$ against x^{-1} plot.

Where no value of r is given K has been obtained from p against log x plot.

* r=Correlation coefficient from linear regression analysis.

** T.W.=Total spectral width.

changes incurred on altering the solvent was too small to allow reliable equilibrium constants to be obtained from the linear plots; instead an approximate value of K was determined from the appropriate sigmoid curve.

Assignments of hyperfine splitting constants for spectra obtained in water were based on S.C.F. calculations for I-VI, XXVI-XXXIII; XXXIV is assigned as in Ref. 1. Plots of p against log x demonstrated the smooth variation in e.s.r. parameters with solvent composition and led to the assignment of the coupling constants in pure HMPA.

Whenever possible the parameter undergoing the largest change from water to HMPA was employed in calculating K. However, in some cases it was not possible to plot two linear graphs. For XXVII, for instance, K has been determined solely from the $1/(p-p_1)$ against x plot, the relatively small variation in the ring proton hyperfine splittings being reflected in a lower value of r (0.929) than that observed in more favourable situations. The second straight line plot, $1/(p-p_2)$ against x^{-1}, could not be used due to extensive overlapping in spectra obtained towards the water end of the solvent range. The same situation obtains for XXXI. For the radical from 3,4,6-trimethoxycatechol (XXXIII), overlapping at the HMPA end prevented the use of the $1/(p-p_1)$ against x plot. For XXXIV, only this plot was found to be linear, yielding an equilibrium constant in good agreement with that from the log plot.

For methyl- and methoxy- substituted semiquinones, different values of K are obtained depending on the e.s.r. parameter employed. Table 10 lists equilibrium constants obtained from p against log x plots, as p is varied, for alkyl- and alkoxy-semiquinones. Different values of K are found if a ring proton splitting is used rather than a methyl or methoxy coupling constant. For XXIX and XXX linear regression analysis was performed on both proton and alkyl/alkoxy- group splittings (Table 9).

When comparing equilibrium constants for different radicals, therefore, it is important to ascertain which parameter has been used to determine K, particularly if the radical is of the type presented in Table 10. In contrast, the total width and the parameter $2a_{3,6}$ yield the same value for 1,2-benzosemiquinone (II), and a_{CH_2} and $2a_{3,6}$ for VI yield a unique equilibrium constant. This implies that the differences observed for the methoxy-substituted radicals of Table 10 may be due to conformational effects of the kind reported previously for methoxy-compounds.[130] Such effects are not possible for the methylenedioxy-substituted radical VI. At present no explanation for the behaviour of methylsemiquinones may be advanced.

The variation in an e.s.r. parameter over the entire range pure water to pure HMPA reveals certain features which might have been overlooked had only the two extreme values been available. It is known, for example, that a_6 in IV is negative[129] when the radical is generated in water; this is confirmed by S.C.F. calculations. By observing the smooth change in a_6 with solvent composition (Fig. 12) it is apparent that a_6 changes

Table 10: Values of K Obtained from p against log x Plots for Methyl- and Methoxy-semiquinones in H_2O-HMPA

Radical	Parameter,p	K from p against log x plot
III	a_6	0.19
	T.W.	0.35
IV	a_{OMe}	1.12
	a_4	1.26
	a_5	0.40
	a_6	0.52
	T.W.	0.40
V	a_3	0.32
	a_{Me}	0.21
	a_5	0.14
	a_6	0.56
	T.W.	0.13
XXVII	Σa_H	0.38
	a_{Me}	0.56
	a_3	0.36
	T.W.	0.47
XXVIII	a_3+a_6	0.11
	a_3	0.63
	a_5	0.63
	a_6	0.11
	a_{OMe}	0.59
XXX	$6a_{OMe}$	0.69
	$2a_H$	0.45
XXXI	a_H	0.50
	a_{Me}	0.63
	T.W.	0.84

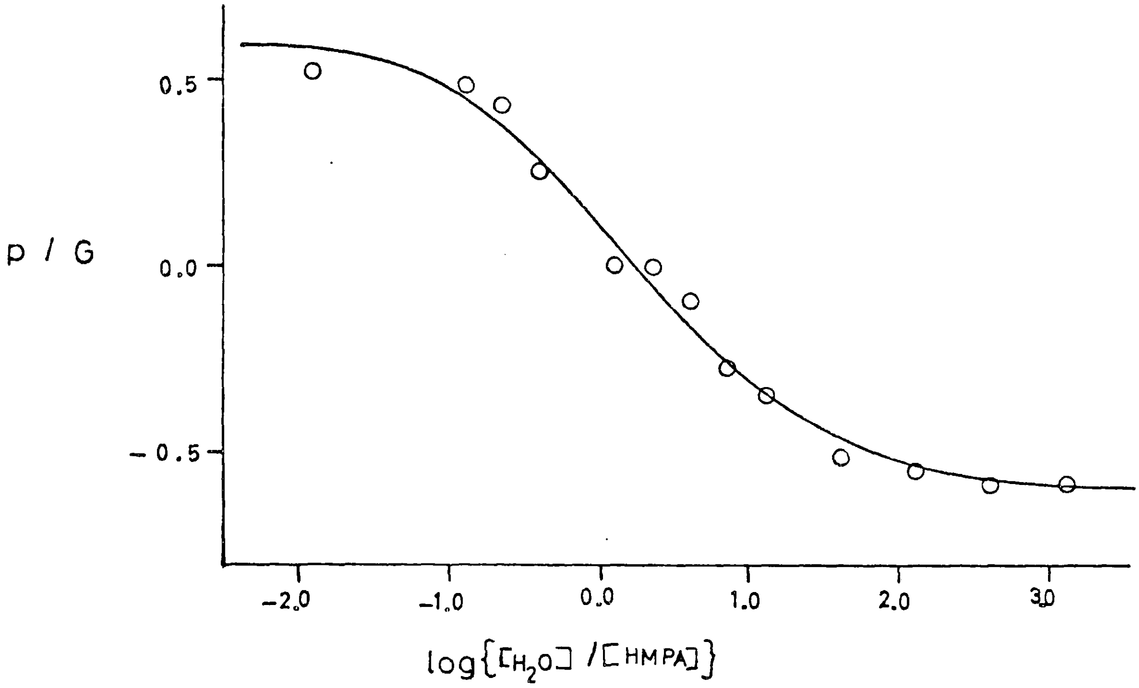


Fig. 12: Variation in a_6 for 3-methoxy-1.2-benzosemiquinone (IV) with solvent composition: p against log x.

sign. The same phenomenon is observed for VI and XXXII (4,5-methlenedioxy- and 4,5-dimethoxy-o-benzosemiquinone, respectively); some spectra for VI are presented in Fig. 13.

It is of interest that five of the seven "best" radicals in Table 9, as suggested by the values of r, are o-semiquinones (II-VI), the remaining two being 2-methoxy- and 2,6-di-t-butyl-p-benzosemiquinone (I and XXVIII, respectively). Omitting XXVIII, in which the change in spectral parameters is too small in other solvents, these six radicals were selected for further study.

3. Equilibrium Constants in Other Solvent Systems

Having verified that the treatment presented in Ch. 3 leads to reasonably consistent equilibrium constants in H_2O-HMPA (Table 9), the method was extended to H_2O-DMSO, H_2O-DMF, EtOH-HMPA and EtOH-H_2O. Initially, a change in the aprotic solvent was studied: Tables 11 and 12 contain equilibrium constants determined in the H_2O-DMSO and H_2O-DMF systems, respectively. In general, the linear regression (with the exception of II) is less satisfactory than in H_2O-HMPA, but is nonetheless acceptable. This result is expected in view of the data presented in Table 7.

Table 13 lists equilibrium constants obtained in the EtOH-HMPA system. Serious practical difficulties were

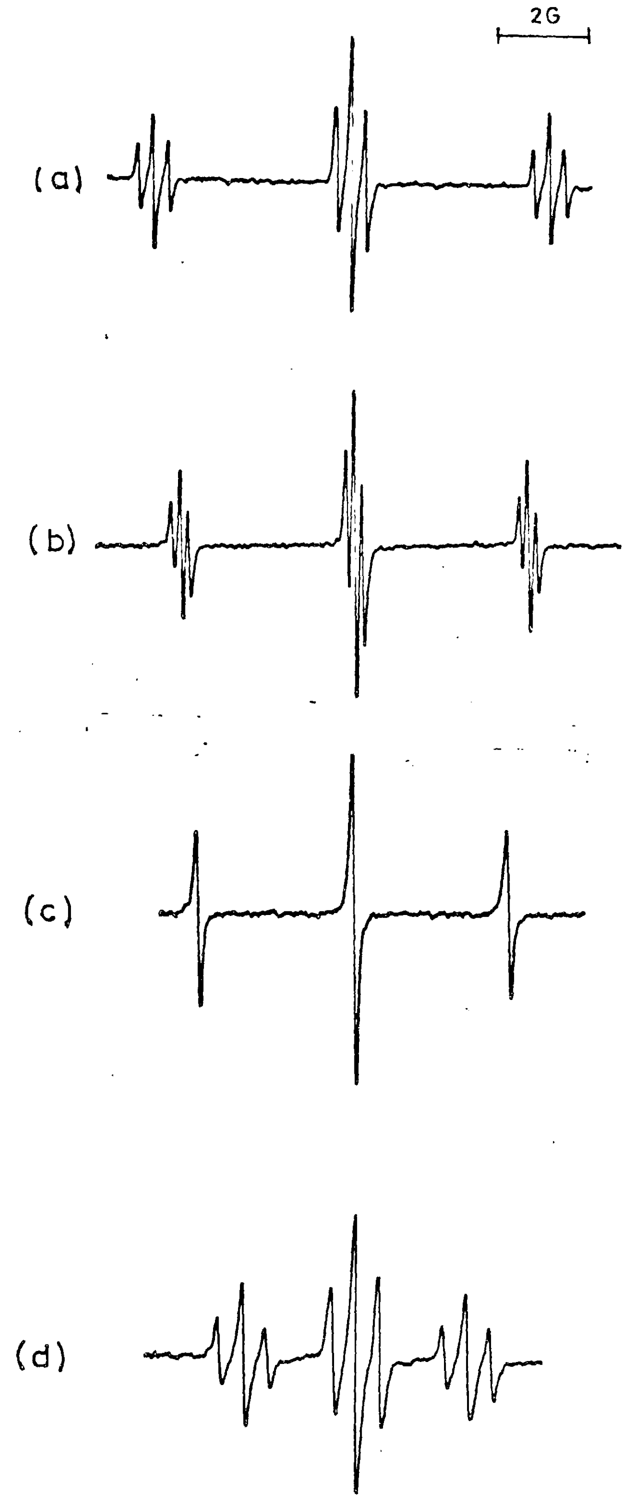
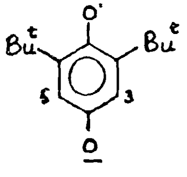


Fig. 13: Spectra of 4,5-methylenedioxy-1,2-benzosemiquinone (VI) in H_2O-HMPA, showing change of sign in ring proton hyperfine splitting.

(a) Pure water : $a_{3,6}$ = (-)0.33 G
(b) x = 19.93 : $a_{3,6}$ = (-)0.17 G
(c) x = 6.51 : $a_{3,6}$ = 0.00 G
(d) Pure HMPA : $a_{3,6}$ = 0.50 G

Table 11: Equilibrium Constants in H_2O-DMSO

(i) Radical	Sol-vent	a_3	a_4 (/G$\pm$0.03)	a_5	a_6	K	r	Parameter used
 I	H_2O DMSO	1.31 2.01		1.31 2.01		(i)2.26 (ii) 1.81	0.993 0.992	T.W.=$2a_{3,6}$

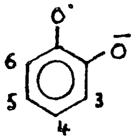
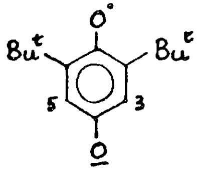
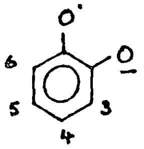
(ii)Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	K	r	Parameter used
Unsubstituted	H_2O	0.75	3.69	3.69	0.75	(i)0.57	0.999	$2a_{3,6}$
II	DMSO	1.39	3.45	3.45	1.39	(ii)0.57	1.000	
3-CH_3	H_2O	a_{Me}=0.63	2.85	4.13	0.28	(i)0.48	0.997	T.W.
III	DMSO	a_{Me}=1.00	2.80	3.70	1.00	(ii)0.37	0.993	
3-OCH_3	H_2O	a_{OMe}=0.65	1.25	4.76	-0.59	(ii)0.63	0.992	a_6
IV	DMSO	a_{OMe}=0.60	1.60	4.00	0.18			
4-CH_3	H_2O	0.07	a_{Me}=4.89	3.89	0.98	(i)0.24	0.956	T.W.
V	DMSO	0.80	a_{Me}=4.08	3.62	1.51	(ii)0.26	0.954	

Table 12: Equilibrium Constants in H_2O-DMF

(i) Radical	Sol-vent	a_3	a_4 (/G±0.03)	a_5	a_6	K	r	Parameter used
 I	H_2O	1.31		1.31		(i)2.42	0.997	T.W.=$2a_{3,5}$
	DMF	2.12		2.12		(ii)2.71	0.992	
(ii)Substituents in	Sol-vent	a_3	a_4	a_5	a_6	K	r	Parameter used
								
Unsubstituted	H_2O	0.75	3.69	3.69	0.75	(i)0.54	0.991	$2a_{3,6}$
II	DMF	1.28	3.48	3.48	1.28	(ii) 0.45	0.999	
3-CH_3	H_2O	a_{Me}=0.63	2.85	4.13	0.28	(i)0.58	0.998	T.W.
III	DMF	a_{Me}=1.06	2.90	3.66	0.98	(ii)0.48	0.998	
3-OCH_3	H_2O	a_{OMe}=0.65	1.25	4.76	-0.59	(i)1.07	0.991	a_6
IV	DMF	a_{OMe}=0.60	1.75	4.00	0.20	(ii)0.91	0.996	
						(i)0.72	0.950	a_5
						(ii)0.41	0.995	

cont.

Table 12 continued:

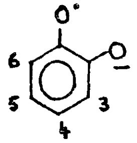
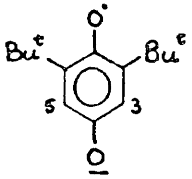
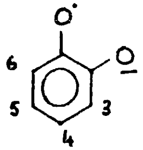
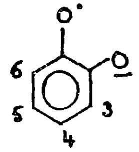
(ii)Substituents in 	Solvent	a_3	a_4	a_5	a_6	K	r	Parameter used
4-CH_3 V	H_2O DMF	0.07 0.89	a_{Me}=4.89 a_{Me}=4.01	3.89 3.65	0.98 1.60	(i)0.97	0.978	a_3
4,5-OCH_2O	H_2O	-0.33	a_{CH_2}=4.22	a_{CH_2}=4.22	-0.33	0.71		a_{CH_2}
VI	DMF	0.43	a_{CH_2}=2.52	a_{CH_2}=2.52	0.43	1.78		$2a_{3,6}$

Table 13: Equilibrium Constants in EtOH-HMPA

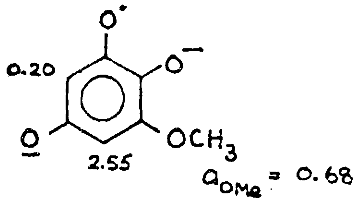
(i) Radical	Sol-vent	a_3	a_4 (/G±0.03)	a_5	a_6	K	r	Parameter used
 I	EtOH	1.21		1.21		(i)1.27	0.998	T.W.=$2a_{3,5}$
	HMPA	2.25		2.25		(ii)1.46	0.998	
(ii) Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	K	r	Parameter used
Unsubstituted	EtOH	0.93	3.59	3.59	0.93	(i)0.99	0.985	$2a_{3,6}$
II	HMPA	1.56	3.34	3.34	1.56	(ii)0.74	0.996	
$3\text{-}CH_3$	EtOH	$a_{Me}=0.80$	2.80	4.07	0.44	(i)0.87	0.944	a_6
III	HMPA	$a_{Me}=1.06$	2.83	3.54	1.06	(ii)0.53	0.966	
$3\text{-}OCH_3$	EtOH	$a_{OMe}=0.65$	1.30	4.59	-0.40	(i)0.59	0.995	a_5
IV	HMPA	$a_{OMe}=0.47$	1.90	3.78	0.46	(ii)0.49	0.995	
						(i)0.67	0.994	a_4
						(ii)0.65	0.993	

cont.

Table 13 continued:

(ii)Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	K	r	Parameter used
4-CH_3	EtOH	0.33	a_{Me}=4.47	3.70	1.10	(i)0.78	0.997	a_3
V	HMPA	1.00	a_{Me}=3.85	3.55	1.69	(ii)0.72	0.989	
4,5-OCH_2O	EtOH	-0.08	a_{CH_2}=3.64	3.64	-0.08	(i)0.65	0.996	$2a_{CH_2}$
VI	HMPA	0.50	a_{CH_2}=2.39	2.39	0.50	(ii)0.66	0.999	

encountered in this system due to the formation of secondary[115] and dimeric radical species;[125] these produced spurious lines in the e.s.r. spectra of the required radicals towards the ethanol end of the solvent range. For example, in solutions of high ethanol concentration 3-methoxycatechol gave rise to radical XXXV:



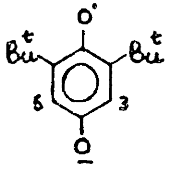
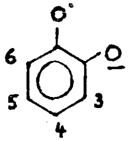
XXXV

similar species were obtained from 4-methyl- and 4,5-methylenedioxycatechol.

Examination of the spectra of VI in EtOH-HMPA indicates that $a_{3,6}$ is of opposite sign in HMPA to that in ethanol, i.e. $a_{3,6}$ is negative in both water and ethanol. This is confirmed by spectra in the EtOH-H_2O system (results in Table 14) which demonstrate that $a_{3,6}$ does not pass through zerowhen the protic solvent is changed from water to ethanol. The result for IV is confirmed in an analogous manner.

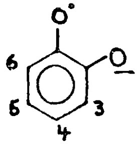
Due to the smaller variations in the e,s.r. parameters in EtOH-H_2O compared with protic-aprotic mixtures, coupled with the inherent difficulties in obtaining "clean" spectra in ethanol, it was not possible to construct linear plots for I, III-V. K was estimated from p against log x plots for these species.

Table 14: Equilibrium Constants in EtOH-H_2O

(i) Radical	Solvent	a_3	a_4 ($/G \pm 0.03$)	a_5	a_6	K	r	Parameter used
 I	H_2O EtOH	1.31 1.21		1.31 1.21		0.2		$2a_{3,5}^{\not+}$
(ii) Substituents in 	Solvent	a_3	a_4	a_5	a_6	K	r	Parameter used
Unsubstituted	H_2O	0.75	3.69	3.69	0.75	(i)0.36	0.994	$2a_{3,6}$
II	EtOH	0.93	3.59	3.59	0.93	(ii)0.34	0.998	
$3-CH_3$	H_2O	$a_{Me}=0.63$	2.85	4.13	0.28	0.45		T.W.
III	EtOH	$a_{Me}=0.80$	2.80	4.07	0.44			
$3-OCH_3$	H_2O	$a_{OMe}=0.65$	1.25	4.76	-0.59	0.54		T.W.
IV	EtOH	$a_{OMe}=0.65$	1.30	4.59	-0.40			

cont.

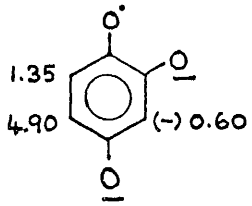
Table 14 continued:

(ii)Substituents in 	Sol-vent	a_3	a_4	a_5	a_6	K	r	Parameter used
4-CH_3	H_2O	0.07	a_{Me}=4.89	3.89	0.98	0.30		T.W.
V	EtOH	0.33	a_{Me}=4.47	3.70	1.10			
4,5-OCH_2O	H_2O	-0.33	a_{CH_2}=4.22	a_{CH_2}=4.22	-0.33	(i)0.25	0.996	$2a_{CH_2}$
VI	EtOH	-0.08	a_{CH_2}=3.64	a_{CH_2}=3.64	-0.08	(ii)0.21	0.999	

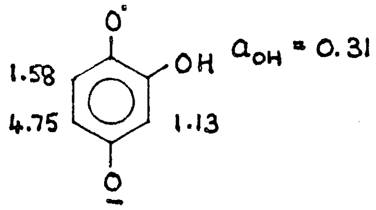
† K approximate as total change is only 0.2 G.

4. Trihydroxy Compounds

As well as the smooth changes with varying solvent ratio typical of the radicals in Tables 9-14, the e.s.r. spectra of the semiquinone from 1,2,4-trihydroxybenzene exhibit an abrupt change in the region $[H_2O]/[HMPA]=2-3$ (Table 15). It is apparent from Fig. 14, some spectra obtained from the trihydroxy compound in H_2O-HMPA mixtures, and from Fig. 15, in which the observed e.s.r. parameters for the radicals produced are plotted as a function of $\log\{[H_2O]/[HMPA]\}$, that there is a change in the nature of the radical. In water the dianion XXXVI is produced, giving rise to an eight-line spectrum. However, when the HMPA concentration is increased beyond the region $[H_2O]/[HMPA]=2$, XXXVI gives way to the corresponding hydroxysemiquinone, XXXVII, which has the following parameters in HMPA:



XXXVI/H_2O



XXXVII/HMPA

Table 15: E.s.r. Parameters of Radicals from 1,2,4-Trihydroxybenzene in H_2O-HMPA

$x = \frac{[H_2O]}{[HMPA]}$	log x	a_3	a_5 (/G$\pm$0.03)	a_6	a_{OH}
H_2O		-0.60	4.90	1.35	
196.6	2.29	-0.61	4.92	1.35	
86.3	1.94	-0.60	4.90	1.39	
48.5	1.69	-0.60	4.91	1.39	
29.6	1.47	-0.60	4.92	1.40	
12.4	1.09	-0.58	4.93	1.40	
10.6	1.02	-0.58	4.99	1.37	
9.72	0.99	-0.57	5.00	1.41	
9.31	0.97	-0.57	5.00	1.41	
7.92	0.90	-0.58	5.03	1.41	
6.90	0.84	-0.58	5.09	1.42	
3.26	0.51	-0.51	5.09	1.42	
2.11	0.32	0.90	4.25	1.75	0.42
1.01	0.003	0.94	4.40	1.70	0.38
0.22	-0.65	1.10	4.70	1.61	0.34
0.20	-0.71	1.05	4.60	1.61	0.30
0.13	-0.88	1.10	4.70	1.60	0.31
0.12	-0.92	1.12	4.68	1.59	0.31
0.01	-1.89	1.15	4.79	1.60	0.31
0.005	-2.31	1.12	4.79	1.59	0.31
0.002	-2.76	1.13	4.77	1.59	0.31
HMPA		1.13	4.75	1.58	0.31

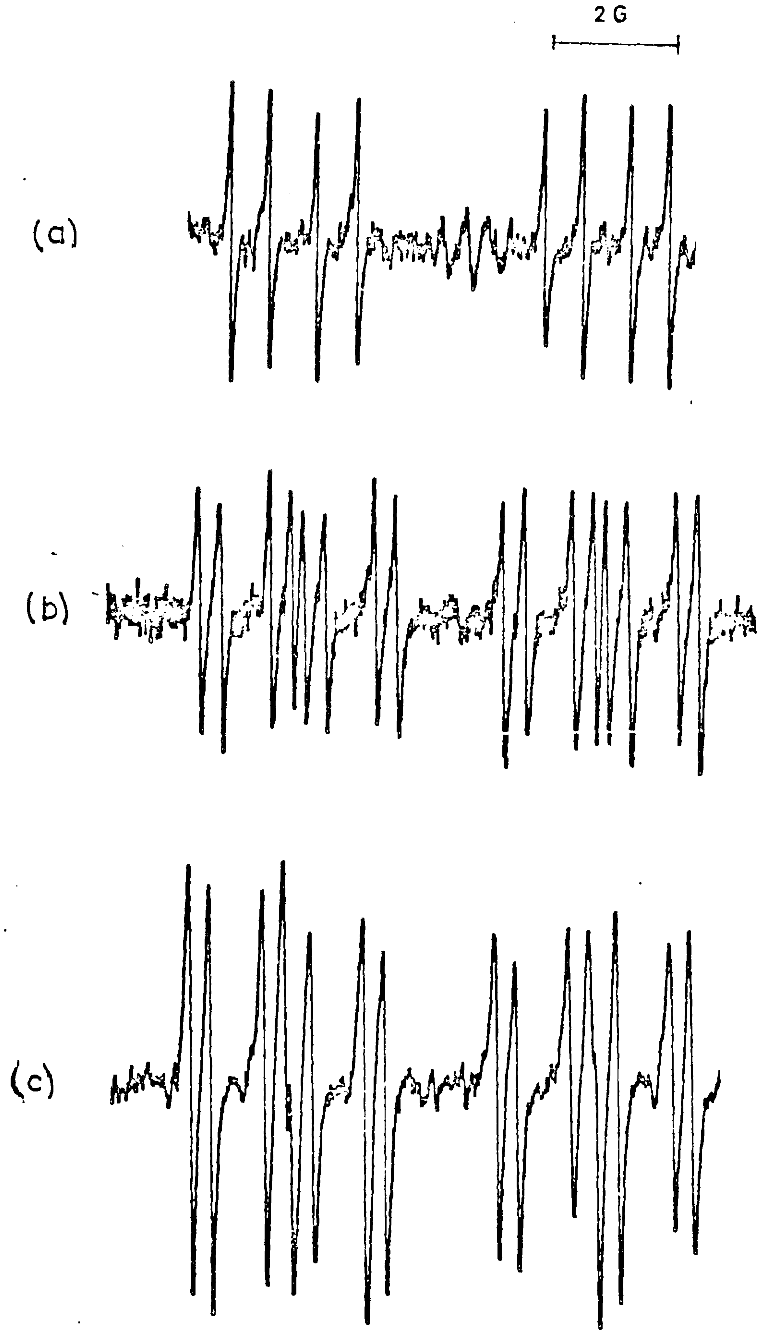


Fig. 14: Spectra from 1,2,4-trihydroxybenzene in H_2O-HMPA. (a) Pure water; (b) x=0.22; (c) Pure HMPA.

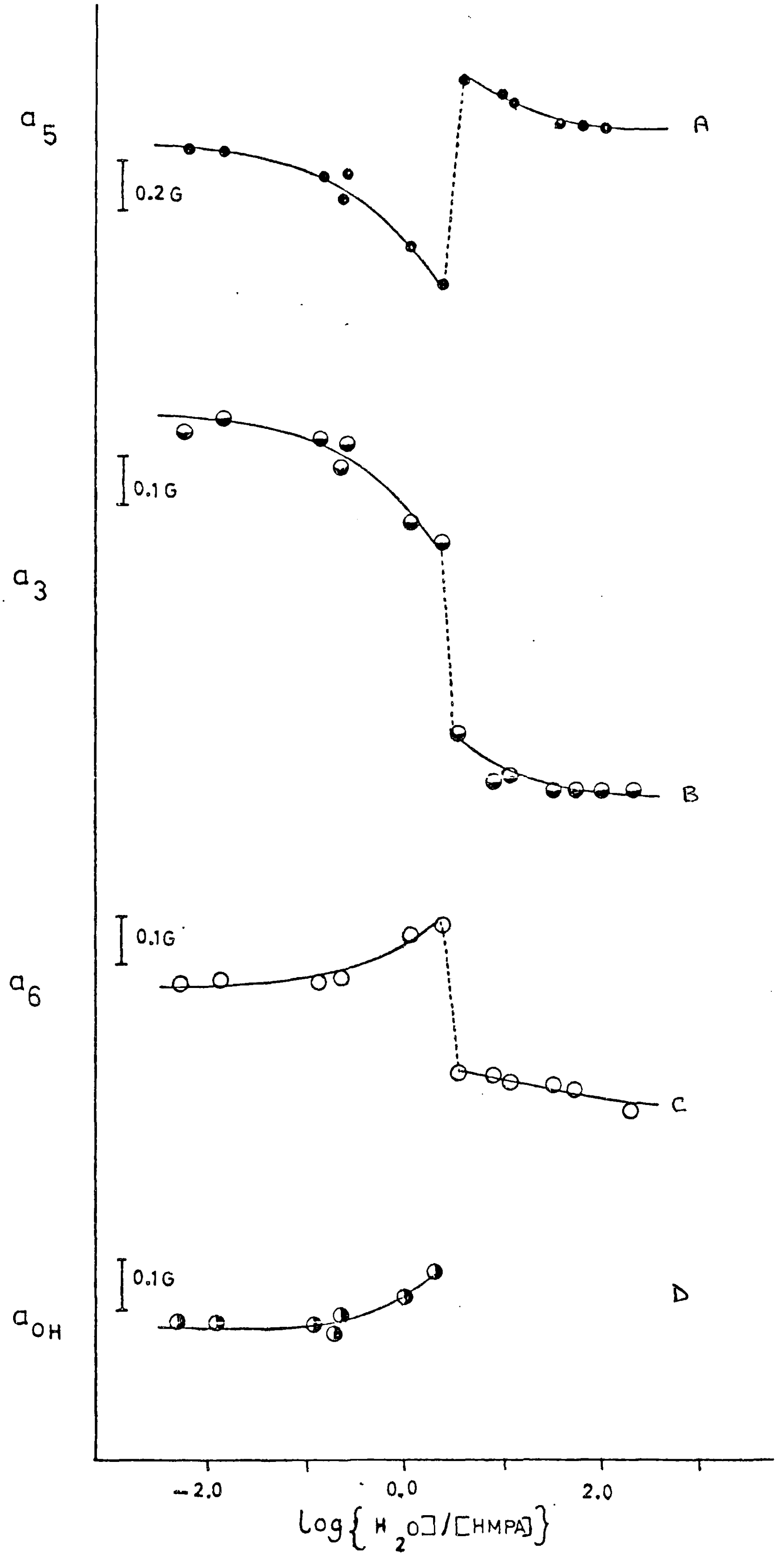
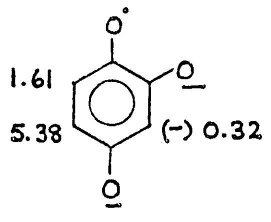


Fig. 15: Radicals from 1,2,4-trihydroxybenzene in H_2O-HMPA: plot of coupling constants against log x.

The assignment of these hyperfine splittings will be rationalised later.

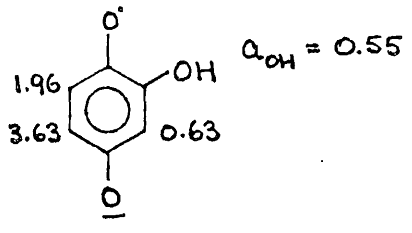
Using the procedure outlined in Ch. 3, it is possible to use the curves of Fig. 15 to obtain a rough estimate of the equilibrium constants for XXXVI and XXXVII. For example, for curve A, if it is assumed that the midpoint of the sigmoid curve expected for XXXVI occurs at the centre of the break, then $\log K^{-1}=(0.32+0.51)/2=0.42$. Now, in going from pure water to $\log x=0.42$ a_5 has changed from 4.90 to 5.14 G. Therefore, the predicted value of a_5 in HMPA is 5.38 G. Using this value of a_5 as p_2, a plot of $1/(p-p_2)$ against x^{-1} may be drawn over the region pure water to $\log x=0.51$. The straight line plot ($r=0.984$) demonstrates, from the intercept, that $p_2=5.36$ G, in good agreement with that obtained from the log plot, and that $K=0.47$ for XXXVI in H_2O-HMPA. This value of K was then used to find the other coupling constants for XXXVI in HMPA by extrapolating curves B-D (Fig. 15) to the value $\log x=\log K^{-1}=0.33$. The extrapolation is valid since it has been shown (Ch. 4-2) that the same equilibrium constant is obtained, regardless of which parameter is plotted, provided the radical does not contain alkyl-/alkoxy- substituents. In this manner the following values were obtained for XXXVI in HMPA:



XXXVI/HMPA

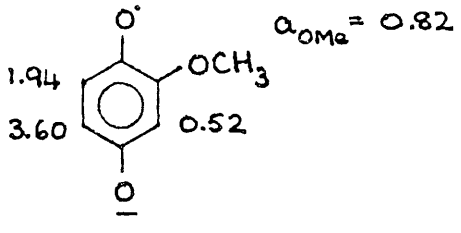
These results are summarised in Table 16.

The calculated parameters for XXXVII in water (Table 16) were obtained in an analogous manner, using the experimental results for this radical in HMPA. In this instance, the plot $1/(p-p_1)$ against x, where $p=a_5$, (r=0.988) was used to establish that K=0.39 for XXXVII in H_2O-HMPA. The predicted values in water are:



XXXVII/H_2O

The assignments of the coupling constants were made by comparison with XXVIII in H_2O:

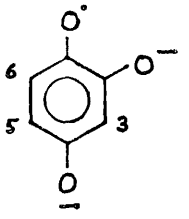


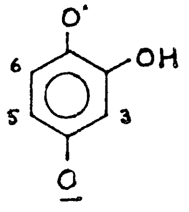
XXVIII/H_2O

The coupling constants for the 2-hydroxy- and 2-methoxy-radicals correspond closely, confirming that for XXXVII a_{OH} has the value 0.31 G in HMPA.

Fig. 16 and Table 17 show that the same phenomenon exists

Table 16: Observed and Calculated Coupling Constants for Radicals from 1,2,4-Trihydroxybenzene

Radical	Parameter p	Value Observed in H_2O (/G)	Value at log x=0.42≠	Calculated value in HMPA
 XXXVI	a_3	-0.60	-0.46	-0.32
	a_5	4.90	5.14	5.38
	a_6	1.35	1.48	1.61

Radical	Parameter p	Value Observed in HMPA	Value at log x=0.41≠	Calculated Value in H_2O
 XXXVII	a_{OH}	0.31	0.43	0.55
	a_3	1.13	0.88	0.63
	a_5	4.75	4.19	3.63
	a_6	1.58	1.77	1.96

≠ Value obtained at log x= log K^{-1} by extrapolation of p against log x plot (Fig. 15).

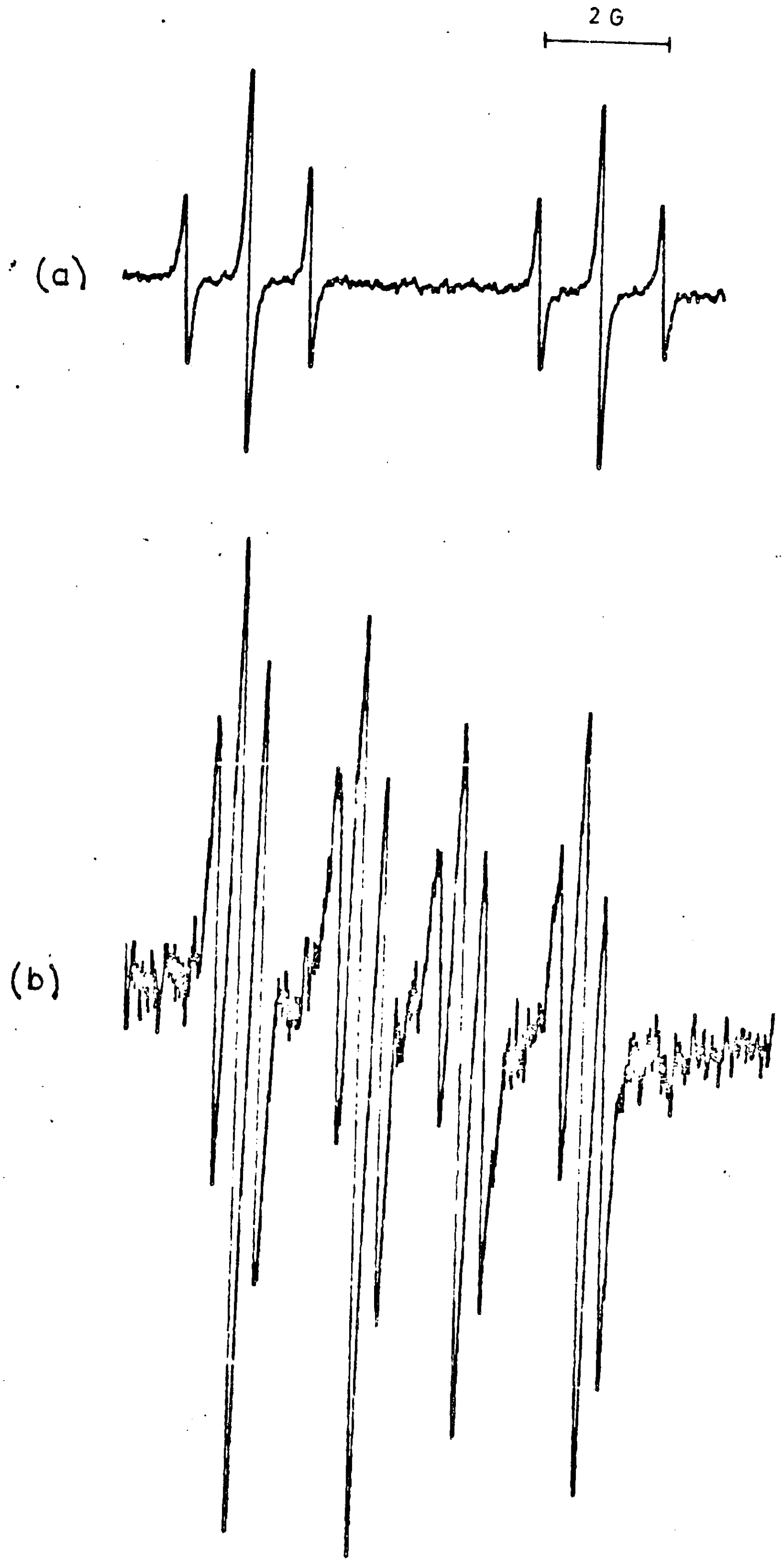


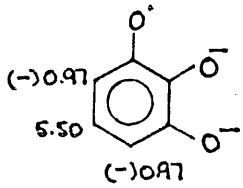
Fig. 16: Spectra from pyrogallol

(a) In water and (b) HMPA.

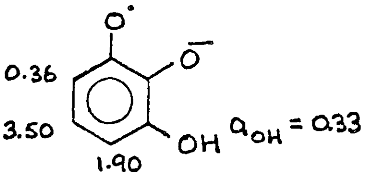
Table 17: E.s.r. Parameters of Radicals from 1,2,3-Trihydroxybenzene (Pyrogallol) in H_2O-HMPA

$x=\frac{[H_2O]}{[HMPA]}$	log x	a_4	a_5 (/G±0.03)	a_6	a_{OH}
H_2O		-0.97	5.50	-0.97	
935.0	2.97	-0.97	5.51	-0.97	
453.6	2.66	-0.98	5.50	-0.98	
180.1	2.26	-0.98	5.52	-0.98	
95.4	1.98	-0.98	5.51	-0.98	
28.8	1.46	-0.98	5.48	-0.98	
9.69	0.99	-0.95	5.32	-0.95	
3.30	0.52	-0.92	5.11	-0.92	
2.10	0.32	1.58	3.90	0.0	0.35
1.45	0.16	1.60	3.80	0.09	0.31
1.23	0.09	1.65	3.79	0.04	0.33
1.18	0.07	1.61	3.85	0.05	0.36
1.11	0.04	1.63	3.81	0.04	0.35
1.00	0.00	1.71	3.75	0.14	0.31
0.52	-0.28	1.75	3.52	0.40	0.34
0.35	-0.46	1.80	3.50	0.22	0.35
0.26	-0.59	1.83	3.48	0.35	0.34
0.20	-0.70	1.85	3.49	0.27	0.34
0.11	-0.96	1.88	3.50	0.38	0.34
0.009	-2.06	1.90	3.45	0.36	0.33
0.002	-2.76	1.90	3.50	0.35	0.33
HMPA		1.90	3.50	0.36	0.33

for pyrogallol (1,2,3-trihydroxybenzene). In water and HMPA XXXVIII and XXXIX, respectively, were obtained. Fig. 17 shows

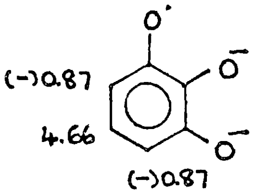


XXXVIII/H_2O



XXXIX/HMPA

plots of the coupling constants observed in H_2O-HMPA against log x. Using the method adopted for 1,2,4-trihydroxybenzene, a plot of $1/(p-p_2)$ against x^{-1}, where $p=a_5$, (r=0.998) indicated that K is 0.33 (i.e. log $K^{-1}=0.49$) for XXXVIII in H_2O-HMPA. The values predicted for XXXVIII in HMPA are:



XXXVIII/HMPA

Similarly, a plot of $1/(p-p_1)$ against x for a_5 gave K=0.36 (log $K^{-1}=0.44$) for XXXIX (r=0.998). For this radical it was also possible to construct a linear plot using a_6, and this yielded the same value within experimental error; K=0.40 (log $K^{-1}=0.40$, r=0.969). The values predicted for XXXIX in

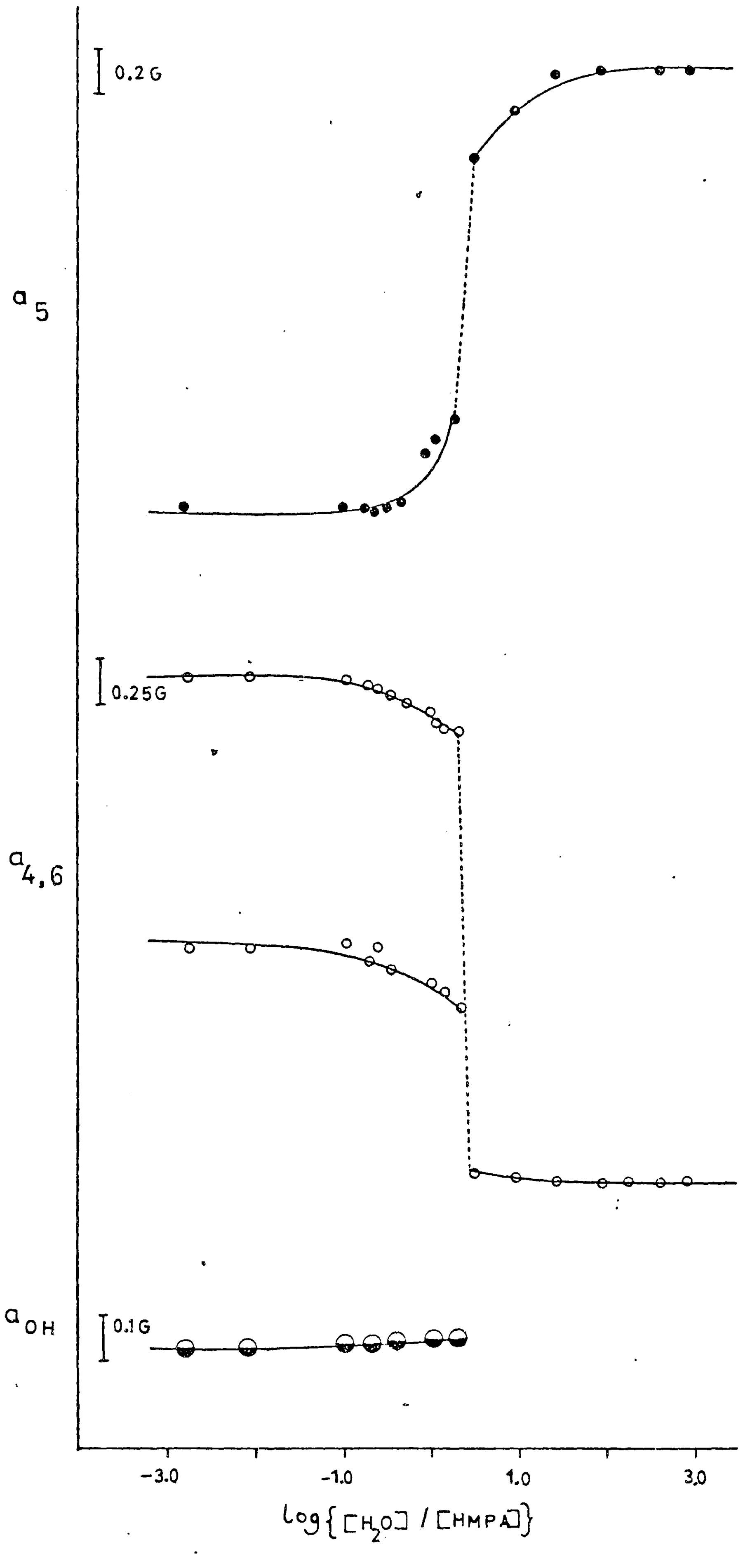
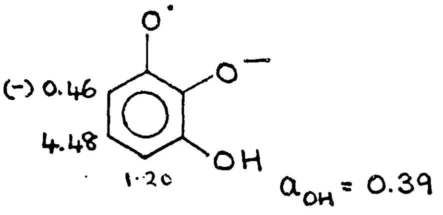


Fig. 17: Radicals from pyrogallol in H_2O-HMPA: plot of coupling constants against log x.

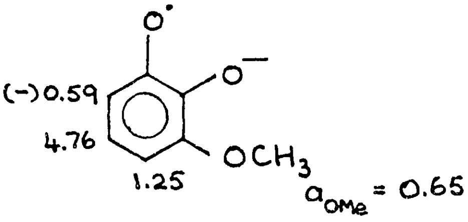
water are:



XXXIX/H_2O

This situation is summarised in Table 18.

The assignments of the coupling constants for XXXIX (Table 18) in water are based on those of IV (Ch. 4-2).

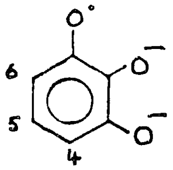


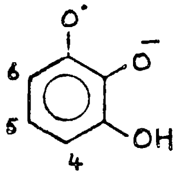
IV/H_2O

In XXXIX a_6, which is predicted to be (-)0.46 G in water, has the value 0.36 G in HMPA; therefore, in HMPA, a_{OH} must be 0.33 G. The magnitude and direction of the changes in the e.s.r. parameters from water to HMPA are highly reminiscent of those for IV (Table 9).

The results from the trihydroxybenzenes suggest that around the region $[H_2O]/[HMPA]=2$ the solvent structure is changing in such a way that at higher HMPA concentrations the dianion radicals can no longer persist. This assertion was

Table 18: Observed and Calculated Coupling Constants for Radicals from Pyrogallol

Radical	Parameter p	Value Observed in H_2O (/G)	Value at log x=0.49†	Calculated Value in HMPA
 XXXVIII	$a_{4,6}$	-0.97	-0.92	-0.87
	a_5	5.50	5.08	4.66

Radical	Parameter p	Value Observed in HMPA	Value at log x=0.42†	Calculated Value in H_2O
 XXXIX	a_{OH}	0.33	0.36	0.39
	a_4	1.90	1.55	1.20
	a_5	3.50	3.99	4.48
	a_6	0.36	-0.05	-0.46

† Value at log x=log K^{-1} from p against log x plot.

investigated independently using n.m.r. (Ch. 5).

Further examples of this specific solvent effect are provided by 4-methyl- and 5-methylpyrogallol. The first trihydroxybenzene gives rise to radicals XL and XLI (Table 19), and the second to XLII and XLIII. (Structure XLI is favoured over the alternative, in which the hydroxy- and methyl- groups are ortho to each other, on steric grounds). Clearly, in HMPA hydroxysemiquinones (XLI, XLIII) are formed, as opposed to dianions in water (XL, XLII). The assignment of a_{OH} for XLI and XLIII in HMPA was guided by the magnitude of a_{OH} in XXXVII and XXXIX. For XLII and XLIII it was possible to observe both species simultaneously in a few H_2O-HMPA mixtures. The dianion, XLII, was observed from pure water to $x=2.30$ ($\log x=0.36$), and the corresponding 3-hydroxy-5-methyl-1,2-benzosemiquinone, XLIII, in the solution $x=9.69$ and solutions of higher HMPA concentration (Table 19). These observations support the statement that dianions cannot exist, under the conditions of a normal "run", unless $x > 2.0$.

5. Correlation of E.s.r. Parameters with Some Measures of Solvent Polarity

In Table 20 the hyperfine splitting constants of three representative semiquinones (I, II and V) are presented, together with some physical properties of the solvents in which

Table 19: Coupling Constants for Radicals from Methyl-substituted Trihydroxybenzenes in Water and HMPA.

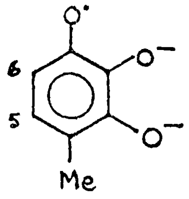
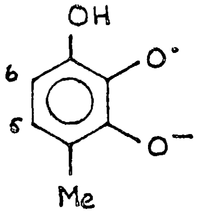
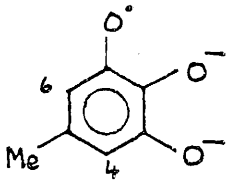
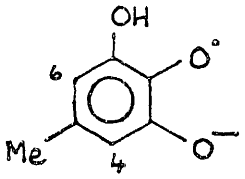
Radical	Solvent	Coupling Constants (/G±0.03)	
 XL	H_2O	$a_{Me}=1.00$ $a_6=0.90$	$a_5=5.65$
 XLI	HMPA	$a_{Me}=2.73$ $a_5=3.55$	$a_{OH}=0.28$ $a_6=0.55$
 XLII	H_2O x=2.30	$a_{Me}=6.30$ $a_{Me}=5.72$	$a_{4,6}=0.82$ $a_{4,6}=0.83$
 XLIII	x=9.69	$a_{Me}=5.25$ $a_H=1.49$	$a_{OH}=0.40$ $a_H=0.61$
	HMPA	$a_{Me}=4.04$ $a_{Me}=2.01$	$a_{OH}=0.35$ $a_H=0.0$

Table 20: Correlation of Coupling Constants of Radicals I, II and $V^{\neq}$ with Some Solvent Polarity Parameters*

Solvent	ε	Z /kcal mol^{-1}	$E_T(30)$ /kcal mol^{-1}	Radical I $2a_{3,5}$(/G)	II $2a_{3,6}$	V a_3
1. HMPA	29.6	62.8	40.9	4.50	3.12	1.00
2. Acetone	20.70	65.5	42.2	3.75		
3. DMF	37.0	68.4	43.8	4.24	2.93	0.89
4. DMSO	46.68	71.1	45.0	4.02	2.78	0.80
5. Sulpholane, $TMSO_2$	43.3	77.5	44.0	3.60	2.48	0.60
6. Ethanol	24.55	79.6	51.9	2.42	1.88	0.33
7. Methanol	32.7	83.6	55.5	2.35	1.84	0.31
8. Formamide	111.0	83.3	56.6	2.95	1.96	0.38
9. Water	78.39	94.6	63.1	2.62	1.50	0.07
10. 2-Methyl-2-propanol, t-BuOH	12.47	71.3	43.9	2.36	1.80	
11. Ethanediol	37.7	75.1	56.3	2.35	1.77	
12. 2-Propanol	19.92	76.3	48.6	3.58		
13. 1-Butanol	17.51	77.7	50.2	2.40	1.91	
14. 1-Propanol	20.33	78.3	50.7	2.48		

≠ Radicals I, II and V are 2,6-di-t-butyl-1,4-benzosemiquinone, 1,2- and 4-methyl-1,2-benzosemiquinone, respectively.

* ε, Z and $E_T(30)$-values are taken from Ref. 24.

the spectra were determined. The e.s.r. parameters of I, II and V are plotted against ε, the dielectric constant of the solvent, in Fig. 18. Overall, the correlation is poor; this has been found for other radicals[21,50-52] by previous workers (Ch. 1-3, p. 29). However, for the solvents H_2O, DMF, DMSO and HMPA, which are of particular interest in the present study, the correlation between p and ε is 0.995, 0.989 and 0.990 for I, II and V respectively. The success of this correlation suggests that the coupling constants of a given radical in any of these solvent systems are a linear function of the dielectric constant.

Table 21 contains data for II in H_2O-EtOH and H_2O-DMSO mixtures, the only solvent systems for which sufficient dielectric constants are available[131] for a plot of p against ε to be drawn (Fig. 19). Over the entire concentration range water to ethanol, there is a straight line relationship between p and ε (r=0.998). This is also true of H_2O-DMSO solutions from pure DMSO to x=2.0 (r=0.993).

Coupling constants for I, II and V are plotted against the Z-value of the solvent (Table 20) in Fig. 20. For I a correlation with $E_T(30)$ is also given. (Z and $E_T(30)$ are defined in Ch. 1-3, pp. 29,30). The correlation between p and Z is generally good, and is better than that found when ε is employed (Fig. 18). The correlation between p and Z is 0.999, 0.998 and 0.998 for I, II and V, respectively, in the solvents water, DMF, DMSO and HMPA. For I, that between $E_T(30)$ and p is 0.998. The excellent correlation suggests that the e.s.r.

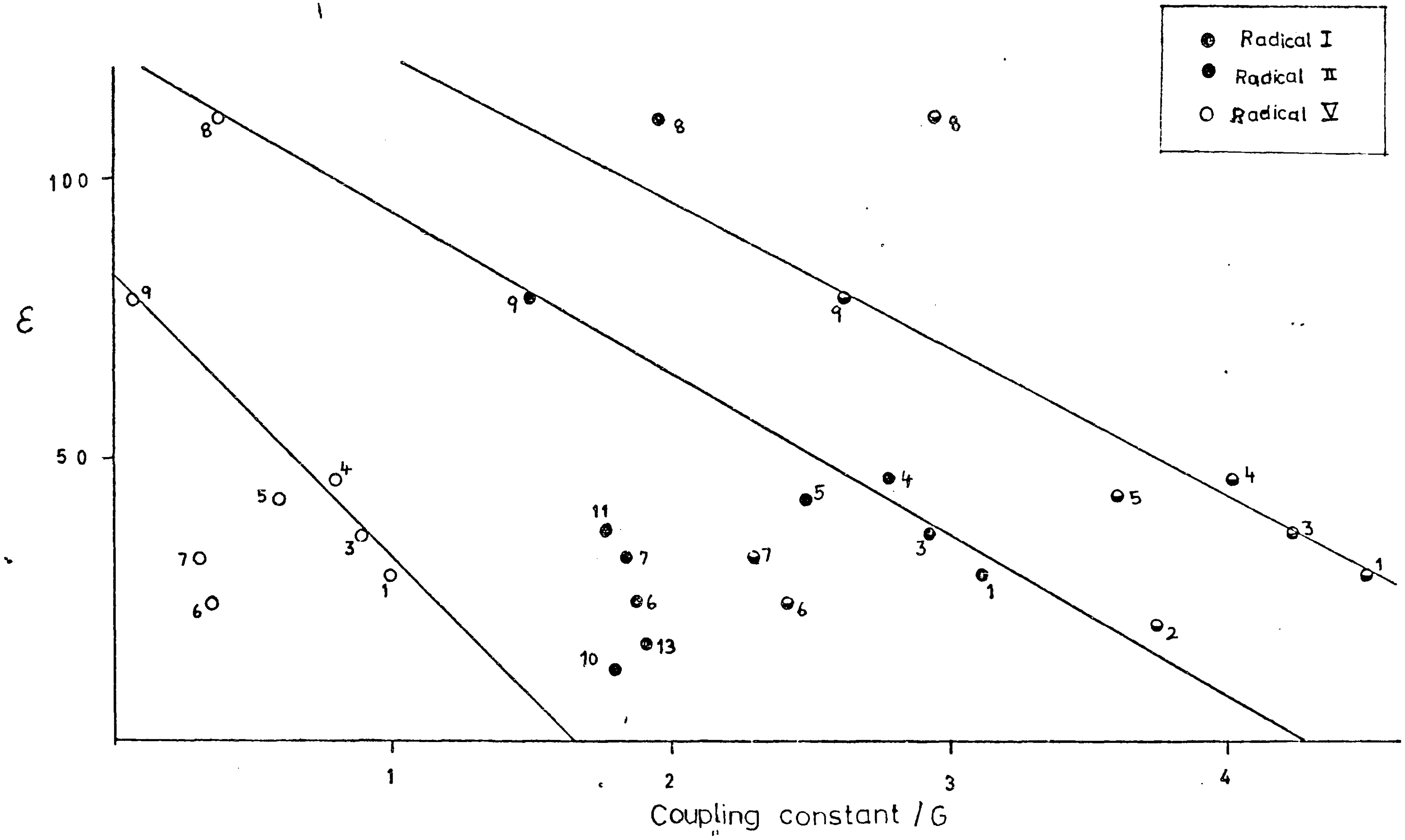


Fig. 18: Correlation of coupling constants of radicals I, II and V with the dielectric constant (ε) of the solvent. (Solvents are numbered as in Table 20).

Table 21: Correlation of Coupling Constants of Radical II with ε and Z for H_2O-EtOH and H_2O-DMSO Mixtures.

H_2O-EtOH

$x=\frac{[H_2O]}{[EtOH]}$	$2a_{3,6}$ (/G $\pm$0.03)	ε^{+}	Z* /kcal mol^{-1}
H_2O	p_1=1.50	78.4	94.46
100.16	1.53	76.5	94.0
32.89	1.54	73.9	93.4
17.52	1.56	70.8	92.75
9.97	1.59	66.0	91.75
4.89	1.66	58.3	90.0
3.32	1.70	53.2	88.75
2.54	1.72	49.3	87.90
2.04	1.73	46.2	87.0
1.83	1.75	44.2	86.6
1.61	1.76	43.0	86.2
1.40	1.77	41.3	85.6
1.23	1.77	40.0	85.1
1.02	1.79	38.0	84.4
0.82	1.79	36.1	83.7
0.75	1.81	35.3	83.3
0.61	1.83	33.8	82.75
0.58	1.82	33.4	82.6
0.51	1.81	32.5	82.25
0.41	1.83	31.5	81.8
0.30	1.84	30.0	81.25
0.21	1.85	28.9	80.6
0.10	1.87	27.7	80.0
0.08	1.87	27.5	80.0
0.03	1.88	26.8	79.5
EtOH	p_2=1.88	24.55	79.28

cont.

Table 21 continued:

H_2O-DMSO

$x=\frac{[H_2O]}{[DMSO]}$	$2a_{3,6}$ (/G $\pm$0.03)	$\varepsilon^{\dagger}$	Z /kcal mol^{-1}
H_2O	p_1=1.50	80.37	94.46
366.3	1.49	80.1	94.0
107.3	1.50	80.0	93.9
30.44	1.56	79.8	93.0
17.51	1.60	79.3	92.0
9.97	1.66	78.6	90.6
5.60	1.76	78.0	89.45
3.16	1.93	75.2	85.7
1.60	2.20	70.0	81.8
0.98	2.29	65.5	79.1
0.62	2.44	61.0	76.85
0.57	2.45	60.0	76.4
0.32	2.54	55.8	74.5
0.11	2.65	50.1	72.5
0.01	2.73	47.2	71.3
DMSO	p_2=2.77	47.1	71.24

† Dielectric constants for mixtures are taken from Ref. 131.

* Z-values from Ref. 132.

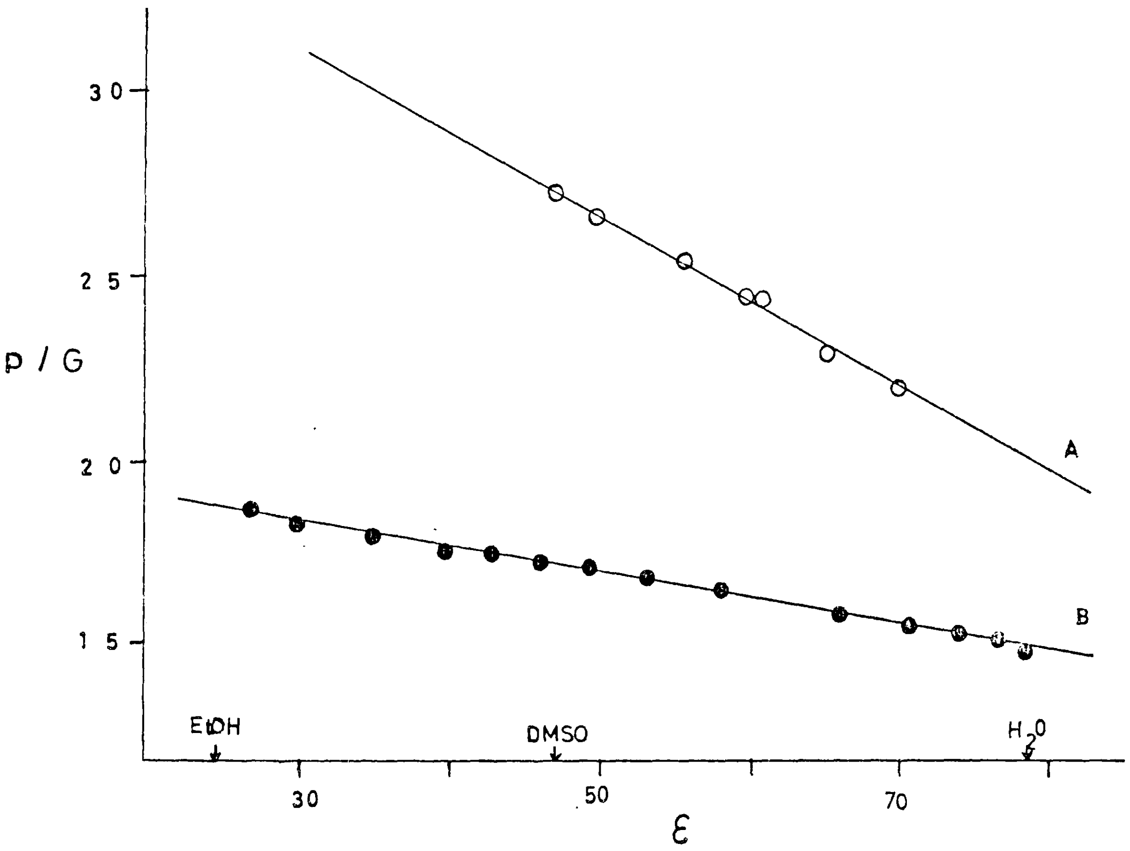


Fig. 19: Coupling constant $2a_{3,6}$ (p) for radical II as a function of the dielectic constant of the solvent. A, H_2O-DMSO mixtures over range x=0 - 2.0; B, H_2O-EtOH from pure water to pure ethanol.

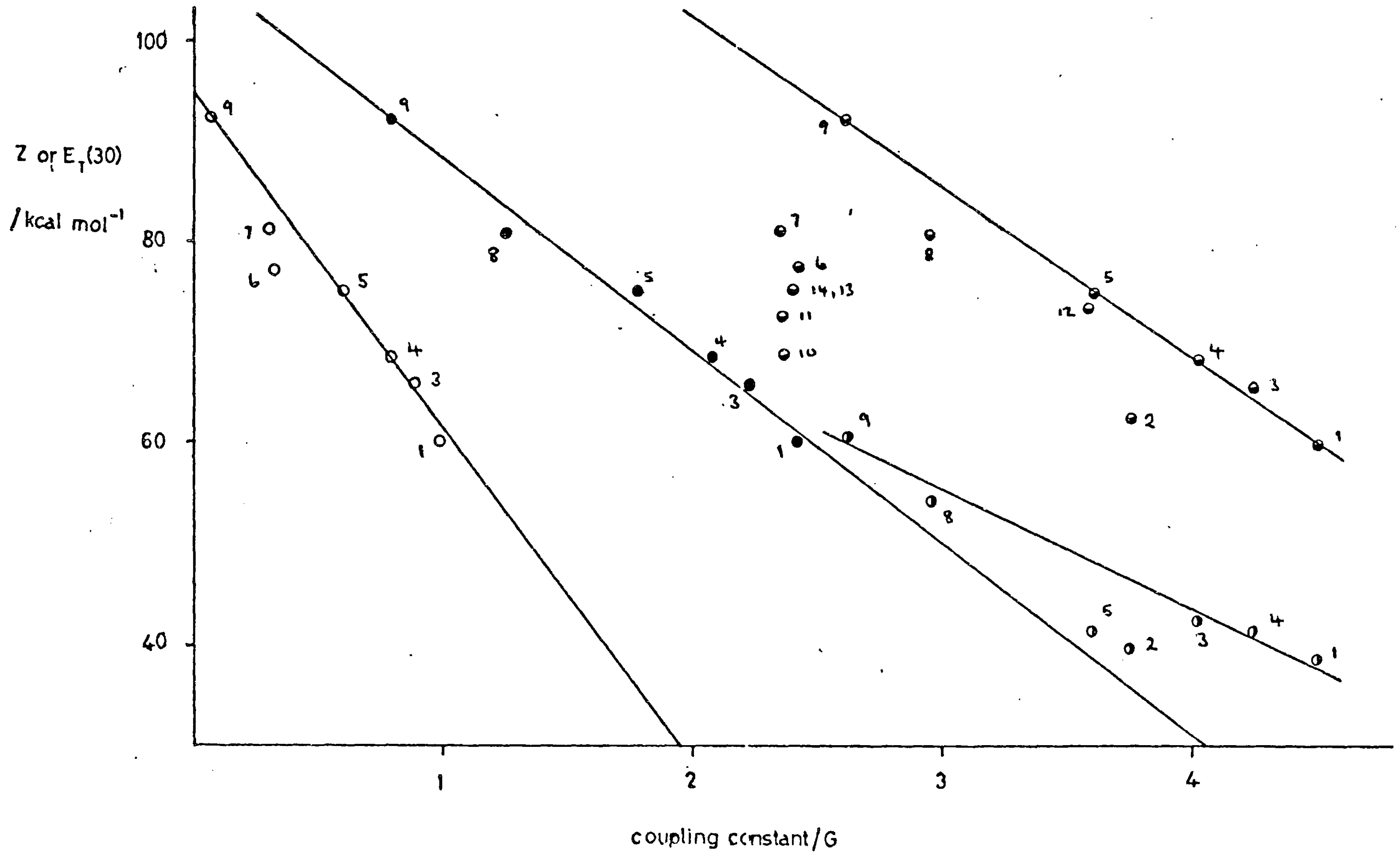


Fig. 20: Correlation of coupling constants of I, II and V with Z- and $E_T(30)$- values of the solvent. (Solvents are numbered as in Table 20).
o, Radical V; ●, Radical II ($2a_{3,6}$-0.7 plotted); ⊖, I:correlation with Z; ⦶, I:correlation with $E_T(30)$.

studies are measuring similar effects to those measured by the Z-value of the solvent.[113] In both studies it is the tendency to pull negative charge towards the solvent molecules which is involved: in one case the charge is derived from the semiquinone, and in the other from the alkyl-pyridinium salt used to determine Z.

The effect of changing solvent polarity within the series of mixtures used for a "run" is investigated in Fig. 21, in which $2a_{3,6}$ (radical II) is plotted against the Z-value of H_2O-EtOH and H_2O-DMSO mixtures[132] (Table 21). This radical was chosen rather than a methyl- or methoxy- substituted one for reasons outlined in Ch. 4-2. From pure EtOH to $[H_2O]/[EtOH]=2.0$ the hyperfine splitting is a linear function $(r=0.989)$ of Z, while in H_2O-DMSO mixtures the correlation $(r=0.999)$ is from pure water to pure DMSO. Z-values are not currently available for other protic-aprotic mixtures. Correlations between e.s.r. parameters and Z have been noted[21,50,56,57] for other radicals in pure solvents (Ch. 1-3, p. 31) but their success appears to depend on the nature of the radical and the type of solvent system studied. For example, for _p_-benzosemiquinone $a(^{13}C)$ and $a(^{17}O)$ are linearly related to the Z-values of solvents such as water, EtOH and DMSO,[56,57] whereas only a poor correlation is observed for 2,6-dimethyl-_p_-benzosemiquinone.[58-60] The major additional factor operative in the latter case is considered to be steric.[58] In the present study, the proton hyperfine splitting for the 2,6-di-_t_-butyl- substituted radical I, although a smooth function of Z, is not linearly related to

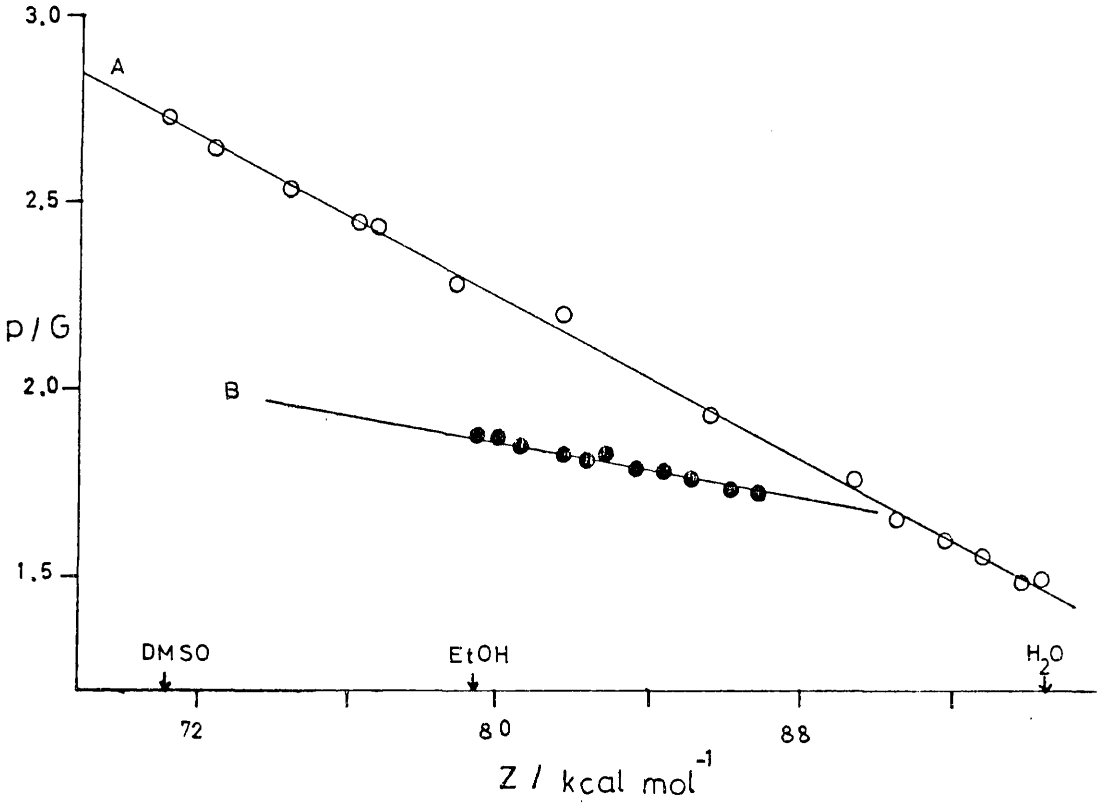


Fig. 21: Coupling constant $2a_{3,6}$ (p) for radical II as a function of the Z-value of the solvent.

A, H_2O-DMSO mixtures from pure water to pure DMSO; B, H_2O-EtOH mixtures over the range pure EtOH to $[H_2O]/[EtOH] = 2.0$.

it; this is in contrast to the behaviour of II. It is likely that the same explanation applies here.

CHAPTER 5

N.M.R. RESULTS

1. The H_2O-HMPA System

The e.s.r. results from trihydroxybenzenes in H_2O-HMPA (Ch. 4-4) suggest that there is a change in the solvent structure around the region x=2. In solutions of high water concentration (x>2) dianions are observed (XXXVI, XXXVIII, XL, XLII), whereas the corresponding singly-charged hydroxysemiquinones (XXXVII, XXXIX, XLI, XLIII) are obtained when more HMPA is present. It appears likely, therefore, that some type of complex is being formed between the two solvents, presumably through hydrogen bonding. N.m.r. studies have shown empirically (Ch. 1-3, p. 37) that a hydrogen-bonded proton resonates at a lower applied magnetic field than one which is not. This makes n.m.r. an ideal technique by which to investigate the possibility of complex formation in H_2O-HMPA.

Table 22 gives the results of the n.m.r. study, showing the change in the proton chemical shift of water as increasing amounts of HMPA are added. In H_2O-HMPA mixtures a single water signal is observed and the proton chemical shift of this peak, p, is a smooth function (Fig. 22) of the concentration ratio $[H_2O]/[HMPA]$. This demonstrates that in mixtures of the two solvents there is fast exchange between water molecules bonded to water, and water molecules bonded to HMPA, so that a single, averaged, result is obtained (Eq.7, p. 16).

Fig. 22 shows the gradual change in p from its value p_1 in pure water to higher field as more HMPA is added. By extrapolation to x=0, the shift of the water signal at infinite

Table 22: Proton Chemical Shift of Water in H_2O-HMPA Mixtures

$x=\frac{[H_2O]}{[HMPA]}$	x^2	$\frac{[H_2O]^2}{[HMPA]}$	Chemical Shift, p (/Hz)	$\frac{1}{(p-p_1)}$
0.05	0.002	0.01	234.3	0.0128
0.13	0.02	0.10	235.3	0.0129
0.18	0.03	0.18	237.7	0.0134
0.26	0.07	0.38	237.7	0.0134
0.30	0.09	0.49	238.4	0.0135
0.39	0.15	0.83	240.7	0.0139
0.46	0.17	1.15	241.1	0.0140
0.61	0.37	1.97	245.1	0.0148
0.66	0.44	2.35	246.2	0.0151
0.83	0.68	3.59	249.9	0.0159
0.85	0.71	3.76	250.75	0.0162
0.99	0.97	5.05	253.25	0.0168
1.08	1.18	6.05	255.55	0.0175
1.37	1.86	9.34	260.8	0.0193
1.56	2.44	12.00	264.55	0.0208
2.14	4.58	21.45	274.0	0.0259
2.61	6.79	30.61	279.45	0.0302
3.02	9.11	39.72	283.8	0.0347
3.53	12.43	52.13	287.6	0.0400
3.88	15.06	61.51	291.05	0.0464
4.57	20.86	81.06	295.55	0.0587
5.20	27.03	100.58	297.2	0.0649
6.02	36.24	127.81	300.8	0.0847
6.50	42.21	144.49	302.0	0.0943
6.97	48.62	161.70	304.7	0.127
7.80	60.84	192.73	305.25	0.136
9.42	88.77	257.33	309.55	0.328
9.96	99.20	279.64	308.7	0.256
10.92	119.33	320.67	310.5	0.476
19.83	393.07	737.62	312.7	10.000
H_2O			p_1=312.6	

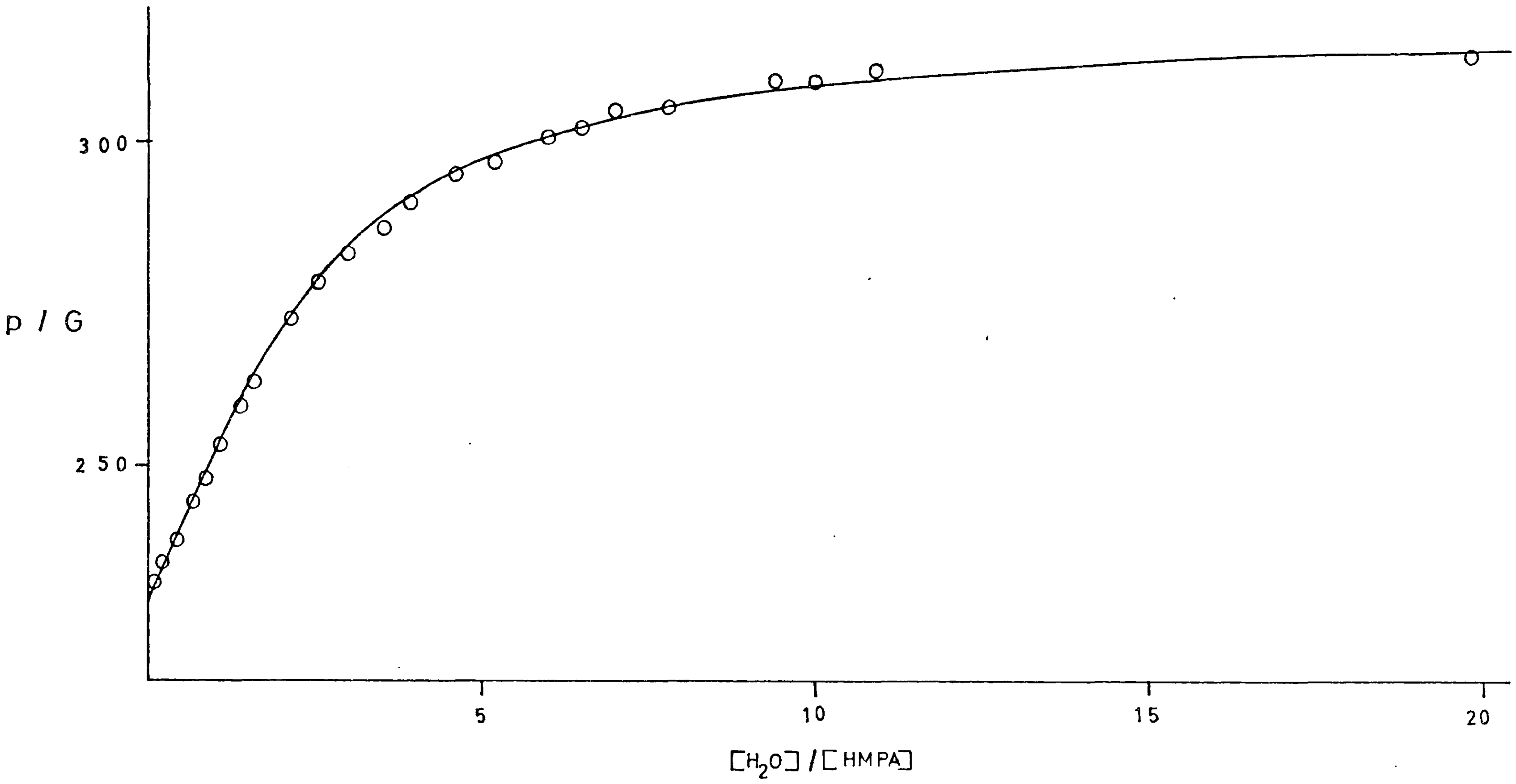


Fig. 22: Straightforward plot of chemical shift of water signal (p) against molar ratio of solvents.

dilution is found to be 233.0 Hz (δ=3.88 p.p.m.) compared with a p_1 value of 312.6 Hz (δ=5.16 p.p.m.), i.e. a total upfield displacement of 79.6 Hz or 1.28 p.p.m. It had been shown previously that this behaviour is expected when an aprotic solvent is added to water.[13] The upfield shift in the water signal with respect to pure water on mixing with HMPA indicates that HMPA brings about a decrease in the hydrogen bonding known to exist in pure water. This decrease results from partial replacement, by HMPA, of water molecules hydrogen bonded to any particular water molecule, i.e. to increased water-HMPA interactions.

By contrast, the chemical shift of the methyl protons in HMPA changes little from its value in pure HMPA (δ=2.94 p.p.m.) to δ=3.07 p.p.m. in the solution of highest water concentration (x=19.83). Of course, the methyl protons cannot participate in hydrogen bonded interactions, and the change is negligible compared with that for water over the same range. Similarly, the spin-spin coupling constant ($J_{Me,\,^{31}P}$) is invariant from pure HMPA ($J_{Me,\,^{31}P}$ = 9.47 Hz) to x=19.83 ($J_{Me,\,^{31}P}$ = 9.33 Hz).

Since exchange is fast, Fig. 22 is of exactly the same form as that obtained when e.s.r. hyperfine splitting constants are plotted against x, so that the treatment developed in Chapter 3 for e.s.r. data can be applied to the n.m.r. results. In Fig. 23, the plot p against log x is sigmoid, in accordance with Eq.30 (p.71), where p is the chemical shift of water.

However, unlike the e.s.r. results, the plot $1/(p-p_p)$ against x is not linear (Fig. 24) even over the range x=0 - 2.0,

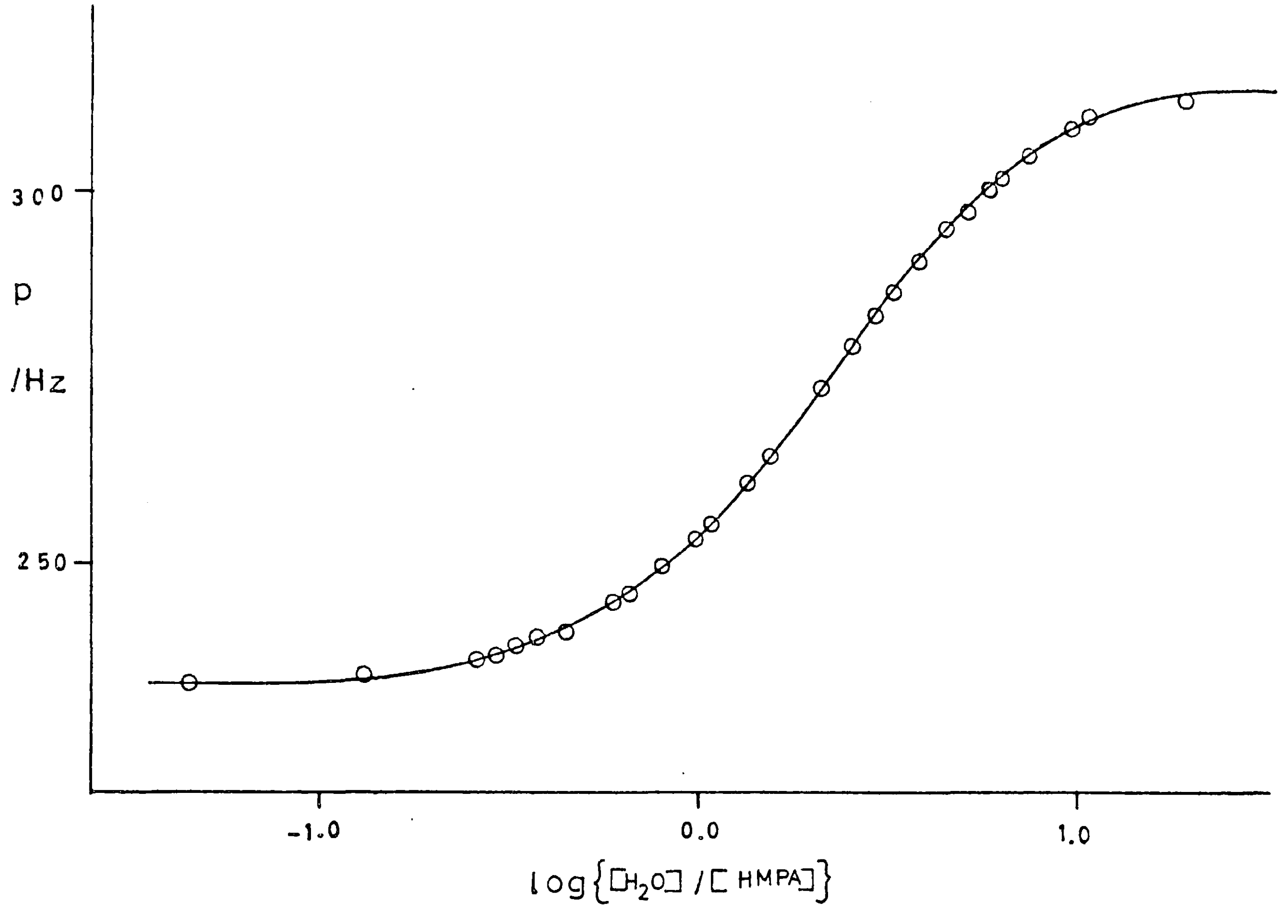


Fig. 23: Plot of chemical shift of water signal (p) against log x.

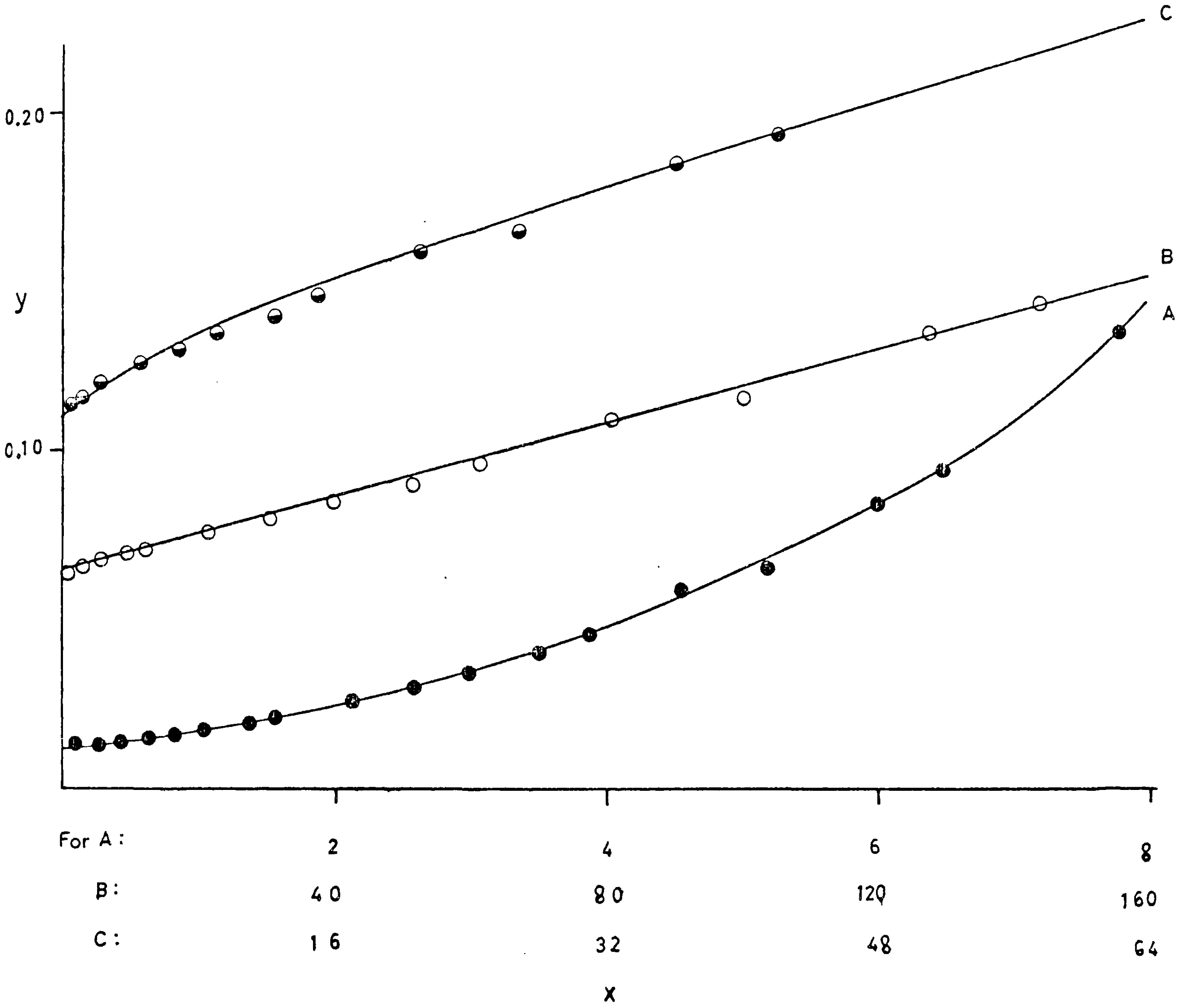


Fig. 24: Plot of chemical shift data against various functions of solvent composition for H_2O-HMPA mixtures.

A, $x = [H_2O]/[HMPA]$; $y = |1/(p-p_1)|$

B, $x = [H_2O]^2/[HMPA]$; $y = |1/(p-p_1)| + 0.05$

C, $x = ([H_2O]/[HMPA])^2$; $y = |1/(p-p_1)| + 0.10$

(Scales adjusted as shown to avoid overlap).

so that Eq.32 (p.75) is not obeyed. This is emphasised in the more detailed study of the x=0-1.0 region presented in Fig. 25. Therefore, the ratio of protons hydrogen bonded to water to those hydrogen bonded to HMPA is not a function of the first power of the solvent ratio. When $1/(p-p_1)$ was plotted against other functions of solvent composition, $[H_2O]^2/[HMPA]$ and $([H_2O]/[HMPA])^2$, for example, the best fit to the experimental data occurred with $[H_2O]^2/[HMPA]$, as shown in Figs. 24 and 25. From pure HMPA to $[H_2O]^2/[HMPA] = 144.49$ (i.e. x=6.50), $1/(p-p_1)$ is a linear function of $[H_2O]^2/[HMPA]$ with r=0.999. That the ratio of protons hydrogen bonded to water varies with $[H_2O]^2$ and inversely with $[HMPA]$ is consistent with the equilibrium:

$$HMPA + 2H_2O \rightleftharpoons HMPA.2H_2O \qquad \text{...Eq.34}$$

Hence the inference from the e.s.r. studies that the solvent structure is changing in the region x=2 is confirmed, and the formation of the comparatively complex stable complex $HMPA{\cdot}2H_2O$ indicated. This suggestion is reasonable as HMPA has approximately 50% ionic character,[133] $(Me_2N)_3\overset{\delta+}{P} = \overset{\delta-}{O}$, and forms stable crystalline stoichiometric complexes with hydrogen donors such as hydroquinone.[134]

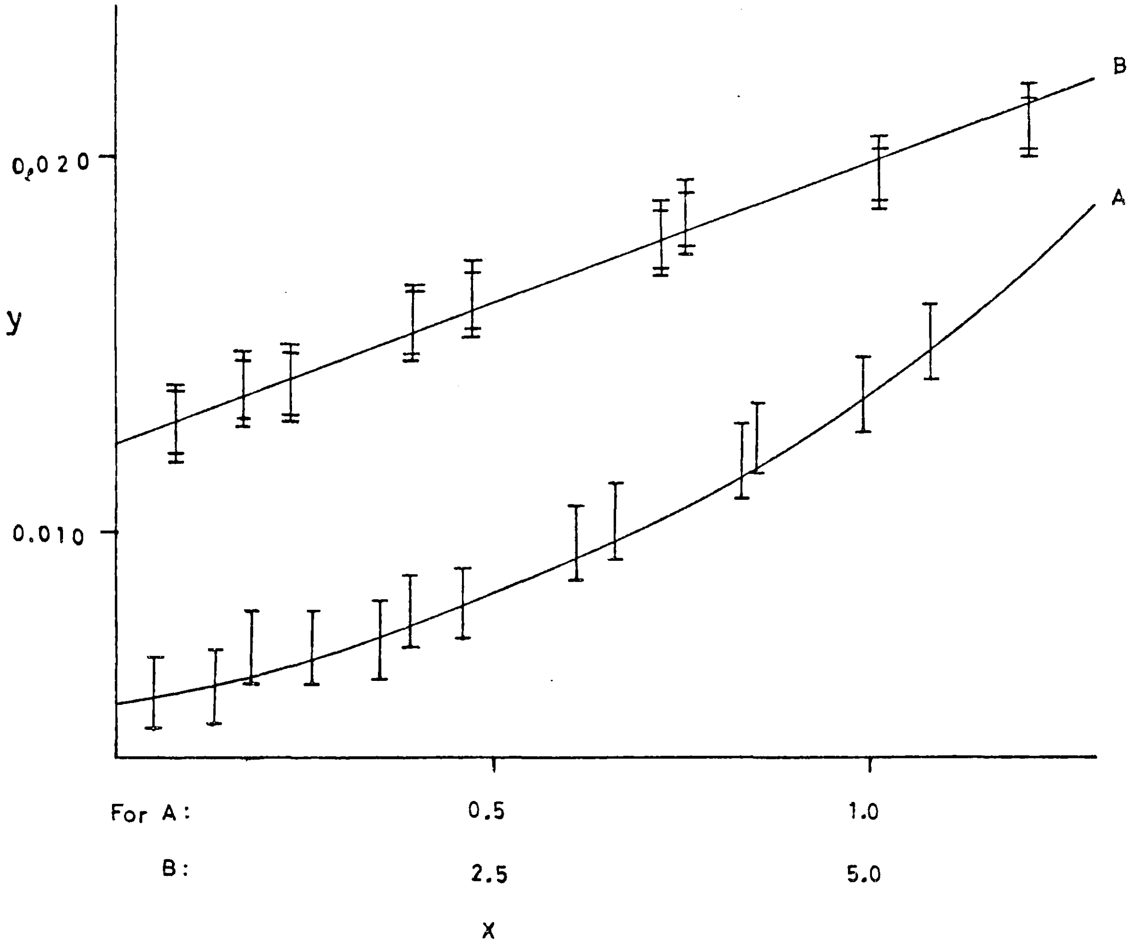


Fig. 25: Comparison of plots obtained for chemical shift data using different solvent functions over the range $[H_2O]/[HMPA] = 0 - 1.08$.

Scales adjusted as follows:

A, $x = [H_2O]/[HMPA]$; $y = |1/(p-p_1)|$

B, $x = [H_2O]^2/[HMPA]$; $y = |1/(p-p_1)| + 0.003$

2. Other Solvent Systems

Other water-aprotic solvent systems are treated analogously in Table 23 and Figs. 26-28. For H_2O-DMSO, the existence of the species DMSO·$2H_2O$ has already been established using dielectric and viscosity measurements,[135] and the results from this system provide a useful indication of the validity of the present method of studying solvent-solvent interactions. It is noteworthy that the addition of DMSO in increasing amounts to water causes the same shift as that produced by HMPA: from pure water to infinite dilution in DMSO the shift is 1.37 p.p.m., in an upfield direction, as compared with a total shift of 1.28 p.p.m. in H_2O-HMPA. This suggests that HMPA and DMSO are equally effective at disrupting the hydrogen bonding between water molecules themselves, and that it is the same type of disruption in each case. This similarity between the two aprotic solvents is confirmed by Figs. 27 and 28. The data for DMSO demonstrates the same trends as that for HMPA, but the correlation of $1/(p-p_1)$ with $[H_2O]^2/[DMSO]$ is slightly poorer (r=0.958). As DMSO·$2H_2O$ is known to be formed, the linearity of this plot lends weight to the suggestion that HMPA·$2H_2O$ is formed in the previous example.

Having established that the treatment developed for the e.s.r. results is applicable to n.m.r. data for binary solvent systems, other mixtures were investigated in this way. DMF induces a change in the chemical shift of water (Fig. 26) of 102.7 Hz (1.71 p.p.m.), which is in good agreement with that

Table 23: Chemical Shift of the Water Signal in H_2O-DMSO and H_2O-DMF.

H_2O-DMSO

$x=\frac{[H_2O]}{[DMSO]}$	$\frac{[H_2O]^2}{[DMSO]}$	Chemical shift, p (/Hz)	$\frac{1}{(p-p_1)}$
0.12	0.19	233.05	0.0124
0.63	4.78	257.1	0.0178
0.98	10.82	269.9	0.0230
1.86	33.14	288.5	0.0402
3.16	78.12	300.4	0.0769
4.05	113.86	304.8	0.116
5.00	155.20	306.1	0.137
5.60	182.25	308.65	0.211
6.97	246.82	307.85	0.180
8.03	298.56	311.0	0.417
9.97	396.40	312.5	1.111
15.03	660.00	312.8	1.667
17.51	792.93	313.4	
H_2O		$p_1=313.4$	

cont.

Table 23 continued:

H_2O-DMF

$x=\frac{[H_2O]}{[DMF]}$	$\frac{[H_2O]^2}{[DMF]}$	Chemical shift, p (/Hz)	$\frac{1}{(p-p_1)}$
0.13	0.22	210.7	0.010
0.19	0.44	227.7	0.012
0.51	3.05	247.6	0.015
0.72	5.70	258.1	0.018
1.10	12.53	266.4	0.021
1.12	12.83	266.55	0.021
1.51	21.95	275.3	0.016
2.01	35.80	282.2	0.032
3.16	74.53	293.7	0.051
4.31	119.81	298.05	0.065
4.88	144.09	298.6	0.068
5.92	190.36	301.9	0.087
6.92	237.12	303.6	0.102
7.97	287.37	305.05	0.120
9.99	387.20	305.8	0.132
15.17		309.4	0.250
16.65		308.9	0.222
94.27		313.8	
H_2O		p_1=313.4	

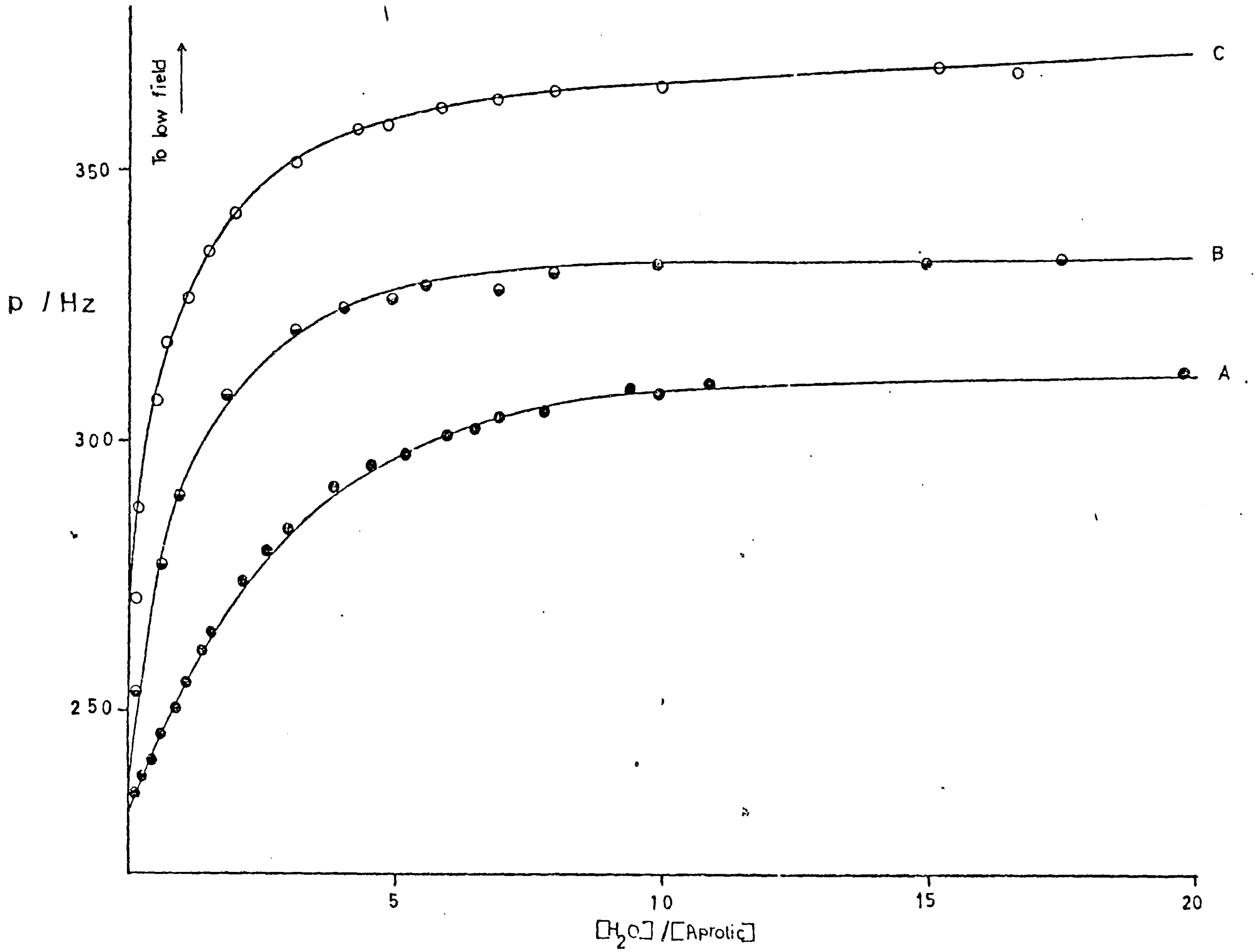


Fig. 26: Chemical shift (p) of water signal in water-aprotic solvent mixtures. A, H_2O-HMPA; B, H_2O-DMSO; C, H_2O-DMF. (For B, p+20 Hz has been plotted; for C, p+60 Hz).

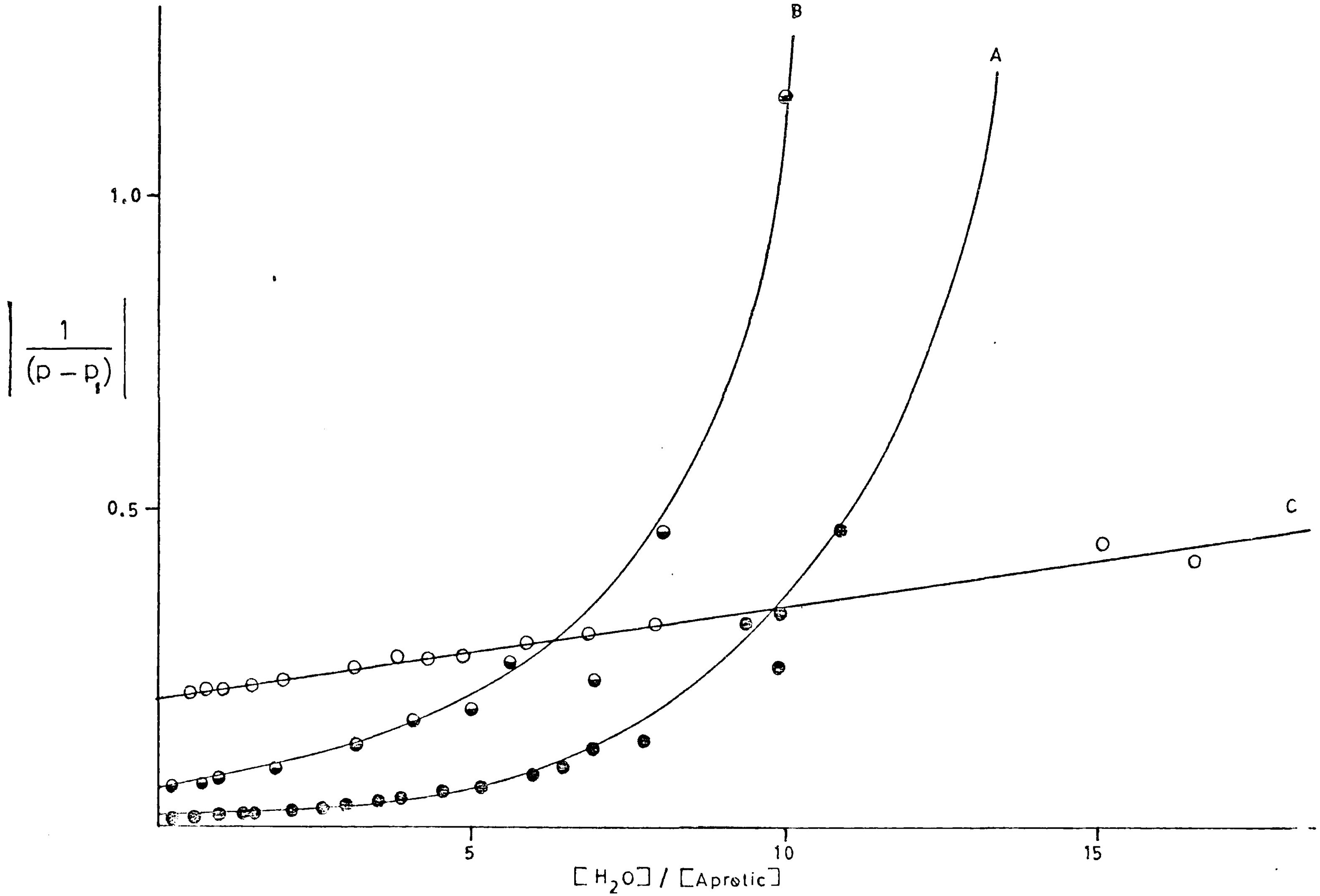


Fig. 27: Chemical shift data for H_2O-aprotic solvent mixtures: plot of $|1/(p-p_1)|$ against $[H_2O]$/[Aprotic]. A, H_2O-HMPA; B, H_2O-DMSO; C, H_2O-DMF. Scales adjusted as follows: B, $|1/(p-p_1)| + 0.05$; C, $|1/(p-p_1)| + 0.2$ shown .

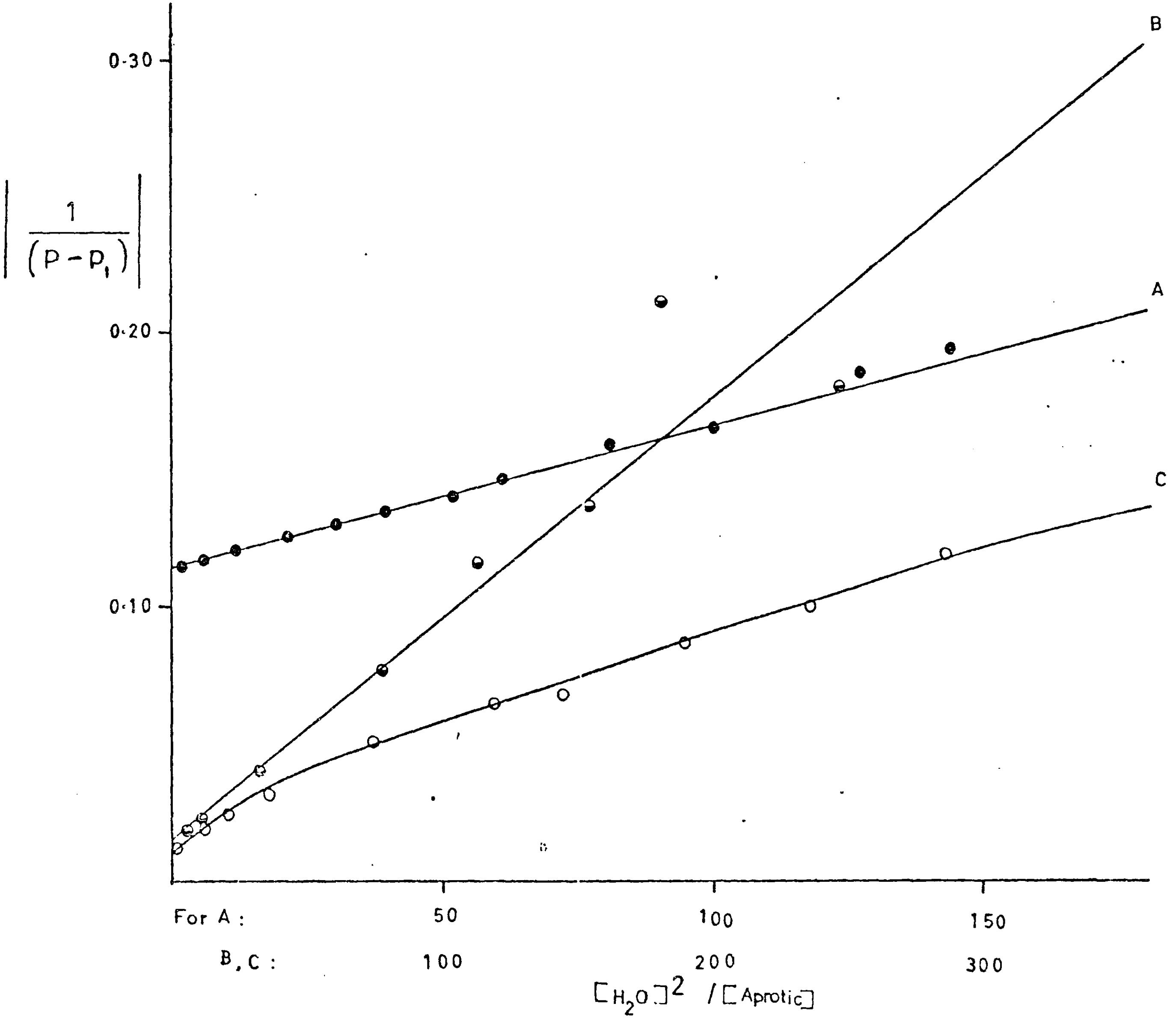


Fig. 28: Plot of $|1/(p-p_1)|$ against $[H_2O]^2/[Aprotic]$. A, H_2O-HMPA; B, H_2O-DMSO; C, H_2O-DMF. (For plot A, $|1/(p-p_1)|$ + 0.10 shown).

found in earlier studies.[†,13] This displacement is some 20 Hz more than that caused by the other aprotic solvents studied. The difference between DMF and the other aprotic solvents is highlighted in Figs. 27 and 28. For DMF the situation is reversed: it is the $1/(p-p_1)$ against x plot which is linear (r=0.991), up to x=17, while $1/(p-p_1)$ against $[H_2O]^2/[DMF]$ is curved. This indicates that the system obeys Eq.35.

$$DMF + H_2O \rightleftharpoons DMF.H_2O \qquad ...Eq.35$$

i.e. that the complex $DMF \cdot H_2O$ is formed. This is in conflict with the suggestion that DMF forms the complex $2DMF \cdot 5H_2O$.[135]

Table 24 contains data for the EtOH-HMPA system. In Fig. 29, the variation in the alcohol -OH resonance is plotted as a function of the solvent ratio [EtOH]/[HMPA]. The results from preliminary studies on EtOH-DMF and EtOH-DMSO are also included in this figure. It is of interest that the effect of HMPA on the alcohol peak is opposite to that of DMF and DMSO. On increasing the HMPA concentration there is a total downfield shift of 16.9 Hz (0.28 p.p.m.). The shift to lower fields as more HMPA is added seems to imply that hydrogen bonding between EtOH and HMPA is stronger than that between

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[†] Using data from Ref. 13, $1/(p-p_1)$ against $[H_2O]/[DMF]$ was plotted for (a) observed $(p-p_1)$ values and (b) values corrected for bulk magnetic susceptibility effects. Such corrections made no difference to the linearity of the plot: both "corrected" and "uncorrected" lines have r>0.995.

Table 24: Chemical Shift of -OH Resonance in EtOH-HMPA Mixtures

$\frac{[EtOH]}{[HMPA]}$	$\frac{[EtOH]^2}{[HMPA]}$	Chemical shift of -OH (p/Hz)	$\frac{1}{(p-p_1)}$
0.11		342.4	0.062
0.12	0.0009	342.5	0.061
0.22	0.0027	343.2	0.059
0.32	0.006	341.9	0.064
0.43	0.011	341.5	0.065
0.49	0.014	341.3	0.066
0.49	0.014	340.6	0.069
0.56	0.017	339.6	0.075
0.63	0.023	338.6	0.081
0.76	0.033	337.7	0.087
0.99	0.055	336.05	0.102
1.14	0.073	334.8	0.116
1.26	0.090	331.15	0.202
1.35	0.10	332.9	0.149
1.65	0.15	331.8	0.179
2.02	0.11	330.75	0.220
3.19	0.53	328.3	0.476
9.92	1.66	326.8	1.67
19.65	3.26	325.65	1.82
30.01	5.01	326.7	
90.79	15.32	325.5	
893.05	149.1	325.3	
EtOH		p_1=326.2	

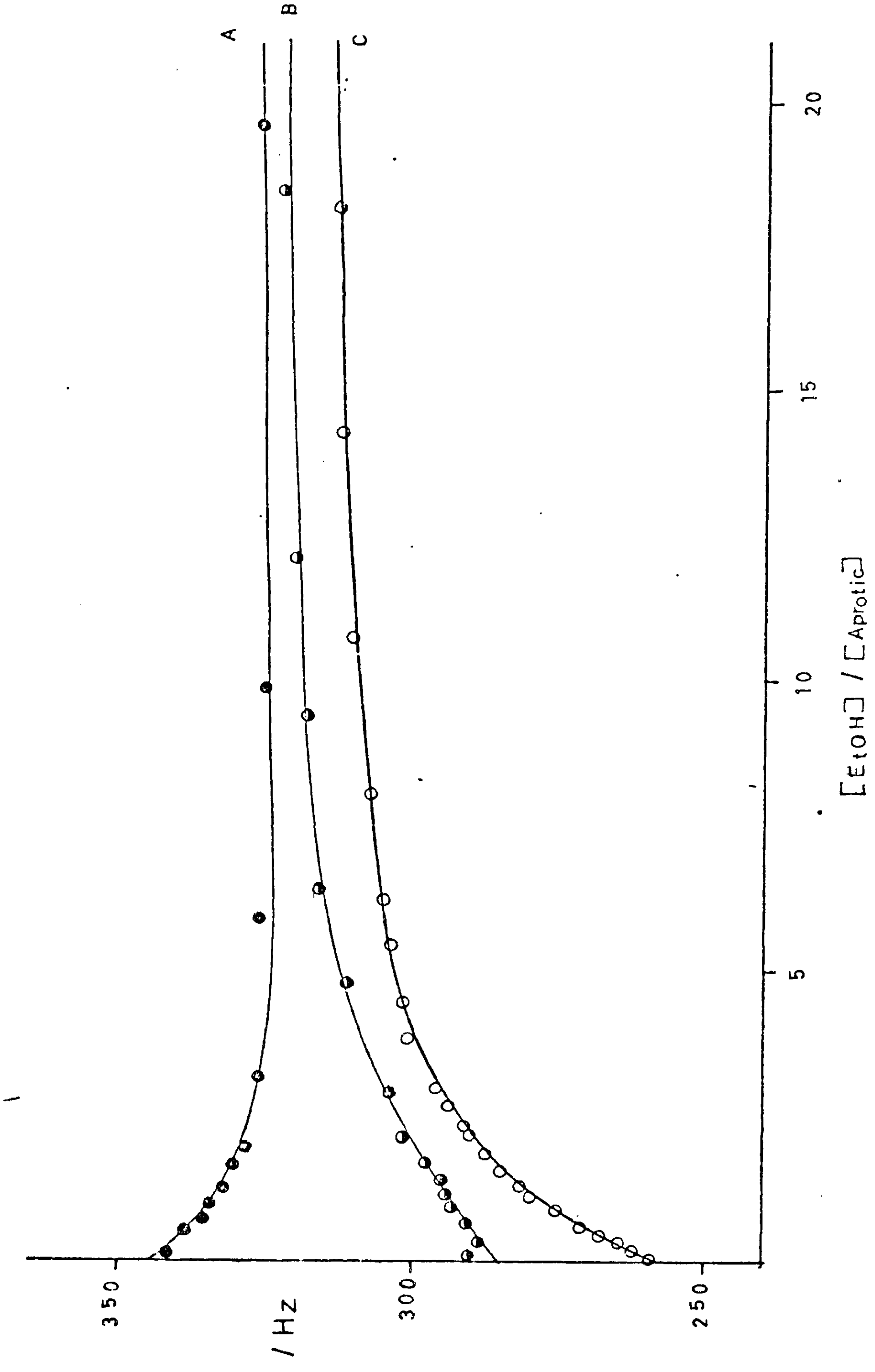


Fig. 29: Chemical shift (p/Hz) of -OH signal in ethanol-aprotic solvent mixtures.
A, EtOH-HMPA; B, EtOH-DMSO; C, EtOH-DMF. (For B, p+5 Hz plotted).

ethanol molecules themselves. By contrast, DMF and DMSO cause upfield shifts of 69.0 Hz (1.15 p.p.m.) and 52.6 Hz (0.88 p.p.m.), respectively. The magnitudes of these two displacements are much larger than that produced by HMPA, whereas in the water-aprotic systems changes were of the same magnitude for all three solvents.

Fig. 30 shows that data for the EtOH-HMPA system gives rise to the linear plot $1/(p-p_1)$ against $[EtOH]^2/[HMPA]$, with r=0.989. The system, therefore, behaves like H_2O-HMPA and H_2O-DMSO, the inferior correlation observed in this case resulting from the smaller overall change in p and the subsequently larger experimental error. Fig. 30, however, also shows that for EtOH-DMF and EtOH-DMSO Eq.32 applies, i.e. there is a 1:1 relationship between these solvents (r=0.998 and 0.997, respectively).

A preliminary attempt was made to study the EtOH-H_2O system but incomplete averaging (leading to two water signals) in some of the mixtures renders the treatment adopted for the other solvent combinations inapplicable.

In summary, the n.m.r. results indicate that in three of the systems investigated Eq.32 is applicable and 1:1 complexes are formed between the aprotic and protic solvents (viz. DMF·H_2O, DMF·EtOH and DMSO·EtOH). For the remaining solvent combinations, this equation is not obeyed and the complexes are of the type aprotic.2 protic (HMPA·$2H_2O$, DMSO·$2H_2O$ and HMPA·2EtOH). The reasons for these observations are, as yet, unclear.

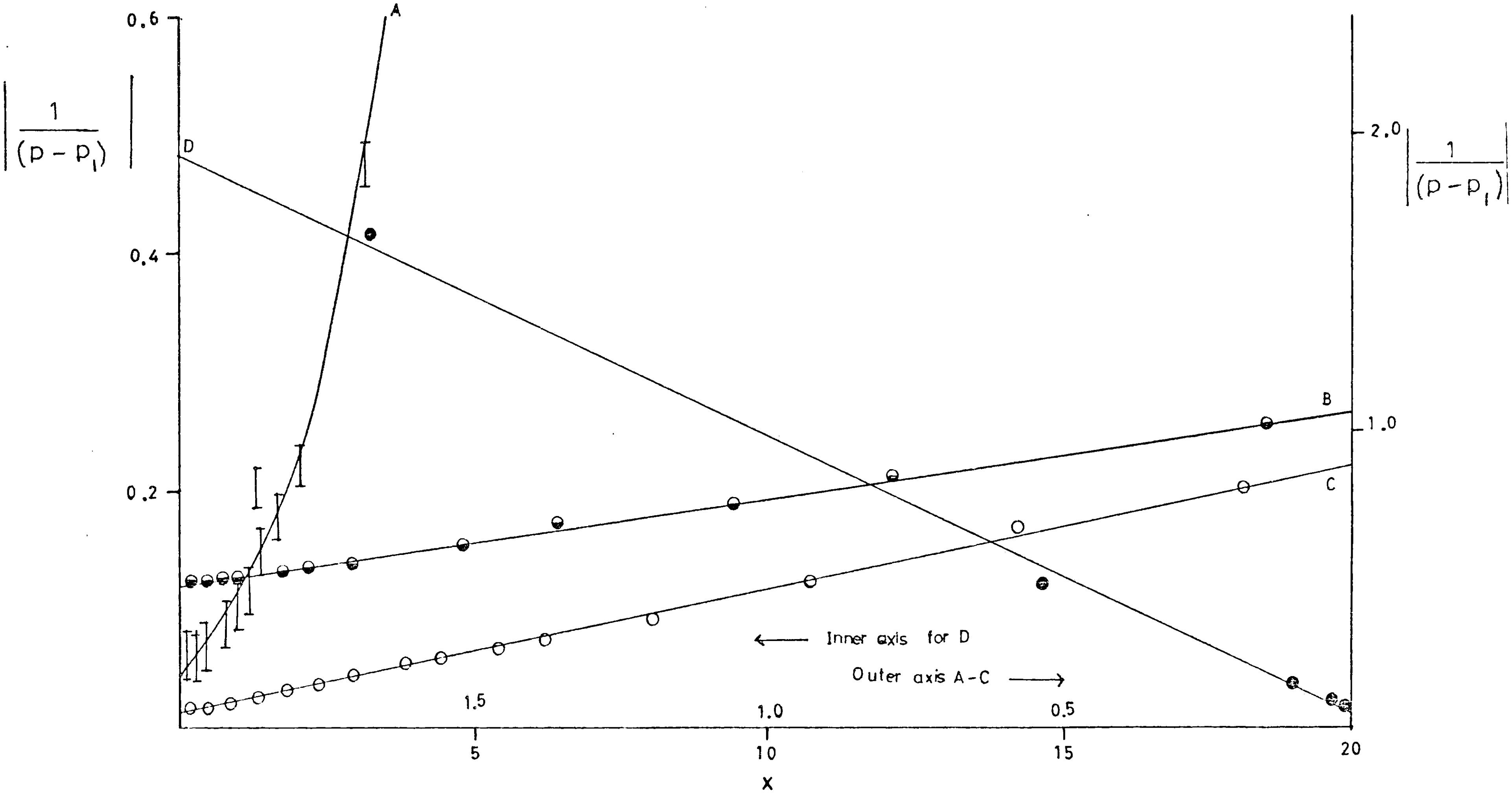


Fig. 30: Plot of $|1/(p-p_1)|$ against solvent composition functions for EtOH-aprotic solvent mixtures. A, x=[EtOH]/[HMPA] ; B, x=[EtOH]/[DMSO] , and $|1/(p-p_1)|$ +0.1 plotted; C, x=[EtOH]/[DMF]; D, $[\mathrm{EtOH}]^2/[\mathrm{HMPA}]$. Left-hand axis refers to y values for A-C; right-hand axis to D.

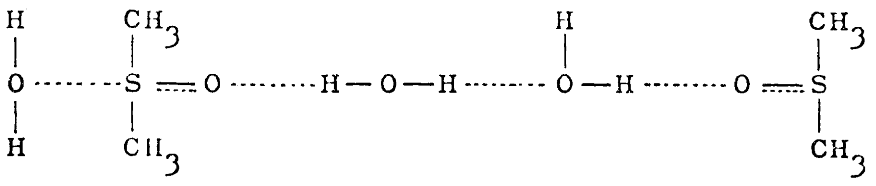
CHAPTER 6

DISCUSSION

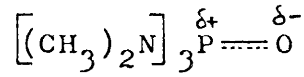
1. Radical-Solvent Interactions

The solvent dependence of the e.s.r. spectra of over forty radicals in the solvents water, ethanol, DMSO, DMF and HMPA has been investigated qualitatively (Tables 7,8,19) and, in favourable cases, quantitatively (Tables 9-14,16,18). In the aprotic solvent HMPA differences from the water hyperfine splitting constants are at a maximum for all radicals. Water is a good anion solvator due to its hydrogen bonding ability, whereas in HMPA anion solvation is mainly via ion-dipole and ion-induced dipole forces.[24] Due to steric hindrance around the phosphorus atom[133] anions are practically unsolvated in HMPA; therefore, in this solvent semiquinones are recorded essentially free from solvent interactions, as opposed to the hydrogen bonded radicals observed in water.

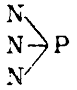
With the other aprotic solvents (Table 7), changes from the water values are smaller, presumably as hydrogen bonded interactions of the type suggested for H_2O-DMSO mixtures:[136]



can occur to some extent between the anion and DMSO or DMF. The table also indicates that deviations from the aqueous values increase in the order: EtOH > DMSO $\geqslant$ DMF > HMPA, i.e. in increasing order of solvent basicity.[133] The unusually high basicity of HMPA results from the 50% ionic character of the P-O bond:



$$\left[(CH_3)_2N\right]_3\overset{\delta+}{P}=\overset{\delta-}{O}$$

The positive charge may be distributed symmetrically over the  grouping; together with the high electron density on oxygen this gives rise to a large dipole moment and a high basicity.

The results demonstrate that the anions are only weakly solvated in aprotic solvents, but the protic solvents employed form hydrogen bonds to the basic sites of sufficient strength to perturb the semiquinones in a readily detectible way.[113] These perturbations are manifested as changes in coupling constants with solvent.

2. Application of the G.F.F. Model to Semiquinones in Mixed Solvents

Tables 9-14 demonstrate conclusively that the simple model presented by G.F.F.[1] applies to the equilibrium involving semiquinones in mixed solvents (Eq.13, Ch. 1-4, p. 46). Data from all five solvent systems investigated comply with this equation, and graphs are of the form predicted by theory (Ch. 3) for each case investigated. In accordance with

Eqs.30-33 good straight line relationships are obtained (r generally $\geqslant 0.99$) over the entire range, i.e. at both protic and aprotic solvent ends. The consistency of the model is supported by the good agreement between equilibrium constants obtained using different plots: p against $\log x$, $1/(p-p_1)$ against x, and $1/(p-p_2)$ against x^{-1}. Therefore, a single equilibrium is being measured throughout the range.

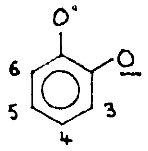
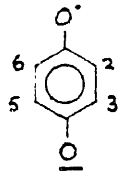
Although the radicals have two functional groups, the modifications to the basic model[1] proposed by Stone and Maki[42] and Symons[114] (Ch. 1-4, p.54) were unnecessary. Presumably this is a consequence of fast averaging in the solutions. More o- than p-semiquinones could be treated quantitatively (Ch. 4). In the p-species the functional groups are at opposite ends of the molecule, so that there is little change in spin density for the carbon atoms carrying the ring protons on hydrogen bonding, i.e. the ring protons are "buffered" (Ch. 1-4, p.45).[113] "Buffering" occurs in o-semiquinones to a lesser extent so that solvent effects are greater. (Compare, for example, radicals II and XXVI, Table 9).

The treatment of results presented in this thesis has been successful even in the absence of complete data. Equilibrium constants were obtained for V, XXVII, XXXI, XXXII and XXXIV (Table 9) even though p_2 was uncertain, and for XXXIII (Table 9) and IV (Table 11) in the absence of p_1. An interesting feature revealed by the graphs defined in this treatment (particularly the p against $\log x$ plot) is the change of sign observed in some coupling constants when water is replaced by HMPA (IV, VI, XXXII, Table 9). Parameters have been estimated for species which could not be observed directly: dianions from trihydroxybenzenes in HMPA (XXXVI, XXXVIII, Tables 16 and 18) and hydroxysemiquinones in water (XXXVII, XXXIX, Tables 16 and 18). By comparison with observed radicals of similar structure (i.e. hydroxy- and methoxysemiquinones) the predicted parameters have been shown to be acceptable and the technique reliable. The fact that dianions cannot exist below x=2.0 means that equilibrium constants are not accessible by the normal method: p_2 for the dianion radicals is unknown. However, using the predicted values of p_2 good regression lines (Ch. 4-4) were obtained ($r > 0.96$) and equilibrium constants estimated.

Table 9 shows that the method is sensitive enough to differentiate between differently substituted semiquinones. For example, for II K has been obtained from two different linear plots and the values differ by 0.06, which is within experimental error. The difference between K for II in H_2O-HMPA and that for any of the other radicals is, in general, greater then the experimental error. The values of K are reproducible and substituent effects constant as expected. The effects of substituents are indicated in Table 25, although the number of examples is limited by the difficulties involved in obtaining suitable radicals for quantitative study (Ch. 4-1).

In 4,5-$(OCH_3)_2$- and 4,5-(OCH_2O)-o-semiquinone (XXXII and VI, respectively), for example, the equilibrium constants are distinct although the substituents have similar effects on the spin density of a radical.[130] Different 2,6- substituents

Table 25: Substituent Effects on Equilibrium Constants Obtained in H_2O-HMPA

Substituent in: 	Radical	K	$\left\|K_{OMe}-K_{Me}\right\|$ ≠	Source of K
$3\text{-}CH_3$	III	0.19	0.33	a_6 against log x plot
$3\text{-}OCH_3$	IV	0.52		
$4,5\text{-}OCH_2O$	VI	0.30		$2a_H$ against log x plot
$4,5\text{-}(OCH_3)_2$	XXXII	0.80		
Substituent in: 				
$2\text{-}CH_3$	XXVII	0.36	0.27	a_3 against log x plot
$2\text{-}OCH_3$	XXVIII	0.63		
$2,6\text{-}Bu^t_2$	I	0.98		linear plots, $p=2a_H$
$2,6\text{-}(CH_3)_2$	XXXI	0.64	0.23	" " "
$2,6\text{-}(OCH_3)_2$	XXX	0.41		" " "

≠ Difference between equilibrium constants for methoxy- and methyl- substituted radicals.

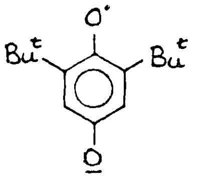
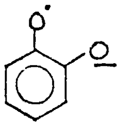
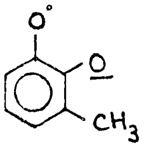
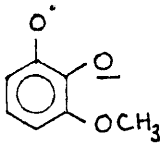
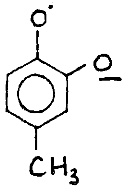
also lead to separate equilibrium constants (I, XXX and XXXI).

Comparing values for the same parameter (i.e. a_H and not a_{Me}, as stressed in Table 10) obtained from the same plot (i.e. either a linear or log plot), the change induced in K by replacing an $-OCH_3$ group by $-CH_3$ is, within experimental error, constant and approximately 0.28, regardless of the position of the substituent: this value is the same for 2- and 2,6- disubstituted p-semiquinones as for 3- substituted o- radicals. This is expected as a given substituent always has the same effect on the spin density distribution within a radical, so that the difference in effects due to $-CH_3$ and $-OCH_3$ is constant.

3. Magnitudes of the Equilibrium Constants

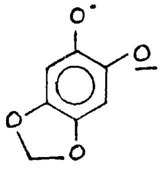
Tables 9-14 show that, with the particular exception of 2,6- disubstituted radicals, which are asymmetrically-solvated,[58-61] equilibrium constants are generally less than unity. This is summarised in Table 26, information on the six "best" radicals. Comparing values obtained using the same parameters, K for H_2O-HMPA is usually quite different from that for other aqueous-aprotic solvent systems. This is particularly marked for radicals I and II, where equilibrium constants for H_2O-DMF/DMSO are similar. In DMF and DMSO, of course, the radicals are not "free" as they are in HMPA.[133] The observed

Table 26: Effect of Solvent on Equilibrium Constants

Radical	Solvent System	K	Parameter used$^{\neq}$
	H_2O-HMPA	0.98	$2a_H$
	H_2O-DMSO	2.04	$2a_H$
	H_2O-DMF	2.57	$2a_H$
I	EtOH-HMPA	1.36	$2a_H$
	H_2O-HMPA	0.36	$2a_{3,6}$
	H_2O-DMSO	0.57	$2a_{3,6}$
	H_2O-DMF	0.50	$2a_{3,6}$
	H_2O-EtOH	0.35	$2a_{3,6}$
II	EtOH-HMPA	0.86	$2a_{3,6}$
	H_2O-HMPA	0.44	T.W.
	H_2O-DMSO	0.43	T.W.
	H_2O-DMF	0.53	T.W.
	H_2O-EtOH	0.45	T.W.*
III	EtOH-HMPA	0.40	T.W.*
	H_2O-HMPA	0.52	a_6
	H_2O-DMSO	0.63	a_6
	H_2O-DMF	0.99	a_6
	H_2O-EtOH	0.54	T.W.*
IV	EtOH-HMPA	0.79	a_6
	H_2O-HMPA	0.34	a_3
	H_2O-DMSO	0.49	a_3
	H_2O-DMF	0.97	a_3
	H_2O-EtOH	0.30	T.W.*
V	EtOH-HMPA	0.75	a_3

cont.

Table 26 continued:

Radical	Solvent System	K	Parameter used†
	H_2O-HMPA	0.22	a_{CH_2}
	H_2O-DMF	0.71	a_{CH_2}*
	H_2O-EtOH	0.23	$2a_{CH_2}$
VI	EtOH-HMPA	0.66	a_{CH_2}

† Unless otherwise stated K has been obtained from the linear plots.

* K from p against log x plot.

order of equilibrium constants changes with the nature of the radical:

$$\begin{array}{rl} \text{I, IV, V:} & K(H_2O\text{-HMPA}) < K(H_2O\text{-DMSO}) < K(H_2O\text{-DMF}) \\ \text{II:} & K(H_2O\text{-HMPA}) < K(H_2O\text{-DMSO}) \approx K(H_2O\text{-DMF}) \\ \text{III:} & K(H_2O\text{-HMPA}) = K(H_2O\text{-DMSO}) < K(H_2O\text{-DMF}) \end{array}$$

K is, therefore, a function of the substitution pattern as well as the solvent combination.

The immediate implications of equilibrium constants less than unity are rather surprising. In the original G.F.F. model,[1] $K=10$ defines a situation in which the complex with solvent S_1 is considerably stronger than that with S_2 (Eq.13). A value of unity corresponds to unselective solvation, such as has been found for nitrobenzene anions.[114] For the H_2O-HMPA system, for example, $K<1$ could be taken (Eq.36) as preferential solvation of the semiquinone radical by HMPA:

$$R\cdots\cdots HMPA + H_2O \rightleftharpoons R\cdots\cdots H_2O + HMPA \qquad K<1 \qquad \ldots Eq.36$$

However, in view of the previous discussion (Section 1, this chapter) this is an unacceptable conclusion. Moreover, values in H_2O-HMPA (Table 26) are lower than those in H_2O-DMF/DMSO, implying that solvation by HMPA is greater than that by DMSO or DMF, which is again unacceptable. Also, results from

EtOH-H_2O suggest (Eq.37) that hydrogen bonding to the radical

$$R\cdots\cdots EtOH + H_2O \rightleftharpoons R\cdots\cdots H_2O + EtOH \qquad K<1 \qquad \ldots Eq.37$$

is stronger for ethanol than water. This is inferred, also, when values for H_2O-HMPA and EtOH-HMPA are compared (Table 26),as K(EtOH-HMPA) is greater than K(H_2O-HMPA).

Standard free energy changes for equilibria involving semiquinones in mixed solvents can be obtained from the van't Hoff isotherm:

$$\Delta G^{\ominus} = -RT \ln K \qquad \ldots Eq.38$$

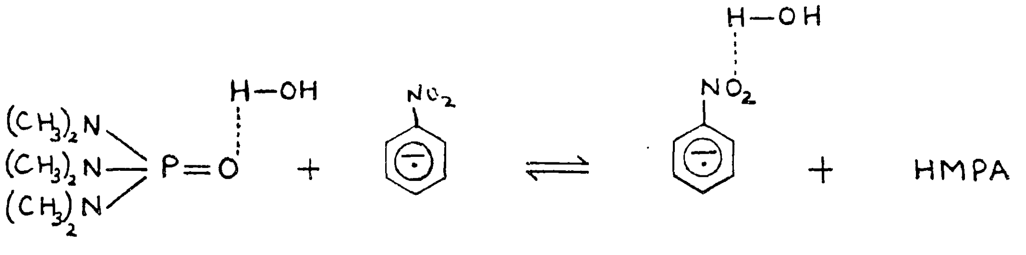
Equilibrium constants less than unity lead to positive $\Delta G^{\ominus}$ values, i.e. the reaction is unspontaneous. It is likely, therefore, that some other effect is operative in this system additional to that represented by the simple G.F.F. equation (Eq.13). However, whatever the physical significance of the determined K values the straight line relationships are undeniable: p clearly depends on $[H_2O]/[HMPA]$.

4. Solvent-Solvent Interactions

The results of Ch. 4-4 and Ch. 5 are strong evidence that the additional effect overlooked in Eq.13 is an interaction between the solvents themselves. The e.s.r. results from trihydroxybenzenes in H_2O-HMPA showed the solvent structure to change in a definite manner, so that dianions of hydroxysemiquinones cannot persist at high HMPA concentrations ($x<2$). N.m.r. confirmed this change to be due to the formation of the relatively stable complex HMPA$\cdot 2H_2O$. Similarly, strong solvent-solvent interactions and complex formation were found for H_2O-DMF, H_2O-DMSO, EtOH-DMF, EtOH-DMSO and EtOH-HMPA. Convincing evidence of solvent interactions, chiefly in H_2O-DMSO, is available from other studies: calorimetric,[94] viscosity,[110,111,135] dielectric constant,[110,111,135] refractive index[110] and density.[137]

For H_2O-DMF an equilibrium constant for hydrogen bonding between the solvents has been determined using i.r.[15] The reported value of 4.4 ± 1.7 dm^3 mol^{-1} corresponds to a negative $\Delta G^{\ominus}$, in contrast to the positive free energy changes found for the radicals. Certainly, the present n.m.r. results suggest, if K can be taken as the value of the solvent function where the concentrations of species are equal, that equilibrium constants for solvent-solvent interactions are large and positive: $K(H_2O\text{-HMPA}) \approx 27$; $K(H_2O\text{-DMSO}) \approx 18$ and $K(H_2O\text{-DMF}) \approx 1.2$. Although n.m.r. is not the most reliable method for obtaining quantitative data on hydrogen bonding,[15] good straight line relationships were observed ($r \gg 0.99$) and it is clear that the equilibrium constants are of a different order of magnitude than those from the e.s.r. studies. This would explain why the $\Delta G^{\ominus}$ values found by e.s.r. are positive: there is actually competition for water molecules between the radical and HMPA, and it is the result of this competition which is being measured by e.s.r.

This conclusion is supported by studies on other types of radical. For the reaction:

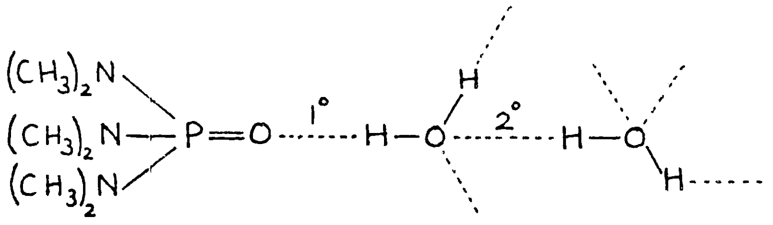


...Eq. 39

K=0.9, indicating that the concentration of hydrogen bonded HMPA is greater than that for the hydrogen bonded ion,[68] an expected result as HMPA forms relatively strong hydrogen bonds.[138] Equilibrium constants less than unity for t-butylnitroxide in mixed aqueous solvents[51] were interpreted in terms of preferential solvation by organic solvents such as dioxan and alcohols. However, using di-t-butylnitroxide as a probe[64] this concept was shown to be totally misleading. Interaction with aprotic solvents is dipolar in nature. As the concentration of this type of solvent is increased, hydrogen bonds to the radical are lost due to the strong affinity of the basic solvent for hydrogen bonds, rather than to increased radical-aprotic solvent interactions. Thus both radical-solvent and solvent-solvent interactions must be considered.

The reliance of p on $[H_2O]/[HMPA]$ might appear to suggest that the equilibrium between the two radical forms is effectively independent of any interaction between the solvents, i.e. that Eq.13 stands. In the ideal case of zero solvent-solvent interactions such a relationship is expected. However, the positive $\Delta G^{\ominus}$ values deny this. Rather, there appear to be two simple situations for a semiquinone: either it is hydrogen bonded or it is not. The effects on spin density distribution within the radical would be expected to depend most critically on the strength of the primary hydrogen bond, that to the radical; thus it would be insignificant whether the radical were hydrogen bonded to a water molecule or to the $HMPA \cdot 2H_2O$ moiety, and $1/|p-p_1|$ could still be a linear funtion of $[H_2O]/[HMPA]$.

The structure of $HMPA \cdot 2H_2O$ is probably the same as that suggested for H_2O-DMSO interactions:[102,108] the first water



molecule is bonded to the oxygen atom of the aprotic solvent (1° solvation), whereas the second water molecule is attached to the first by secondary solvation (2°), as shown above.

Although it is often assumed that 1^{o} solvation is complete before the onset of 2^{o} solvation, i.r. studies on tetra-alkylammonium halides[109] have established that this is incorrect.

The structure proposed for HMPA$\cdot$2H_2O has the capacity to form further hydrogen bonds. Depending on the relative concentrations, these can be either to the radical or to other water molecules. Thus the measured e.s.r. parameters are averages resulting from exchange between hydrogen bonded radicals, either bonded to water or to HMPA$\cdot$2H_2O, and radicals solvated through dipolar interactions with HMPA. However, further details are not obtainable from the present results.

This explanation is compatible with the results of Ch.4-5, in which the e.s.r. parameters were found to correlate simultaneously with ε and Z, one a bulk, macroscopic property of the solvent and the second a measure of interactions at the molecular level. If the present picture of hydrogen bonding to the radical by HMPA$\cdot$2H_2O or water itself is accepted, the observed correlations are consistent: p must depend on the nature of the 1^{o} bond, i.e. on what is happening at the radical and therefore on Z, and also on interactions throughout the solvent as a whole and therefore on ε.

Whatever the physical significance of the equilibrium constants it is clear from the linear relationships that unique values are being measured. Thermodynamic considerations confirm this.

5. Thermodynamic Considerations

If the measured K values are true thermodynamic equilibrium constants, then $\Delta G^{\ominus}$ values calculated from them (Eq.38) must be additive. Therefore, if two equilibrium constants are known, a third can be calculated and compared with the experimentally observed value. An example is detailed for radical II (Table 27).

Table 27: Prediction of K(H_2O-EtOH) for Radical II

$$\text{(i)}\quad \text{R....HMPA} + H_2O \rightleftharpoons \text{R....}H_2O + \text{HMPA} \qquad K^{\neq} = 0.29$$

$$\text{(ii)}\quad \text{R....HMPA} + \text{EtOH} \rightleftharpoons \text{R....EtOH} + \text{HMPA} \qquad K^{\neq} = 0.84$$

$$\text{(iii)}\quad \text{R....EtOH} + H_2O \rightleftharpoons \text{R....}H_2O + \text{EtOH}$$

$$\begin{aligned} \Delta G^{\ominus}(\text{iii}) &= \Delta G^{\ominus}(\text{i}) \quad \Delta G^{\ominus}(\text{ii}) \\ &= -RT \ln 0.30 + RT \ln 0.84 \qquad \text{where } T = 293\text{K} \\ &= 2.508 \text{ kJ mol}^{-1} \end{aligned}$$

K (iii, calculated) = 0.36

$K^{\neq}$(iii, experimental) = 0.35

$\neq$ From $2a_{3,6}$ against log x plot.

Values for other radicals in H_2O-EtOH were obtained similarly (Table 28). The limiting factor to accuracy in these calculations

Table 28: Predicted Equilibrium Constants for Radicals in H_2O-EtOH

Radical	K(H_2O-HMPA) Experimental	K(EtOH-HMPA) Experimental	K(EtOH-H_2O) Experimental	K(EtOH-H_2O) Calculated	Source of K Experimental
II	0.29	0.84	0.35	0.36	$2a_{3,6}$ against log x
III	0.19	0.71	0.45[†]	0.27	a_6 against log x
IV	0.40	0.60	0.54[†]	0.67	a_5 against log x
V	0.13	0.56	0.30	0.23	T.W. against log x
VI	0.16	0.63	0.25	0.22	a_{CH_2} against log x

[†] K(H_2O-EtOH) from T.W. against log x plot.

is the H_2O-EtOH experiment. Values in this system are probably only correct to ±0.2 due to the small changes involved and the fact that K can only be determined from the less reliable p against log x plot; for other systems K is estimated to be correct to ±0.1. For consistency only values obtained from log plots have been used and, where possible, the same parameter has been employed in the calculation of K. In all cases the agreement between predicted and experimental values of K is good and, in fact, disparities are only greater than 0.1 when values obtained from different plots have had to be compared (III, IV). This supports the suggestion that a single, true equilibrium is being observed in the e.s.r. studies, that between hydrogen bonded and non-hydrogen bonded radicals.

REFERENCES

1. J. Gendell, J. H. Freed and G. K. Fraenkel, J. Chem. Phys., 1962, 37, 2832.

2. J. Burgess and M. C. R. Symons, Quart. Rev., 1968, 22, 276.

3. M. C. R. Symons, Ann. Rep. Chem. Soc. A, 1976, 73, 91.

4. M. C. R. Symons, J. Phys. Chem., 1967, 71, 172.

5. N. M. Atherton, Electron Spin Resonance (Ellis Horwood Ltd., Chichester, 1973); J. E. Wertz and J. R. Bolton, Electron Spin Resonance, elementary theory and applications (McGraw-Hill, London, 1972).

6. A. Carrington, Quart. Rev., 1963, 17, 67.

7. H. M. McConnell, J. Chem. Phys., 1956, 25, 709.

8. J. Ronayne and D. H. Williams, Annual Review of NMR Spectroscopy, ed. E. F. Mooney (Academic Press, London, 1969), vol. 2, p. 83.

9. L. M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry (Pergamon Press, Oxford, 2nd. edn., 1969).

10. M. I. Foreman, Nuclear Magnetic Resonance (Specialist Periodical Report, Chemical Society, London, 1976), vol. 5, p. 292.

11. J. H. Swinehart and H. Taube, J. Chem. Phys., 1962, 37, 1579.

12. J. A. Pople, W. G. Schneider and H. J. Bernstein, High-resolution Nuclear Magnetic Resonance (McGraw-Hill, New York, 1959).

13. A. Fratiello, Mol. Phys., 1963, 566.

14. A. D. Buckingham and J. A. Pople, Proc. Camb. Phil. Soc., 1957, 53, 262;
T. W. Marshall and J. A. Pople, Mol. Phys., 1958, 1, 199.

15. M. D. Joesten and L. J. Schaad, Hydrogen Bonding (Marcel Dekker, New York, 1974).

16. T. C. Waddington (ed.), Non-aqueous Solvent Systems (Academic Press, New York, 1965).

17. B. G. Segal, M. Kaplan and G. K. Fraenkel, J. Chem. Phys., 1965, 43, 4191.

18. P. J. Zandstra, J. Chem. Phys., 1964, 41, 3655.

19. T. Kawamura, S. Matsunami and T. Yonezawa, Bull. Chem. Soc. Japan, 1967, 40, 1111.

20. H. Hayat and B. L. Silver, J. Phys. Chem., 1973, 77, 72.

21. R. Brière, H. Lemaire and A. Rassat, Bull. Soc. chim. France, 1965, 3273.

22. A. L Buchachenko, Chem. Abstracts, 1965, 62, 2390g.

23. C. Jolicoeur and H. L. Friedman, Ber. Bunsenges. phys. Chem., 1971, 75, 248; J. Solution Chem., 1974, 3, 15.

24. C. Reichardt, Solvent Effects in Organic Chemistry (Verlag Chemie, Weinheim, 1979).

25. S. I. Weissman, J. Chem. Phys., 1954, 22, 1378;
S. I. Weissman and D. Banfill, J. Amer. Chem. Soc., 1953, 75, 2534.

26. E. Fermi, Z. Phys., 1930, 60, 320.

27. H. M. McConnell, J. Chem. Phys., 1956, 24, 764; R. Bersohn, ibid., p. 1066; S. I. Weissman, ibid., 1956, 25, 890; H. S. Jarrett, ibid., p. 1289.

28. H. M. McConnell and D. B. Chesnut, J. Chem. Phys., 1958, 28, 107; H. M. McConnell, ibid., p. 1188.

29. H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, J. Amer. Chem. Soc., 1960, 82, 766.

30. H. M. McConnell and C. H. Holm, J. Chem. Phys., 1957, 27, 314.

31. A. Carrington and A. D. McLachlan, Introduction to Magnetic Resonance (Harper and Row, London, 1967).

32. F. C. Adam and S. I. Weissman, J. Amer. Chem. Soc., 1958, 80, 1518.

33. J. Oakes, J. Slater and M. C. R. Symons, Trans. Faraday Soc., 1970, 66, 546.

34. D. Kivelson, J. Chem. Phys., 1964, 41, 1904.

35. T. J. Stone, T. Buckman, P. L. Nordio and H. M. McConnell, Proc. Nat. Acad. Sci. U.S.A., 1965, 54, 1010.

36. C. J. W. Gutch and W. A. Waters, J.C.S. Chem. Comm., 1966, 39; W. E. Griffiths, C. J. W. Gutch, G. F. Longster, J. Myatt and P. F. Todd, J. Chem. Soc. B, 1968, 785.

37. D. H. Geske and A. H. Maki, J. Amer. Chem. Soc., 1960, 82, 2671.

38. L. H. Piette, P. Ludwig and R. N. Adams, J. Amer. Chem. Soc., 1961, 83, 3909.

39. L. H. Piette, P. Ludwig and R. N. Adams, J. Amer. Chem. Soc., 1962, 84, 4212.

40. N. M. Atherton and S. I. Weissman, J. Amer. Chem. Soc., 1961, 83, 1330.

41. Y. Deguchi, Bull. Chem. Soc. Japan,1962, 35, 260.

42. E. W. Stone and A. H. Maki, J. Chem. Phys., 1962, 36, 1944; J. Amer. Chem. Soc., 1965, 87, 454.

43. F. W. Heineken, M. Bruin and F. Bruin, J. Chem. Phys., 1962, 37, 452.

44. A. V. Il'yasov, Zh. strukt. Khim, 1962, 3, 95; Chem. Abstracts, 1963, 58, 7523d.

45. E. A. C. Lucken, J. Chem. Soc., 1963, 5123.

46. P. B. Ayscough and F. P. Sargent, J. Chem. Soc. B, 1966, 907.

47. P. Ashworth, Mol. Phys., 1975, 30, 313.

48. P. Ludwig, T. Layloff and R. N. Adams, J. Amer. Chem. Soc., 1964, 86, 4568.

49. J. Q. Chambers, T. Layloff and R. N. Adams, J. Phys. Chem., 1964, 68, 661.

50. R. Brière, H. Lemaire and A. Rassat, Tetrahedron Letters, 1964, 1775; G. Chapelet-Letourneux, H. Lemaire and A. Rassat, Bull. Soc. chim. France, 1965, 444.

51. G. Stout and J. B. F. N. Engberts, J. Org. Chem., 1974, 39, 3800.

52. B. R. Knauer and J. J. Napier, J. Amer. Chem. Soc., 1976, 98, 4395.

53. E. M. Kosower, J. Amer. Chem. Soc., 1958, 80, 3253; J. Chim. phys., 1964, 61, 230; E. M. Kosower and M. Mohammad, J. Amer. Chem. Soc., 1968, 90, 3271; ibid., 1971, 93, 2713; J. Phys. Chem., 1970, 74, 1153.

54. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlman, Annalen, 1963, 661, 1; C. Reichardt, ibid., 1971, 752, 64.

55. Th. A. J. W. Wajer, A. Mackor and Th. J. de Boer, Tetrahedron, 1969, 25, 175.

56. T. E. Gough and M. C. R. Symons, Trans. Faraday Soc., 1966, 62, 269.

57. E. A. C. Lucken, J. Chem. Soc., 1964, 4234.

58. T. A. Claxton, J. Oakes and M. C. R. Symons, Trans. Faraday Soc., 1967, 63, 2125.

59. P. S. Gill and T. E. Gough, Trans. Faraday Soc., 1968, 64, 1997.

60. J. Oakes and M. C. R. Symons, Trans Faraday Soc., 1968, 64, 2579.

61. T. A. Claxton and D. McWilliams, Trans. Faraday Soc., 1968, 64, 2593.

62. L. Grossi, F. Minisci and G. F. Pedulli, J.C.S. Perkin II, 1977, 943.

63. E. F. Ullmann, L. Call and J. H. Osiecki, J. Org. Chem., 1970, 35, 3623; J. Amer. Chem. Soc., 1970, 92, 7210.

64. Y. Y. Lim, E. A. Smith and M. C. R. Symons, J.C.S. Faraday I, 1976, 72, 2876.

65. G. R. Stevenson and L. Echegoyen, J. Amer. Chem. Soc., 1974, 96, 3381.

66. A. E. Alegria, R. Concepcion and G. R. Stevenson, J. Phys. Chem., 1975, 79, 361.

67. G. R. Stevenson and L. Echegoyen, J. Phys. Chem., 1973, 77, 2339.

68. G. R. Stevenson and H. Hidalgo, J. Phys. Chem., 1973, 77, 1027.

69. G. R. Stevenson, L. Echegoyen and H. Hidalgo, J. Phys. Chem., 1975, 79, 152.

70. L. P. Hammett, Physical Organic Chemistry (McGraw-Hill, New York, 2nd. edn., 1970); Chem. Rev., 1935, 17, 135.

71. Brown's σ^+ values from C. D. Ritchie and W. F. Sager, Progress in Physical Organic Chemistry, ed. S. G. Cohen, A. Streitweiser, Jr. and R. W. Taft (Interscience, New York, 1964), vol. 2, p. 323.

72. G. R. Luckhurst and L. E. Orgel, Mol. Phys., 1964, 8, 117.

73. J. A. Pedersen and J. Spanget-Larsen, Chem. Phys. Lett., 1975, 35, 41.

74. P. J. Zandstra and E. M. Evleth, J. Amer. Chem. Soc., 1964, 86, 2664.

75. K. Mukai, H. Nishiguchi, K. Ishizu, Y. Deguchi and H. Takaki, Bull. Chem. Soc. Japan, 1967, 40, 2731.

76. S. Aono and M. Suhara, Bull. Chem. Soc. Japan, 1968, 41, 2553.

77. J. Pannell, Mol. Phys., 1964, 7, 317.

78. H. G. Aurich and J. Trösken, Annalen, 1971, 745, 159; H. G. Aurich, W. Dersch and H. Forster, Chem. Ber., 1973, 106, 2854.

79. A. D. Buckingham, T. Schaefer and W. G. Scheider, J. Chem. Phys., 1960, 32, 1227.

80. W. T. Raynes, A. D. Buckingham and H. J. Berstein, J. Chem. Phys., 1962, 36, 3481.

81. P. Laszlo, Progress in NMR Spectroscopy, ed. J. W. Emsley, J. Feeney and L. H. Sutcliffe (Pergamon Press, Oxford, 1968), vol. 3, p. 231.

82. J. Homer, Appl. Spectroscopy Rev., 1975, 9, 1.

83. H. J. Bernstein, Pure Appl. Chem., 1972, 32, 79.

84. M. I. Foreman, Nuclear Magnetic Resonance (Specialist Periodical Report, Chemical Society, London, 1973), vol. 2, p. 355; ibid., 1977, 6, 233.

85. J. T. Arnold and M. E. Packard, J. Chem. Phys., 1951, 19, 1608; U. Liddel and N. F. Ramsey, ibid., 1951, 19, 1608.

86. A. S. N. Murthy and C. N. R. Rao, Appl. Spectroscopy Rev., 1969, 2, 69; J. C. Davis and K. K. Deb, Advances in Magnetic Resonance ed. J. S. Waugh, (Academic Press, New York, 1970), vol. 4, p. 201.

87. J. Homer, Nuclear Magnetic Resonance (Specialist Periodical Report, Chemical Society, London, 1978), vol. 7, p. 318.

88. A. Fratiello and D. P. Miller, Mol. Phys., 1966, 11, 37.

89. D. R. Cogley, J. N. Butler and E. Grunwald, J. Phys. Chem., 1971, 75, 1477.

90. G. W. Stockton and J. S. Martin, J. Amer. Chem. Soc., 1972, 94, 6921.

91. A. Carrington, F. Dravnieks and M. C. R. Symons, Mol. Phys., 1960, 3, 174.

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

93. W. Karzijn and J. B. F. N. Engberts, Rec. Trav. chim., 1977, 96, 95.

94. B. G. Cox, J.C.S. Perkin II, 1973, 607 and Refs. therein; B. G. Cox, R. Natarajan and W. E. Waghorne, J.C.S.Faraday I, 1979, 75, 1780.

95. L. Rodehüser and H. Schneider, Z. phys. Chem. (N.F.), 1976, 100, 119.

96. O. L. Chapman and R. W. King, J. Amer. Chem. Soc., 1964, 86, 1256.

97. B. Kingston and M. C. R. Symons, J.C.S. Faraday II, 1973, 69, 978.

98. W. Y. Wen and H. G. Hertz, J. Solution Chem., 1972, 1, 17.

99. J. Oakes, J.C.S. Faraday II, 1972, 68, 1464.

100. M. Marciacq-Rousselot and M. Lucas, J. Phys. Chem., 1973, 77, 1056.

101. A. K. Covington and K. E. Newman, Modern Aspects of Electro-chemistry (Plenum Press, New York, 1977), vol. 12, p. 41.

102. J. M. Harvey, M. C. R. Symons and R. J. Naftaltn, Nature, 1976, 261, 435; J. M. Harvey, S. E. Jackson and M. C. R. Symons, Chem. Phys. Letters, 1976, 37, 551.

103. A. Coccia, P. L. Indovina. F. Podo and V. Viti, Chem. Phys., 1975, 7, 30.

104. D. N. Glew, H. D. Mak and N. S. Rath, J.C.S. Chem. Comm., 1968, 264.

105, W. M. Litchman, M. Alei and A. E. Florin, J. Amer. Chem. Soc., 1969, 91, 6574.

106. J. E. Sarneski, H. L. Surpenant, F. K. Molen and C. N. Reilley, Analyt. Chem., 1975, 47, 2116.

107. J. F. Hinton and C. E. Westerman, Spectrochim. Acta A, 1970, 26, 1387; J. F. Hinton and K. H. Ladner, ibid., 1972, 28, 1731; J. F. Hinton, K. H. Ladner and W. E. Stewart,

J. Magnetic Resonance, 1973, 12, 90.

108. M. C. R. Symons, J. M. Harvey and S. E. Jackson, J.C.S. Faraday I, 1980, 76, 256.

109. M. C. R. Symons and S. E. Jackson, J.C.S. Faraday I, 1979, 75, 1919.

110. T. Tokuhiro, L. Menafra and H. H. Szmant, J. Chem. Phys. 1974, 61, 2275 and Refs. therein.

111. T. Tokuhiro, J. Freer and L. Menafra, J.C.S. Faraday II, 1979, 75, 1388 and Refs. therein.

112. M. Karplus and G. K. Fraenkel, J. Chem. Phys., 1961, 35, 1312.

113. M. C. R. Symons, Pure Appl. Chem., 1977, 49, 13.

114. J. M. Gross and M. C. R. Symons, Trans. Faraday Soc., 1967, 63, 2117.

115. P. Ashworth and W. T. Dixon, J.C.S. Perkin II, 1972, 1130.

116. F. R. Hewgill and L. R. Mullings, J. Chem. Soc. B, 1969, 1155.

117. A. I. Vogel's Textbook of Practical Organic Chemistry, revised by B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell (Longmans, London, 4th edn., 1978).

118. R. C. Weast (ed.), Handbook of Chemistry and Physics, (Chemical Rubber Co., Cleveland, Ohio, 52nd edn., 1971).

119. J. Heilbron, A. H. Cook, H. M. Bunbury and D. H. Hey (ed.), Dictionary of Organic Compounds (Eyre and Spottiswoode, London, 4th edn, 1965).

120. H. J. Teuber and W. Rall, Chem. Ber., 1953, 86, 1036.

121. W. Baker, *J. Chem. Soc.*, 1941, 662; W. Baker and H. Raisrick, *ibid.*, 1941, 670; W. Baker, E. H. T. Jukes and C. A. Subrahmanyam, *ibid.*, 1934, 1681.

122. E. Chapman, A. G. Perkin and R. Robinson, *J. Chem. Soc.*, 1927, 3015.

123. F. Dallacker, W. Edelman and A. Weiner, *Annalen*, 1968, *719*, 112.

124. W. D. Crow, R. D. Haworth and P. R. Jeffries, *J. Chem. Soc.*, 1952, 3705.

125. W. A. Waters, *J. Chem. Soc.*, 1964, 408.

126. D. M. Holton and D. Murphy, *J.C.S. Perkin II*, paper 0/602, in the press.

127. W. T. Dixon, P. M. Kok and D. Murphy, *Tetrahedron Letters*, 1976, *8*, 623.

128. P. Ashworth, *J.C,S. Perkin II*, 1974, 739.

129. W. T. Dixon, M. Moghimi and D. Murphy, *J.C.S. Faraday II*, 1974, *70*, 1713.

130. P. D. Sullivan, *J. Phys. Chem.*, 1970, *74*, 2563; *ibid.*, 1971, *75*, 2195;
W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1976, 1823; *J.C.S. Faraday II*, 1977, *73*, 1475.

131. E. W. Washburn (ed.), *International Critical Tables* (National Research Council U.S.A., 1929), vol. VI, p. 101;
G. Douheret, *Bull. Soc. chim. France*, 1968, 3122.

132. J. A. Gowland and G. H. Schmid, *Canad. J. Chem.*, 1969, *47*, 2953.

133. N. Normandt, *Angew. Chem. (Int. Edn)*, 1967, *6*, 1046.

134. A. C. MacKinnis, Chem. Abstracts, 1957, 51, 1275g.

135. D. Jannakoudakis, G. Papanastasiou and P. G. Mavradis, Chim. Chron., 1976, 5, 167.

136. A. J. Parker, Quart. Rev., 1962, 16, 163.

137. C. de Visser, W. J. M. Heuvelsland, L. A. Dunn and G. Somsen, J.C.S. Faraday I, 1978, 74, 1159.

138. T. Olsen, Acta Chem. Scand., 1970, 24, 3081.

PUBLICATIONS

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Quantitative Aspects of the Solvation of Semiquinones in Water+HMPA Mixtures

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The e.s.r. spectra of semiquinones generally vary smoothly with the molar ratio of water to hexamethylphosphoramide (HMPA). Detailed analysis of this variation leads to equilibrium constants which are a measure of the affinity of a radical for HMPA compared to that for water. When there is sufficient HMPA in the solution, the dianions of hydroxysemiquinones give way to the corresponding singly-charged species, providing additional evidence for the formation of a stable complex between the two solvents, of the form HMPA . $2H_2O$.

Solvent effects in e.s.r. spectra have long since been noted [1-3] and have often been rationalized in terms of specific interactions between sites on the radical concerned and sites on the solvent molecules.[4-6] However, little quantitative work [7] on the thermodynamic aspects of such interactions in mixed solvents has been reported. The simple theoretical model proposed by Gendell, Freed and Fraenkel [3] for the competition between solvents for a radical was not actually applied by these authors to their own data, no doubt due to the small magnitude of the effects they observed, and has not received much attention since. In this paper we deal with the determination of thermodynamic equilibrium constants, which are measures of the affinities of various semiquinones for the solvent HMPA [8] [hexamethylphosphoramide $OP(NMe_2)_3$], relative to water. In favourable cases the solvent effects are large enough for us to prove that the simple model does apply and we can deduce something about the interaction between the two solvents.

EXPERIMENTAL

Mixtures of the two solvents were made up by weight fractions. The radicals were generated in the usual way by autoxidation, using $KOBu^t$ (solid) as the base.[9] All the materials were commercially available and were purified by the usual methods.

ANALYSIS OF RESULTS

In eqn (1),[3] R_2 is the radical solvated by solvent S_2 and R_1 is the radical solvated by solvent S_1

$$R_2+S_1 \rightleftharpoons R_1+S_2. \tag{1}$$

If the concentrations of the species in this equation are r_2, s_1, r_1, s_2 respectively, then for a given parameter "p", which has a value p_1 in S_1 and a value p_2 in S_2, we have the equilibrium eqn (2)

$$\left(\frac{p-p_2}{p_1-p}\right)\frac{s_2}{s_1} = K \tag{2}$$

where K is a constant measuring the tendency of solvent S_1 to displace solvent S_2 molecules associated with the radical.

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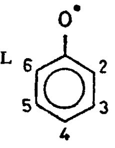
† Deceased 12th August, 1977.

TABLE 1.—PARAMETERS FOUND FOR DERIVATIVES OF PHENOXYL COUPLING CONSTANTS ($G = 10^{-4}$ T) (±0.03 G)



substituents	solvent	a_2	a_3	a_4	a_5	a_6	$1/K$
4-O$^-$	H$_2$O	2.37	2.37		2.37	2.37	1±0.5
	HMPA	2.43	2.43		2.43	2.43	
2-CH$_3$, 4-O$^-$	H$_2$O	$a_{\text{Me}} = 2.13$	1.75		2.61	2.42	1±0.25
	HMPA	$a_{\text{Me}} = 1.86$	2.06		2.73	2.49	
2-O$^-$, 4-O$^-$	H$_2$O		0.60		4.90	1.35	
2-OH, 4-O$^-$	HMPA	$a_{\text{OH}} = 0.31$	1.13		4.75	1.58	
2-OMe, 4-O$^-$	H$_2$O	$a_{\text{OMe}} = 0.86$	0.52		3.69	2.00	1.75±0.25
	HMPA	$a_{\text{OMe}} = 0.48$	1.15		3.50	2.31	
2,6-Bu$^t_2$, 4-O$^-$	H$_2$O		1.31		1.31		1±0.05
	HMPA		2.25		2.25		
2-O$^-$	H$_2$O		0.73	3.69	3.69	0.73	4±0.25
	HMPA		1.57	3.33	3.33	1.57	
2-O$^-$, 4-CH$_3$	H$_2$O		0.07	$a_{\text{Me}} = 4.89$	3.89	0.92	5±0.5
	HMPA		1.00	$a_{\text{Me}} = 3.85$	3.55	1.69	
2-O$^-$, 4,5-CH$_2$<O/O	H$_2$O		(−)0.33	$a_{\text{CH}_2} = 4.22$		(−)0.33	6±0.25
	HMPA		(+)0.53	$a_{\text{CH}_2} = 2.37$		(+)0.53	
2-O$^-$, 3-O$^-$	H$_2$O			0.97	5.50	0.97	
2-O$^-$, 3-OH	HMPA		$a_{\text{OH}} = 0.36$	1.90	3.50	0.33	
2-O$^-$, 3-OMe	H$_2$O		$a_{\text{OMe}} = 0.65$	1.28	4.75	0.59	2.75±0.25
	HMPA		$a_{\text{OMe}} = 0.48$	1.90	3.79	0.46	

From eqn (2), the variation of a parameter with solvent composition should be of the type shown in fig. 1, as has been observed by a number of authors [3, 6] already.

In the systems we are studying, the inaccuracies in individual measurements are liable to be quite significant, and it is therefore desirable to find a legitimate procedure

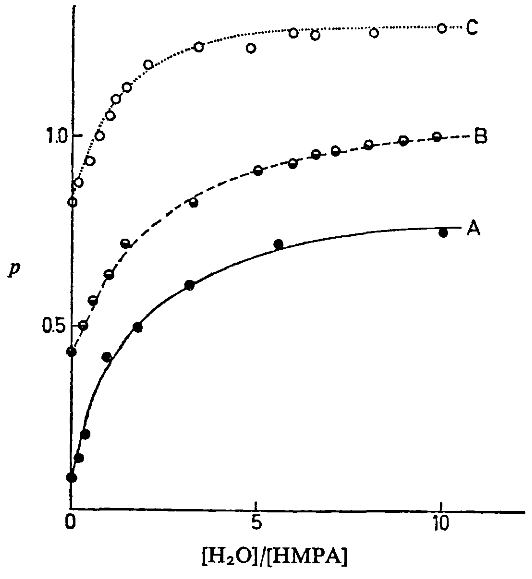


FIG. 1.—Straightforward plot of parameter " p " against molar ratio of solvents for semiquinones A, from 3-methoxycatechol (a_5/G); B, from catechol (a_3/G); and C, from methoxyhydroquinone (a_3/G). Scales of p are adjusted so that the curves do not overlap.

to determine whether eqn (2) is being obeyed. It is better to plot the parameter against log (s_2/s_1) than against s_2/s_1 because then, according to eqn (2), a sigmoid curve should arise, the point of inflection being at a point where "p" is the mean between the two extremes, *i.e.* $(p_1+p_2)/2$. The value of log (s_2/s_1) at this point will simply be log K (see fig. 2).

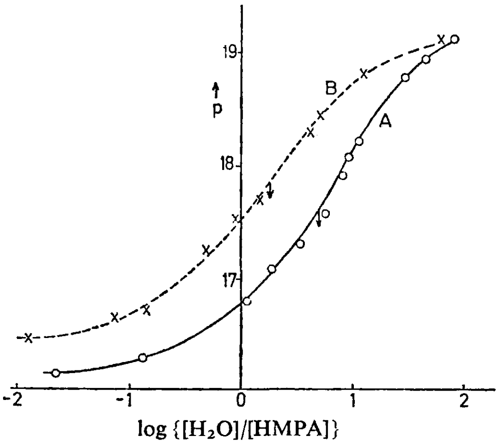


FIG. 2.—Plot of parameter "p" (total spectral width/G) against log(molar ratio) for 4-methylcatechol. A, for water-HMPA ; B, for water-DMF (for comparison).

However, just as there are many ways of arriving at curves resembling those in fig. 1, so there are an infinite number of relationships, of which eqn (2) is only one, which could give rise to sigmoid curves as in fig. 2. A more exacting way of approach- the problem is to use eqn (3) and (4) derived from eqn (2)

$$\frac{p_1-p_2}{p_1-p} = Ks_1/s_2+1 \tag{3}$$

$$\frac{p_1-p_2}{p-p_2} = s_2/Ks_1+1. \tag{4}$$

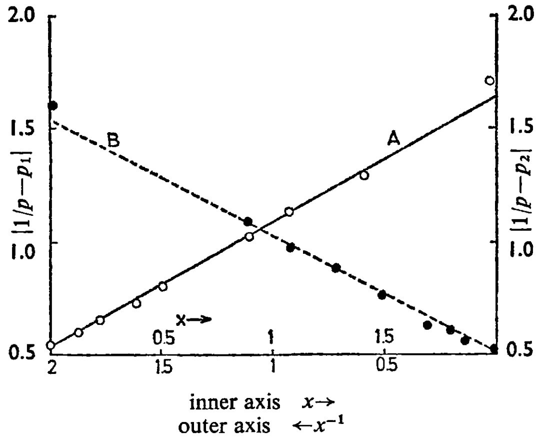


FIG. 3.—Plots for data from 2,6-di-t-butylhydroqui one suggested by eqn (3) and (4). A, $x \rightarrow |1/(p-p_1)|$; B, $1/x \rightarrow |1/(p-p_2)|$; where $x = [H_2O]/[HMPA]$, $p = (a_3+a_5)/G$ p_1, p_2 = values of "p" in water, HMPA respectively.

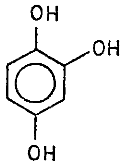
Thus, using eqn (3), we plot $1/(p_1-p)$ against s_1/s_2. The result should be a straight line from which K can easily be calculated. When we plot our data for semiquinones in this way we obtain straight lines, as shown in fig. 3, showing that eqn (2) is obeyed.

Eqn (3) and (4) are particularly useful when it is difficult to determine accurately one, or even both, of the extreme values of the parameters. The values obtained in this way for the constant K are given in table 1 ; S_1 ≡ water, S_2 ≡ HMPA.

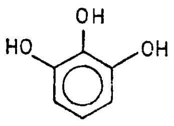
In the cases where the range of variation is small there is a corresponding uncertainty in " K ", for example in the worst case, that of *p*-benzosemiquinone, it is possible to bracket the point of inflection (as in fig. 2) to within ±0.5.

RESULTS FROM TRIHYDROXYBENZENES

The e.s.r. spectra of the semiquinones from the trihydroxybenzenes A and B



A



B

showed not only the gradual changes with changing solvent ratio, as discussed above, but in addition showed a sharp change in the region s_1/s_2 = 2-3, (see fig. 4).

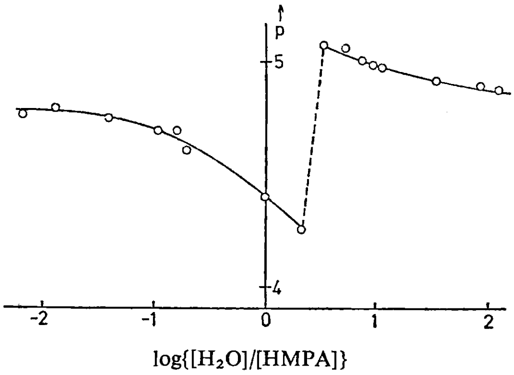


FIG. 4.—Plot of large coupling constant/G in spectrum from 1,2,4-trihydroxybenzene, showing change of nature of radical.

It was clear that when the solvent ratio $s_1/s_2 \lesssim 2$, hydroxysemiquinones were being observed, whereas when $s_1/s_2 \gtrsim 2$, the corresponding dianion only could be seen. The coupling constants of these various radicals are given in table 1.

DISCUSSION

The ratio of the two solvated forms of a given semiquinone varies with the first power of the molar ratio of the two solvents, as would be expected in an ideal case where there is no interaction between the solvents. It seems, therefore, that there are two situations for a semiquinone, one where it is hydrogen-bonded to water and the other where it is not. However, the equilibrium between possible long-lived complexes of water and HMPA has to be taken into account. The results from the

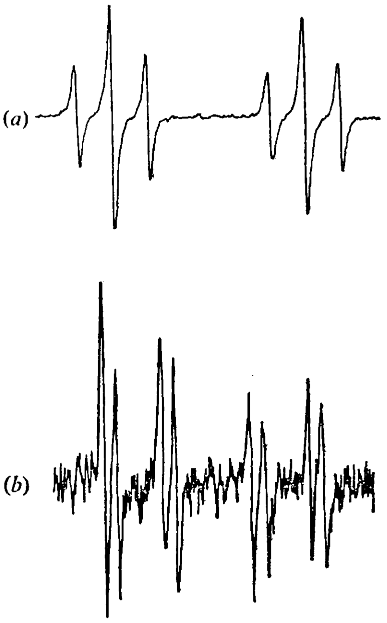


FIG. 5.—E.s.r. spectra from 1,2,3-trihydroxybenzene. (a), $[H_2O]/[HMPA] = 3.3$; (b), $[H_2O]/[HMPA] = 2.1$.

trihydroxybenzenes show that around the region $[H_2O]/[HMPA] = 2$, the solvent structure changes in such a way that at higher HMPA concentrations, the dianion radicals no longer persist.

An investigation of the proton chemical shift of water in mixtures of HMPA and water, using the principles developed above, showed that the ratio of protons hydrogen-bonded to HMPA to those hydrogen-bonded to water varies with the square of the water concentration and inversely with the first power of the HMPA concentration, (see fig. 6). This is consistent with the equilibrium (5)

$$HMPA + 2H_2O \rightleftharpoons HMPA . 2H_2O \tag{5}$$

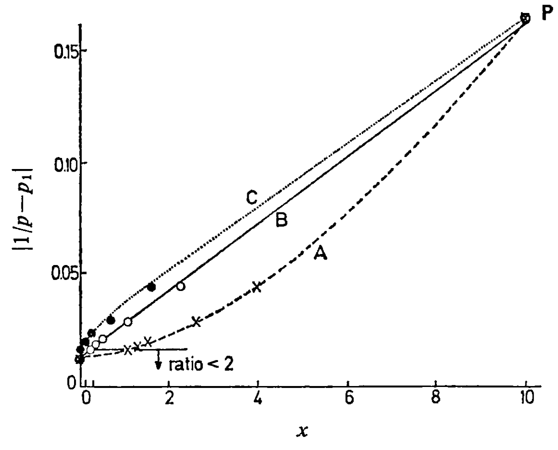


FIG. 6.—Plot of chemical shift data against A, $x = [H_2O]/[HMPA]$; B, $x = [H_2O]^2/[HMPA]$; C, $x = ([H_2O]/[HMPA])^2$. "p" = proton chemical shift relative to TMS, p_1 = value of "p" in pure water. The scales of "x" are adjusted so that the three points at a ratio 10 : 1 coincide at P.

where HMPA . $2H_2O$ is probably the same type of stable complex as those formed, for example, by dimethylsulphoxide and by dimethylformamide with water.[10] HMPA . H_2O could either be a similar type of compound or water " solvated " by HMPA, *i.e.* by means of hydrogen-bonding.

These results suggest that the dianion radicals from the trihydroxybenzenes cannot persist unless there is enough " free " water in the system, *i.e.* water not bound to HMPA. In contrast to this, the equilibrium between the two solvated forms of a semiquinone appears to be independent of any interaction between the two solvents.

[1] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.
[2] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **36**, 1944.
[3] J. Gendell, J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.
[4] C. Trapp, C. A. Tyson and G. Giacometti, *J. Amer. Chem. Soc.*, 1968, **90**, 1394.
[5] J. A. Pedersen, *Mol. Phys.*, 1974, **28**, 1031.
[6] P. Ashworth, *Mol. Phys.*, 1975, **30**, 313.
[7] J. Oakes, J. Slater and M. C. R. Symons, *Trans. Faraday Soc.*, 1970, **66**, 546.
[8] N. Normant, *Angew. Chem.* (*Int. Edn*), 1967, **6**, 1046.
[9] W. T. Dixon, P. M. Kok and D. Murphy, *Tetrahedron Letters*, 1976, 623.
[10] D. Giannakoudakis, G. Papanastasiou and P. G. Mavridis, *Chem. Chron.*, 1976, **5**(2), 167.

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AN E.S.R. STUDY OF RADICALS OBTAINED BY THE OXIDATION OF 3,6-DIHYDROXYPYRIDAZINES

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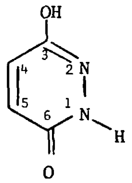
One electron oxidation of the plant growth substance 3,6-dihydroxypyridazine (maleic hydrazide) gives a cyclic α-carbonylhydrazyl, the e.s.r. parameters of which are assigned by comparison with five related radicals.

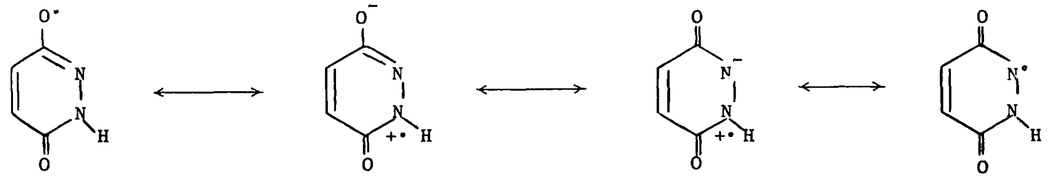
3,6-Pyridazinedione[1] is one of a growing number of cyclic α-carbonylazo-compounds investigated in the search for highly reactive dienophiles which have proved most valuable in the synthesis of difficultly accessible ring systems. The diazaquinone is conveniently prepared by the reaction of the potassium salt of 3,6-dihydroxypyridazine (maleic hydrazide) with t-butyl hypochlorite in acetone at -78°C. In this work, the one electron oxidation of the hydrazide has been studied by e.s.r. spectroscopy in order to determine the nature of any radical intermediates.

Maleic hydrazide exists almost entirely in the monolactim form (*1*). Oxidation of a 5×10^{-3} mol dm^{-3} solution of (*1*) with 5×10^{-3} mol dm^{-3} cerium(IV) sulphate in 0.1 mol dm^{-3} sulphuric acid using a flow system[2] resulted in an intense e.s.r. spectrum, splittings 3.75 (1N), 6.50 (1N), 6.50 (1H) and 0.40×10^{-4} T (1H). As these values cannot be unambiguously assigned, a series of substituted derivatives of (*1*) were prepared and examined in a similar way; the results are given in the table, radicals (*2*)-(*7*). It has been demonstrated[3] that in a large number of radicals containing N-H groups, $a_N \approx a^{H}_{NH}$, so that the observed splittings can be assigned as in (*2*)-(*7*).



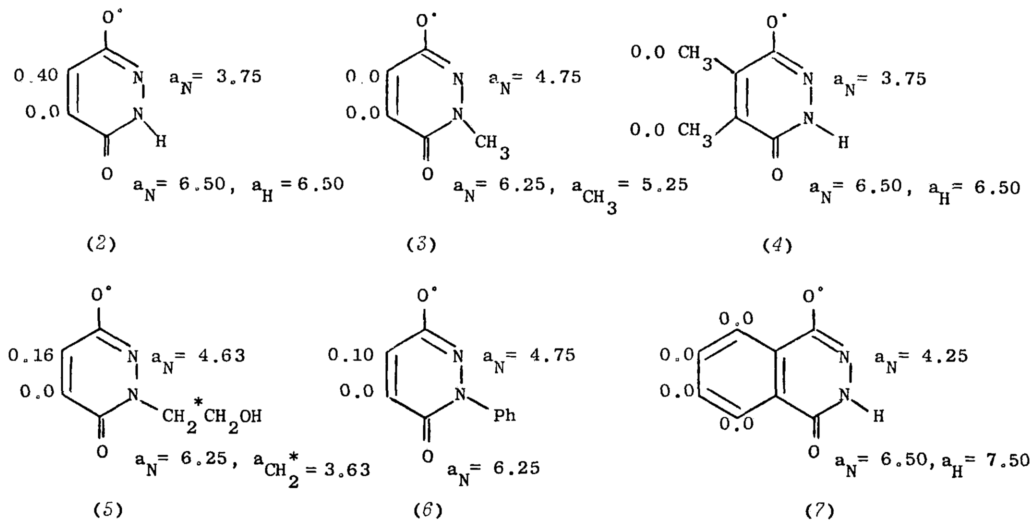
(*1*)

The stability of the radicals as indicated by the intense e.s.r. signals is due to delocalisation as in (*2a*)-(*2d*). Studies of other α-carbonylhydrazyl radicals[4] have suggested



(*2a*) (*2b*) (*2c*) (*2d*)

Table 1. E.s.r. parameters ($a/10^{-4}$ T) for radicals from 3,6-dihydroxypyridazines


O•
0.40
0.0
a_N = 3.75
a_N = 6.50, a_H = 6.50
(2)
0.0
0.0
a_N = 4.75
a_N = 6.25, a_{CH_3} = 5.25
(3)
0.0 CH₃
0.0 CH₃
a_N = 3.75
a_N = 6.50, a_H = 6.50
(4)
0.16
0.0
a_N = 4.63
a_N = 6.25, $a_{CH_2^*}$ = 3.63
(5)
0.10
0.0
a_N = 4.75
a_N = 6.25
(6)
0.0
0.0
0.0
0.0
a_N = 4.25
a_N = 6.50, a_H = 7.50
(7)

that in the presence of the carbonyl group, forms (*2b*) ⟷ (*2c*) with the unpaired electron mainly on N(1) are major contributors to the structure. Thus, in the experimental conditions used in this work (*2b*), which may be protonated in the acid solutions, is consistent with the observed splittings, with $a_{N(1)} > a_{N(2)}$.

Attempts to obtain diazasemiquinone by autoxidation of (*1*) in alkaline solution[5] were unsuccessful.

As it is shown that (*1*) is readily oxidised to give a free radical (*2*) it is possible that the plant growth inhibiting action[6] of (*1*) is connected with such an intermediate. The more stable, but related, bipyridinyl radicals are potent herbicides[7].

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REFERENCES

1. T.J. Kealy, J. Amer. Chem. Soc., 1962, 84, 996.
2. W.T. Dixon and R.O.C. Norman, J. Chem. Soc., 1963, 3119
3. A.T. Bullock and C.B. Howard, Trans. Faraday Soc., 1970, 66, 1861
4. Y.M. Ryzhmanov, Y.V. Yablokov, B.M. Kozynev, L.I. Stashkov and R.O. Matevosyan, Doklady Chem., 1965, 162, 443
5. W.T. Dixon, P.M. Kok and D. Murphy, Tetrahedron Lett., 1976, 623
6. L.J. Audus, Plant Growth Substances, (Hill, London, 2nd Edn., 1959)
7. W.R. Boon, Endeavour, 1967, 26, 27; Outlook Agr., 1963 and refs. therein.

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Electron Spin Resonance Spectra of Tri-, Tetra- and Penta-alkoxybenzene Radical Cations

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Radical cations of tri-, tetra- and pentaalkoxybenzenes have been generated in a flow system by oxidation of the ethers with cerium(IV) in aqueous sulphuric acid solution. The observed splitting patterns have been confirmed by calculations using the McLachlan SCF method, and have been interpreted in terms of the symmetry properties of the odd electron molecular orbitals.

In a previous paper [1] we reported a flow technique for the observation of e.s.r. spectra of alkyl aryl ether radical cations in which the ethers were oxidised with cerium(IV) sulphate in $H_2SO_4 . 4H_2O$ virtually inside the cavity of our Varian E4 spectrometer.[2] Radical cations of the methoxybenzenes had been reported previously,[3] but with the techniques then available, many of the spectra were incompletely resolved. Only in the case of the radical cations from *p*-dimethoxybenzene had extensive e.s.r. studies been made.[4, 5] We have now been able to obtain relatively well resolved e.s.r. spectra (*e.g.*, see fig. 1) of a range of penta-, tetra- and tri-alkoxybenzene radical cations, which together with those published previously [1] gives a more complete insight into the symmetry properties of the odd electron orbitals in these compounds.

EXPERIMENTAL

E.S.R. SPECTRA

E.s.r. spectra were obtained by the oxidation of 5×10^{-3} mol dm^{-3} solutions of the ethers in $H_2SO_4 . 4H_2O$ with 5×10^{-3} mol dm^{-3} cerium(IV) sulphate in $H_2SO_4 . 4H_2O$ in the flow system described previously.[2] *g*-Values were measured using Fremy's salt ($g = 2.0055$)[6] as an external standard. Second-order effects were manifested in the broadening of the centre lines in the spectra of the 1,3-benzodioxole radical cations and in some cases the second-order splittings ($\approx 0.1\times10^{-4}$ T) could just be resolved. Corresponding corrections to the *g*-values were within the general experimental error.

MATERIALS

2,5-Dimethoxy-3,4-methylenedioxy-1-allylbenzene [7a] (parsley apiol), m.p. 28-29°, 2,3-dimethoxy-4,5-methylenedioxy-1-allylbenzene [7b] (dill apiol), m.p. 29-30° and 3-methoxy-4,5-methylenedioxy-1-allyl benzene [7c] (myristicin), b.p. 150°/15 Torr were obtained by steam distillation of the crushed fruits of parsley, dill and nutmeg, respectively. Pentamethoxybenzene, m.p. 58-59°, 1,2,3,4-tetramethoxybenzene, m.p. 88-89° and 1,2,3,5-tetramethoxybenzene, m.p. 45-46°, were prepared as in ref. (8). 3,4,5-Trimethoxy-1,2-methylenedioxybenzene, m.p. 46° and 3,4,6-trimethoxy-1,2-methylenedioxybenzene, m.p. 27-29°, were prepared by treatment of the corresponding trimethoxy-1,2-dihydroxybenzenes with diiodomethane;[8-11] 1,2,4,5-tetramethoxybenzene, m.p. 103° and 1,2; 4,5-bis-methylenedioxybenzene,[11] m.p. 141°, were prepared from commercial 4,5-dimethoxy-1,2-benzoquinone and 4-hydroxy-1,2-methylenedioxybenzene, respectively. All of these compounds had physical constants which agreed well with those given in the cited literature.

Other compounds used were commercial materials which after purification by recrystallisation, distillation under reduced pressure or vacuum sublimation had physical constants which corresponded to those in the literature.

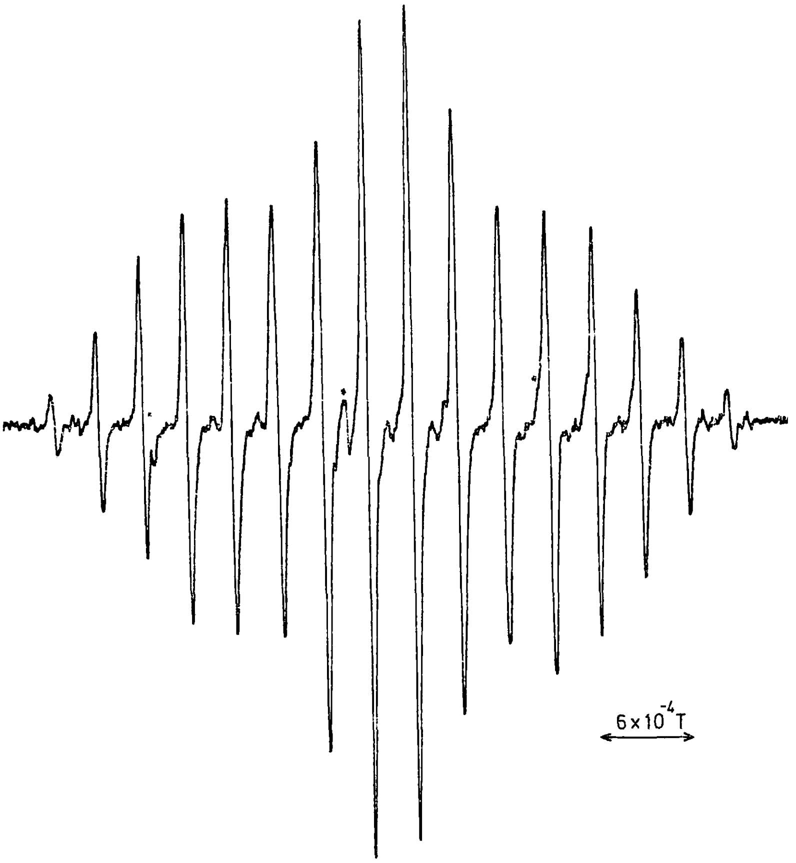
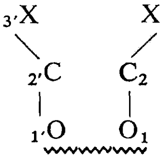


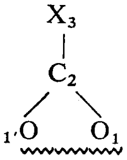
FIG. 1.—E.s.r. spectrum of 2,3-dimethoxy-4,5-methylenedioxy-1-allylbenzene (* lines due to the external standard).

RESULTS AND DISCUSSION

The e.s.r. parameters of a number of polyalkoxybenzene radical cations are given in table 1. Two points arise from this table. Firstly, most of the methoxy splittings not resolved in the previous work [3] have been resolved and satisfactorily assigned. Secondly, the relationship between splittings of *o*-dimethoxy protons (A) and those of the corresponding methylenedioxy protons (B) provides a reliable guide for the assignment



(A)



(B)

of splittings. The aliphatic proton splittings in (A) and (B) both arise from hyperconjugation,[1, 5] and are, therefore, proportional to the spin densities on the adjacent oxygen atoms. The relevant secular equations for calculating spin delocalisation due to hyperconjugation are, for (A), as follows.

$$(\alpha_C - E_O)(C_2 + C_{2'}) + \beta_{12}C_1 + \beta_{1'2'}C_{1'} + \beta_{23}C_3 + \beta_{2'3'}C_{3'} = 0$$

$$\beta_{23}C_2 + \beta_{2'3'}C_{2'} + (\alpha_x - E_O)(C_3 + C_{3'}) = 0$$

and for (B):

$$(\alpha_C - E'_O)C_2 + \beta_{12}C_1 + \beta_{1'2'}C_{1'} + \beta_{23}C_3 = 0$$

$$\beta_{22}C_2 + (\alpha_x - E'_O)C_3 = 0$$

where α_C and α_x are the coulomb integrals of the carbon π orbital and hydrogen group orbital of π symmetry, respectively, and are assumed to be equal for the two different alkoxy fragments in (A); β_{12}, $\beta_{1'2'}$, β_{23} and $\beta_{2'3'}$ are resonance integrals and C the coefficients of the atomic orbitals. E_O and E'_O are the energies of the odd electron orbitals in the two cases and we would expect that $(E_O - E'_O)$ is small. The spin density ρ_x in the hydrogen group orbital " x " is then calculated to be for (A)

$$\rho_x = C_3C_{3'} \approx \frac{\beta_{12}\beta_{1'2'}}{\beta_{23}\beta_{2'3'}}\rho_O$$

and for (B)

$$\rho_x = C_3^2 \approx \frac{4\beta_{12}\beta_{1'2'}}{\beta_{23}^2}\rho_O$$

where ρ_O is the spin density on the oxygen atom.

The splittings of the aliphatic protons will depend on the dihedral angles, (θ), which in turn determine the nature of the hydrogen group orbitals. The splittings in the two cases are:

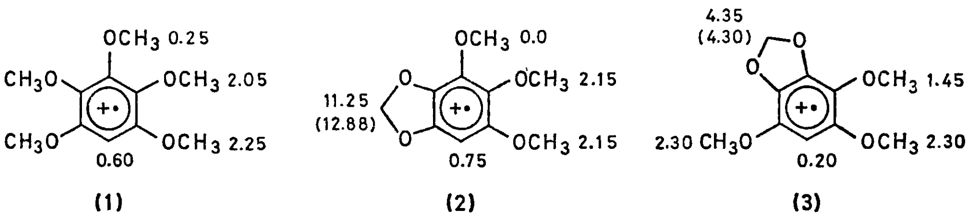
$$a_A = \tfrac{1}{3}\rho_x \times 508 \times 10^{-4}T\,(\theta = 45°,\ \text{rotational average})$$

$$a_B = \tfrac{1}{2}\rho_x \times 508 \times 10^{-4}T\,(\theta = 30°).$$

The product of β_{23} and $\beta_{2'3'}$ (for A) is expected to be approximately equal to β_{23}^2 (for B) and consequently the predicted ratio of the aliphatic coupling constants reduces to

$$\frac{a_A}{a_B} \approx \frac{\frac{1}{3}}{\frac{1}{2}\times 4} = \tfrac{1}{6}.$$

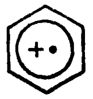
The calculated value for a_{CH_2} in (2) (scheme I) is, therefore, $(\sqrt{2.25} \times \sqrt{2.05}) \times 6 = 12.88 \times 10^{-4}$T. Thus, since the assignments in (1) have been proven by SCF calculations, the position of the methylenedioxy group in (2) and (3) can be inferred.

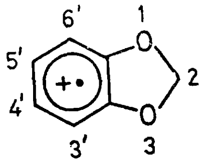


(1) (2) (3)

SCHEME 1.—Experimental splittings for radicals (1)-(3); values calculated from hyperconjugation model in brackets.

TABLE 1.—E.S.R. PARAMETERS ($a/10^{-4}$ T) FOR ALKOXYBENZENE

(i) substituents 	a_1	a_2
(1) 1,2,3,4,5-$(OCH_3)_5$	a_{OCH_3} = 2.25(1.53)	a_{OCH_3} = 2.05(1.53)
1,2,3,4-$(OCH_3)_4$	a_{OCH_3} = 2.80(2.47)	a_{OCH_3} = 0.55(0.44)
1,2,3,5-$(OCH_3)_4$	a_{OCH_3} = 2.20(0.85)	a_{OCH_3} = 4.70(3.09)
1,2,4,5-$(OCH_3)_4$	a_{OCH_3} = 2.35(1.53)	a_{OCH_3} = 2.35(1.53)
1,2,3-$(OCH_3)_3$	a_{OCH_3} = 2.05(1.57)	a_{OCH_3} = 5.25(4.05)
1,2,3-$(OCH_3)_3$,4-CHO	a_{OCH_3} = 1.75(1.44)	a_{OCH_3} = 5.70(4.06)
1,2,3-$(OCH_3)_3$,5-CHO	a_{OCH_3} = 2.30(1.68)	a_{OCH_3} = 5.30(4.10)
1,2,3-$(OCH_3)_3$,5-CO_2H	a_{OCH_3} = 2.25(1.68)	a_{OCH_3} = 3.23(4.10)
1,2,3-$(OCH_3)_3$,5-CH_3	a_{OCH_3} = 1.80(1.35)	a_{OCH_3} = 5.0(3.75)
1,2,3-$(OCH_3)_3$,5-CH_2CO_2H	a_{OCH_3} = 2.0	a_{OCH_3} = 5.20
1,2,3-$(OCH_3)_3$,5-$(CH_2)_2NH_3^+$	a_{OCH_3} = 2.0	a_{OCH_3} = 5.15
1,2,4-$(OCH_3)_3$,5-CO_2H	a_{OCH_3} = 3.40(3.01)	a_{OCH_3} = 1.85(1.38)
1,3,5-$(OCH_3)_3$,2-CH_3	a_{OCH_3} = 0.50(0.77)	a_{CH_3} = 15.60(12.09)

(ii) substituents in 	a_2	a_3'
(2) 3′,4′,5′-$(OCH_3)_3$	11.25(10.66)	a_{OCH_3} = 0.05(−0.09)
(3) 3′,4′,6′-$(OCH_3)_3$	4.35(3.53)	a_{OCH_3} = 1.45(1.29)
3′,4′-$(OCH_3)_2$,5′-$CH_2CH{=}CH_2$	12.15(12.35)	a_{OCH_3} = 0.0(0.04)
(4) 3′,6′-$(OCH_3)_2$,4′-$CH_2CH{=}CH_2$	17.42(11.16)[b]	a_{OCH_3} = 1.32(0.36)
3′-OCH_3,5′-$CH_2CH{=}CH_2$	18.90(16.82)	a_{OCH_3} = 1.35(1.03)
3′-CH_3,6′-$CH(CH_3)_2$	21.23(21.08)	a_{CH_3} = 0.67(0.13)
4′-CH_3,5′-CHO	21.25(19.63)	0.65(−1.25)
4′,5′-(OCH_2O)	11.75(9.71)	1.025(−1.75)

[a] Parameters from ref. (14) —O^-; $h_O = 1.6$, $k_{CO} = 1.3$, —CH_3; $h_C = -0.7$, $h_{H_3} = -1.0$, $k_{C-CH_3} = 0.7$, $k_{C-H_3} = 2.5$, —OCH_3; $h_O = 2.3$, $h_C = -0.7$, $h_{H_3} = -1.0$, $k_{C-OCH_3} = 1.1$, $k_{O-CH_3} = 0.7$, $k_{C-H_3} = 2.5$ where $\alpha_x = \alpha + h_x\beta$ and $\beta_{Cx} = k_{Cx}\beta$.

As we have observed previously,[1] where there are alkyl substituents in the ether radical cations, the nature of the alkyl group has virtually no effect on the spin distribution.

EMPIRICAL SCF THEORY

As most of the observed splitting patterns obtained from the methoxybenzene radical cations cannot be unambiguously assigned, we have used McLachlan's simplified SCF procedure,[12-14] neglecting overlap and non-nearest neighbour inter-

RADICAL CATIONS (CALCULATED VALUES IN PARENTHESES)[a]

a_3	a_4	a_5	a_6	g-values (±0.0001)
a_{OCH_3} = 0.25(−0.10)	a_{OCH_3} = 2.05(1.53)	a_{OCH_3} = 2.25(1.53)	0.60(−1.80)	2.0039
a_{OCH_3} = 0.55(0.44)	a_{OCH_3} = 2.80(2.47)	3.0(2.78)	3.0(2.78)	2.0039
a_{OCH_3} = 2.20(0.85)	0.20(0.56)	a_{OCH_3} = 2.60(1.50)	0.20(0.56)	2.00385
0.95(−1.87)	a_{OCH_3} = 2.35(1.53)	a_{OCH_3} = 2.35(1.53)	0.95(−1.87)	2.0039
a_{OCH_3} = 2.05(1.57)	0.45(−1.30)	6.25(5.86)	0.45(−1.30)	2.0038
a_{OCH_3} = 2.25(1.74)	0.0(−0.11)	5.55(5.73)	0.45(−1.14)	2.0040
a_{OCH_3} = 2.30(1.68)	0.80(−1.45)	a_{CH} = 0.10(0.05)	0.80(−1.45)	2.0043
a_{OCH_3} = 2.25(1.68)	0.75(−1.45)		0.75(−1.45)	2.0040
a_{OCH_3} = 1.80(1.35)	0.05(−0.97)	a_{CH_3} = 8.95(4.48)	0.05(−0.97)	2.0037
a_{OCH_3} = 2.0	0.33	a_{CH_2} = 5.20	0.33	2.0037
a_{OCH_3} = 2.0	0.30	a_{CH_2} = 5.65	0.30	2.0038
0.35(−1.28)	a_{OCH_3} = 2.65(1.73)		0.35(0.63)	2.00385
a_{OCH_3} = 0.50(0.77)	2.50(2.09)	a_{OCH_3} = 4.50(2.51)	2.50(2.0)	2.00315

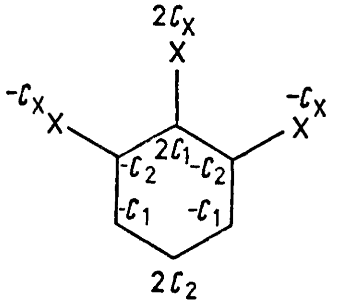
a'_4	a'_5	a'_6	g-values (±0.0001)
a_{OCH_3} = 2.15(1.35)	a_{OCH_3} = 2.15(1.41)	0.75(−1.70)	2.0040
a_{OCH_3} = 2.30(1.56)	0.20(−1.70)	a_{OCH_3} = 2.30(1.46)	2.0040
a_{OCH_3} = 3.0(1.69)	a_{CH_2} = 6.10(3.80)	0.0(−0.25)	2.0038
a_{CH_2} = 7.70(5.42)	0.60(−1.77)	a_{OCH_3} = 1.32(1.61)	2.0038
0.25(−0.44)	a_{CH_2} = 7.65(3.93)	0.65(−1.39)	2.0044
4.61(3.52)	4.61(3.52)	a_{CH} = 0.27(0.13)	2.0039
a_{CH_3} = 6.85(3.46)	a_{CH} = 0.25	0.25(0.14)	2.0042
[11.75(9.71)]		1.025(−1.75)	2.00435

[b] See scheme 2.

actions, to obtain information about the magnitudes and signs of the coupling constants. The variable parameters for a heteroatom x are its coulomb integral $\alpha_x = \alpha + h_x\beta$ and resonance integral $\beta_{cx} = k_{cx}\beta$, where α and β are the coulomb and resonance integrals, respectively, for aromatic carbon p_π orbitals. Previous work has shown that this semi-empirical theory gives large numbers of successful predictions [14] from comparatively few parameters where more sophisticated theories fail.[13] Using the set of parameters given fully elsewhere [14] we have calculated values for the coupling constants observed; these are given in table 1. Agreement is generally good, although as in previous work, predicted splittings for methyl substituents *para* to oxygen are too small.

TRIALKOXYBENZENE RADICAL CATIONS

The experimental values for all of the radicals related to 1,2,3-trihydroxybenzene, which were consistently confirmed by SCF theory, showed that the odd electron is in an orbital (ψ_s), which is symmetrical with respect to the symmetry plane perpendicular to the aromatic ring.[15]



ψ_s

The ratio of the observed aliphatic proton splittings for the methoxy groups on C(2) and on C(1) in the 1,2,3-trimethoxybenzene radical cation (see table 1) is generally less than that predicted from this model (4 : 1), due to the expected [3] effects of steric hindrance.

Replacement of two methoxy groups by the methylenedioxy group or the introduction of a range of alkyl or of carbonyl substituents had very little effect on the spin distribution.

No resolved e.s.r. spectrum could be obtained from either 1,2,4- or 1,3,5-trimethoxybenzene. Introduction of a carboxyl substituent (2,4,5-trimethoxybenzoic acid) and a methyl substituent (2,4,6-trimethoxytoluene), respectively, led to well resolved spectra. In the latter case the unpaired electron is in a symmetrical orbital; the observed splittings are very close to those previously estimated[16] and are confirmed by our calculations.

TETRA-ALKOXYBENZENE RADICAL CATIONS

The radical cations from ethers related to 1,2,3,4-tetrahydroxybenzene (apionol) form an interesting class. With the exception of one example, radical (4) from 2,5-dimethoxy-3,4-methylenedioxy-1-allylbenzene, the splitting patterns, confirmed by calculation, show that the unpaired spin density is mainly concentrated at the 1,4,5,6-positions, with very small values for the 2,3-substituents.

A systematic development of the orbitals of apionol using the interleaving theorem [17, 18] is given in fig. 2. Using this approach the m.o. energy levels of a system can be generated by building up from simple units such as diatomic molecules and symmetric homonuclear systems which can be treated algebraically. An improved estimate of the relative spacings between adjacent energy levels results when the molecule is constructed by alternative routes as in fig. 2, without recourse to actual computation. The figure shows that the unpaired electron orbital is antisymmetric with respect to a plane (σ) bisecting the C_2—C_3 and C_5—C_6 bonds. The exceptional example (4) has, however, a large methylene splitting on a group which must lie in the nodal plane of the antisymmetric orbital.

Two kinds of explanation have been advanced for this situation where two completely different splitting patterns arise in closely related systems. One is the observation of triple oxidation of the substrate when one electron and three electron oxidation, respectively, give two sets of coupling constants which reveal the shapes of two adjacent molecular orbitals. This effect has been observed with pyrogallol[15] and with 1,4-bis(dimethylphosphino)benzene, where a single and a triple electron reduction gives rise to the same effect.[19] It is very unlikely that this explanation applies to radical (4) since three electron oxidation must lead to decomposition and the observed splitting pattern accounts for all six substituents in the benzene ring.

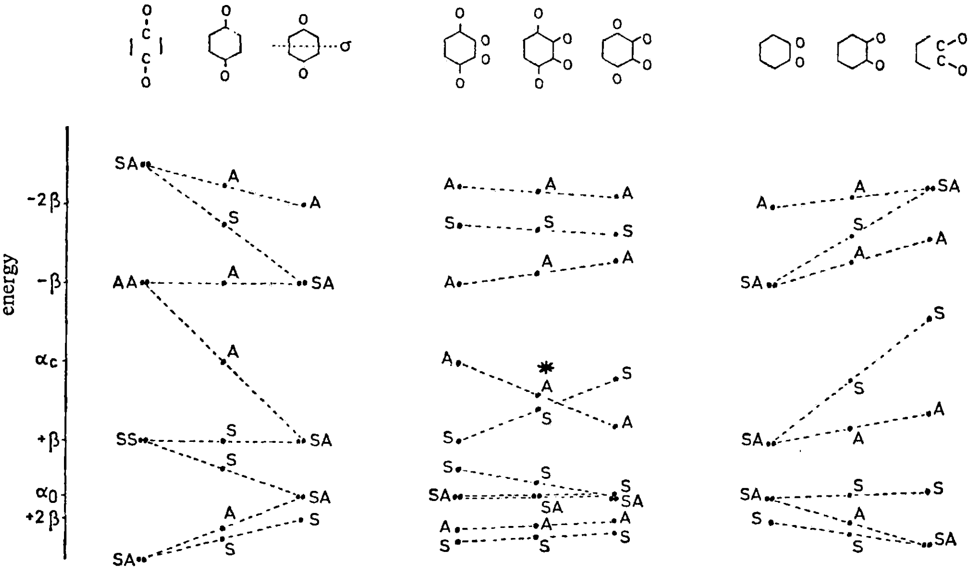
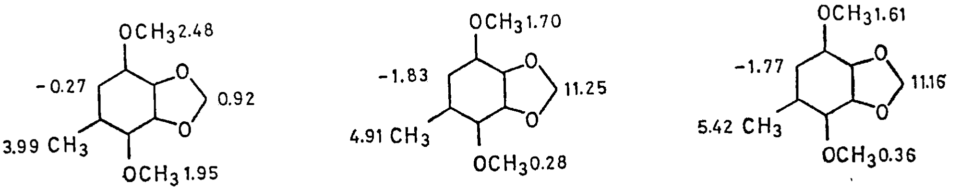


FIG. 2.—Schematic development of the orbitals of 1,2,3,4-tetrahydroxybenzene using the interleaving theorem, σ, symmetry plane, *, odd electron orbital.

A second effect which may explain our result has been observed in radicals related to 1,3,5-trihydroxybenzene(phloroglucinol).[16] The correlation diagram (fig. 2) shows that degeneracy must occur somewhere near to the 1,2,3,4-tetrasubstituted system because of the crossing [18] of two orthogonal orbitals. The results from the 1,3,5-substituted radicals [16] have shown that in cases where there is approximate degeneracy, some substituents can have the effect of reversing the order of some of the orbitals. This is due, in the case of a methyl substituent [17] for example, to the high coulomb energy of the hydrogen group orbital of π symmetry. It is likely, therefore, that perturbation of the orbitals of apionol caused by the various alkyl groups in radical (4) has led to a change in the order of two orbitals so that the 7th orbital (the odd electron orbital) is now symmetrical with respect to the symmetry plane (σ). The McLachlan SCF calculations have shown that whereas most of the calculated spin densities in the methoxybenzene radical cations were relatively insensitive to small changes in the parameters,[13, 14] in the case of radical (4) the pattern was extremely sensitive to any small change which effectively increased the interaction of the methylenedioxy group relative to that of the methoxy groups.

Scheme 2 shows that variations of this type increase the predicted methylenedioxy splitting by a factor of 12; other changes are relatively small. Such changes can be justified in terms of steric hindrance, and the sensitivity of the calculated values is analogous to that previously encountered [16] in isomers of the 1,3,5-trimethoxybenzene radical cation.

Similar small changes in the parameters were made during calculations for a number of the radicals, but only in the case of radical (4) was there a significant effect.



$k_{\text{C—OCH}_3} = 1.1$ $k_{\text{C—OCH}_3} = 1.1$ $k_{\text{C—OCH}_3} = 1.0$

$k_{\text{C—OCH}_2\text{O}} = 1.1$ $k_{\text{C—OCH}_2\text{O}} = 1.2$ $k_{\text{C—OCH}_2\text{O}} = 1.1$

SCHEME 2.—Effect of changing $k_{\text{C—OR}}$ in calculations for radical (4). [The other parameters are unchanged and are as in ref. (14).]

The observed splitting pattern for the radical cation from 1,2,3,5-tetramethoxybenzene accounts for all 14 protons. This radical can best be classified with the 5-substituted 1,2,3-trimethoxybenzene radical cations, which have the largest spin density at position 2.

We confirm the earlier result [3] for 1,2,4,5-tetramethoxybenzene.

PENTA-ALKOXY BENZENE RADICAL CATIONS

A splitting pattern accounting for all 16 protons was obtained from the e.s.r. spectrum of radical (1). This result and those from radicals (2) and (3), all supported by m.o. calculations, confirm the prediction [3] that the odd electron is in an orbital which has a nodal plane through positions 3 and 6.

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[1] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1976, 1823.
[2] W. T. Dixon, W. E. J. Foster and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.
[3] A. Zweig, W. C. Hodgson and W. H. Jura, *J. Amer. Chem. Soc.*, 1964, **86**, 4124.
[4] W. F. Forbes, P. D. Sullivan and H. M. Wang, *Canad. J. Chem.*, 1966, **44**, 1501.
[5] P. D. Sullivan, *J. Phys. Chem.*, 1970, **74**, 2563.
[6] J. Q. Adams, S. W. Nicksic and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.
[7] (*a*) W. Baker and R. I. Savage, *J. Chem. Soc.*, 1938, 1602; (*b*) W. Baker, E. H. T. Jukes and C. A. Subrahmanyam, *J. Chem. Soc.*, 1934, 1681; (*c*) F. B. Power and A. H. Salway, *J. Chem. Soc.*, 1907, 2037.
[8] W. Baker, *J. Chem. Soc.*, 1941, 662.
[9] W. Bonthrone and J. W. Cornforth, *J. Chem. Soc. C*, 1969, 1202.
[10] A. P. Bashall and J. F. Collins, *Tetrahedron Letters*, 1975, 3489.
[11] F. Dallacker, W. Edelmann and A. Weiner, *Annalen*, 1968, **719**, 112.
[12] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[13] W. T. Dixon, M. Moghimi and D. Murphy, *J.C.S. Faraday II*, 1974, **70**, 1713.
[14] W. T. Dixon, P. M. Kok and D. Murphy, *J.C.S. Faraday II*, 1977, **73**, 709.
[15] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1975, 850.
[16] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1977, **73**, 1475.
[17] W. T. Dixon, *J.C.S. Faraday II*, 1977, 73, 67.
[18] W. T. Dixon, *J.C.S. Faraday II*, 1978, **74**, 511.
[19] W. Kain and H. Bock, *J. Amer. Chem. Soc.*, 1978, **100**, 6504.

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Determination of Acid Dissociation Constants of some Phenol Radical Cations

Part 2.

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The variation of the ratio of acid–base forms of some phenol radical cations with acid strength is followed by e.s.r. spectroscopy. The acid dissociation constants (K) are given in the form of $-\log K$ where

$$K = \frac{[\text{base form}]}{[\text{acid form}]}\left(\frac{h}{W^4}\right)^n;$$

h and $55.5W$ are the number of moles of sulphuric acid and water, respectively, used to make up 1 dm^3 of solution and $n = 1$ or 2 depending upon the structure of the radical. The implications of this relationship are discussed and it is shown that application of the method to acid–base data for carbon protonation of phenols produces a deviation from linearity of the same order as that observed when H_0 is used.

The acidity constants of a number of phenol radical cations were reported in a previous paper [1] in this series. These values were obtained from a study of the variation with acid strength of time averaged e.s.r. spectra of radicals resulting from the oxidation of phenols by cerium(IV). The observed changes in the e.s.r. parameters were entirely consistent with a situation in which the spectra resulted from rapid averaging of mixtures of the phenoxyl radicals and their conjugate acids.[1, 2] Under the conditions of the experiments it was found that the dissociation of radical cations without oxygen substituents *m*- or *p*- to the oxygen involved in the protonation equilibrium was represented by eqn (1) over the range of acidities studied:

$$\text{Ar}^{+\cdot}\text{OH} + 4\text{H}_2\text{O} \rightleftharpoons \text{ArO}^{\cdot} + \text{H}_9\text{O}_4^+ \tag{1}$$

where $H_9O_4^+$ represents a hydrogen ion bound to four water molecules.

From eqn (1), the equilibrium constant (K) for the dissociation can be expressed as in eqn (2), where h and $55.5W$

$$K = \frac{[\text{ArO}\cdot]}{[\text{Ar}^{+}\cdot\text{OH}]}\frac{h}{W^4} \tag{2}$$

are the number of moles of H_2SO_4 and water, respectively, used to make up 1 dm^3 of solution (concentration of water in pure water = 55.5 mol dm^{-3}). If an e.s.r. parameter, p, (usually the relative g-factor) has values p_0 in the phenoxyl radical and p_+ in the corresponding radical cation, eqn (3) may be written and K can be calculated from linear plots of $|1/(p-p_+)|$ against h/W^4 or $|1/(p_0-p)|$ against W^4/h

$$K = \left(\frac{p-p_+}{p_0-p}\right)\frac{h}{W^4}. \tag{3}$$

A different relationship was found to apply to radicals which had *m*- or *p*-oxygen substituents relative to the site of protonation (*e.g.*, 1,3-dihydroxybenzene). For these radicals the ratio of acid : base forms was found to vary with the square of h/W^4, so that eqn (4) was obeyed over the whole range.

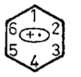
$$K = \left(\frac{p-p_+}{p_0-p}\right)\left(\frac{h}{W^4}\right)^2. \tag{4}$$

In an attempt to explain the nature of these unexpected straight line relationships the range of radicals studied in this way has been extended and more conventional acid–base data have been treated in this manner.

EXPERIMENTAL

E.s.r. spectra were obtained by the oxidation of 10^{-2} mol dm^{-3} solutions of the phenols with 10^{-2} mol dm^{-3} cerium(IV) sulphate, both in aqueous sulphuric acid, in the flow system described previously.[3] The sulphuric acid+water mixtures were made up by weight fraction using commercial 98 % H_2SO_4. For each of the phenols, sharply resolved spectra were obtained from low acid concentrations to a limiting value, usually 10 mol dm^{-3} but 12 mol dm^{-3} in the case of phenoxyl,[2] when the signals broadened out. g-Values were measured using Fremy's salt (g = 2.0055)[4] as an external standard; relative g-shift =

TABLE 1.—E.S.R. PARAMETERS ($a/10^{-4}$ T) AND ACID DISSOCIATION CONSTANTS (K) FOR RADICALS FROM PHENOL DERIVATIVES[a] OBEYING THE EQUATION $K = (p-p_+/p_0-p)(h/W^4)$

substitutents	e.s.r. parameters[b] ($\pm 0.05\times10^{-4}$ T)						acid dissociation constants	
in 	a_2	a_3	a_4	a_5	a_6	$g(\pm0.0001)$	$K(\pm5\ \%)$	pK
1-O$^-$, 4-NO_2	7.20	−2.40	a_N = 2.40	−2.40	7.20	2.005 45	62	−1.79
1-OH, 4-NO_2	7.20	−2.40	a_N = 2.40	−2.40	7.20	2.004 84		
1-O$^-$, 3-NO_2	7.40	a_N = 0.35	9.80	−2.10	6.75	2.005 03	60	−1.78
1-OH, 3-NO_2	7.30	a_N = 0.35	9.80	−2.00	6.60	2.004 32		
1-O$^-$, 2-NO_2	a_N = 1.25	−1.25	10.35	−2.25	7.50	2.005 02	96	−1.98
1-OH, 2-NO_2	a_N = 1.25	−1.15	10.40	−2.10	7.35	2.004 57		
1-O$^-$, 4-$COCH_3$	6.75	−2.20	a_{CH_3} = 0.10	−2.20	6.75	2.005 20	72	−1.86
1-OH, 4-$COCH_3$	6.45	−1.90	a_{CH_3} = 0.50	−1.90	6.45	2.004 36		
1-O$^-$, 3-$COCH_3$	7.10		9.90	−1.90	6.70	2.004 80	65	−1.81
1-OH, 3-$COCH_3$	6.95		9.90	−1.90	6.00	2.003 93		
1-O$^-$, 2-$COCH_3$		−1.50	10.10	−2.15	7.20	2.004 97	250	−2.40
1-OH, 2-$COCH_3$		−0.10	10.50	−2.05	7.20	2.004 10		
1-O$^-$, 4-F	6.50	−1.45	a_F = 27.50	−1.45	6.50	2.005 03	39	−1.59
1-OH, 4-F	5.80	−0.90	a_F = 29.75	−0.90	5.80	2.004 26		
1-O$^-$, 3-F	5.00	a_F = 5.80	10.75	−2.25	7.90	2.004 56	90	−1.95
1-OH, 3-F	2.60	a_F = 4.25	11.05	−2.05	7.90	2.003 51		
1-O$^-$, 2-F	a_F = 17.25	−1.40	10.00	−2.15	5.80	2.004 75	49	−1.69
1-OH, 2-F	a_F = 17.20	−1.00	10.20	−2.05	5.35	2.004 17		
1-O$^-$, 4-CF_3	7.20	−2.20	a_F = 11.20	−2.20	7.20	2.004 91	29	−1.46
1-OH, 4-CF_3	7.05	−2.05	a_F = 11.20	−2.05	7.05	2.004 28		
1-O$^-$, 3-CF_3	7.10	a_F = 1.50	10.05	−2.00	6.70	2.004 90	34	−1.53
1-OH, 3-CF_3	7.10	a_F = 1.50	10.30	−2.00	6.75	2.004 25		
1-O$^-$, 2-CF_3	a_F = 4.00	−1.35	10.50	−2.15	7.50	2.004 74	36.5	−1.56
1-OH, 2-CF_3	a_F = 3.85	−1.25	10.55	−2.05	7.35	2.004 26		
1-O$^-$, 4-Cl	6.40	−1.75	a_{Cl} = 1.90	−1.75	6.40	2.005 97	20	−1.30
1-OH, 4-Cl	6.05	−1.35	a_{Cl} = 2.20	−1.35	6.05	2.005 66		
1-O$^-$, 3-Cl	6.20	a_{Cl} = 0.25	10.50	−2.10	7.50	2.004 50	56	−1.75
1-OH, 3-Cl	5.65	a_{Cl} = 0.05	10.85	−2.10	7.25	2.003 80		
1-O$^-$, 2-Cl	a_{Cl} = 1.05	−2.00	9.80	−1.60	6.00	2.005 35	19	−1.27
1-OH, 2-Cl	a_{Cl} = 1.05	−2.10	10.15	−1.40	5.85	2.004 98		
1-O$^-$, 3,5-$(CH_3)_2$	6.30	a_{CH_3} = 1.60	10.70	a_{CH_3} = 1.60	6.30	2.004 38	36	−1.55
1-OH, 3,5-$(CH_3)_2$	4.70	a_{CH_3} = 0.08	11.85	a_{CH_3} = 0.08	4.70	2.002 84		

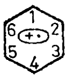
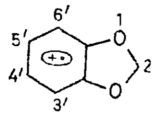
[a] Results not in ref. (1) and (2); [b] signs of coupling constants inferred as in ref. (2) and (6).

g-shift in 10^{-4} T relative to that of the external standard[2]; the temperature of the solutions was 22.5±0.5°C. The methylenedioxy compounds were prepared as in ref. (5); other phenols were commercial materials, purified where necessary by the usual methods.

RESULTS

The e.s.r. parameters of some phenoxyl radicals and their corresponding radical cations are given in tables 1 and 2. For each pair of radicals, K was determined as described above; an example is given in fig. 1 for the radicals from 3,5-dimethylphenol. If the intercept of the $|1/(p_0-p)|$ against W^4/h plot is I, where $I = |1/(p_0-p_+)|$, the value of $1/K$ is given by the point on the W^4/h axis corresponding to $|1/(p_0-p)| = 2I$. Alternatively, K may be determined from the $|1/(p-p_+)|$ against h/W^4 plot, using the value of h/W^4 at which $|1/(p-p_+)| = 2I'$. Clearly, for perfect data, $I = I'$, and in the example given the values $1/K = 0.0272$ and $K = 34$ are in reasonable agreement. Tables 1 and 2 list the values of K, together with corresponding pK values, for the radicals studied. No useful correlations between the pK values and Hammett σ constants[7-9] could be found, indicating that the dissociation constants of the phenol radical cations do not vary in a simple manner with inductive and mesomeric effects of the substituents.

TABLE 2.—E.S.R. PARAMETERS ($a/10^{-4}$T) AND ACID DISSOCIATION CONSTANTS (K) FOR RADICALS FROM PHENOL DERIVATIVES[a] OBEYING THE EQUATION $K = (p-p_+/p_0-p)(h/W^4)^2$

substituents	e.s.r. parameters[b] ($\pm 0.05\times10^{-4}$ T)						acid dissociation constants	
(i) in 	a_2	a_3	a_4	a_5	a_6	$g(\pm 0.0001)$	$K(\pm 5\ \%)$	pK
1-O$^-$, 4-OH, 2-CH$_3$	$a_{CH_3} = 3.85$	0.28		1.24	3.85	2.004 32	15	−1.18
1,4-(OH)$_2$, 2-CH$_3$	$a_{CH_3} = 2.72$	1.36		3.05	2.00	2.003 47		
1-O$^-$, 3-OH, 4-CH$_3$	3.20		$a_{CH_3} = 12.30$	−2.05	9.20	2.004 06	21	−1.32
1,3-(OH)$_2$, 4-CH$_3$	0.25		$a_{CH_3} = 14.70$	−1.70	8.80	2.003 13		
1-O$^-$, 3,5-(OH)$_2$, 2-CH$_3$	$a_{CH_3} = 13.10$		5.75		5.75	2.004 01	15	−1.18
1,3,5-(OH)$_3$, 2-CH$_3$	$a_{CH_3} = 17.70$		3.10		3.10	2.003 03		
(ii) in 	a_2	$a_{3'}$	a_4	$a_{5'}$	$a_{6'}$	$g(\pm 0.0001)$	$K(\pm 5\ \%)$	pK
4′-O$^-$, 5′-OH	6.25	−0.45			−0.45	2.004 33	7	−0.84
4′,5′-(OH)$_2$	11.05	−1.00			−1.00	2.003 94		
3′-O$^-$	3.60		6.50	−0.50	2.50	2.004 63	120	−2.08
3′-OH	18.80		−0.98	5.95	−0.52	2.003 91		
4′-O$^-$	6.50	1.95		8.00	−1.10	2.004 30	29	−1.46
4′-OH	13.50	0.00		6.25	−0.40	2.003 95		
3′-O$^-$, 4′-COCH$_3$	5.60			−1.70	5.05	2.004 81	382	−2.58
3′-OH, 4′-COCH$_3$	17.55			5.15	0.01	2.004 13		

[a] Results not in ref. (1) and (2); [b] signs of coupling constants from ref. (2) and (6).

DISCUSSION

Eqn (3) and (4) have now been used to determine the acidity constants of some forty phenol radical cations. It was, therefore, felt necessary to re-examine the

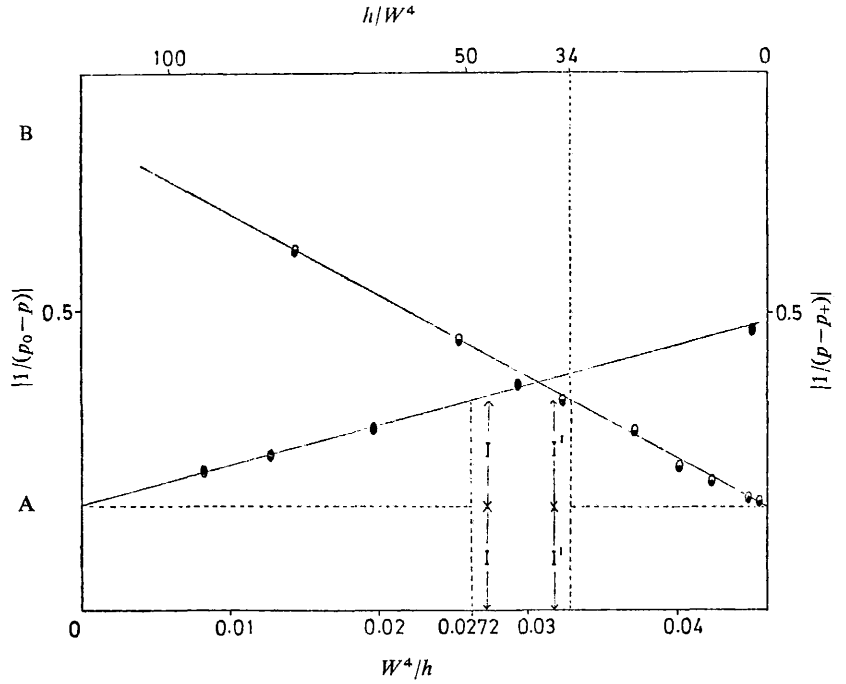


FIG. 1.—Curve A is a plot of $|1/(p_0-p)|$ against W^4/h and curve B is a plot of $|1/(p-p_+)|$ against h/W^4 for radicals from 3,5-dimethylphenol (p = relative g-shift).

relationships embodied in these equations in the context of more established treatments in the literature.[10] The dissociation constant defined by eqn (1) is more rigorously expressed as in eqn (2*a*) where

$$K_a = \frac{[\text{ArO}\cdot][\text{H}_9\text{O}_4^+]}{[\text{Ar}\cdot^+\text{OH}][\text{H}_2\text{O}]^4} \times \frac{\gamma\text{ArO}\cdot\gamma\text{H}_9\text{O}_4^+}{\gamma\text{Ar}^+\cdot\text{OH}\gamma^4\text{H}_2\text{O}} \qquad (2a)$$

the activity coefficients, γ, are a measure of the deviation of the system from ideality. In terms of the measured e.s.r. parameters eqn (2*a*) may be written as in eqn (3*a*). Clearly, eqn (3*a*) reduces to eqn (3) as infinite dilution is approached, so that plots

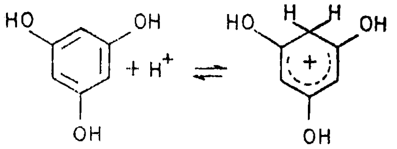
$$K_a = \frac{(p-p_+)}{(p_0-p)}\frac{h}{W^4}\frac{\gamma\text{ArO}\cdot\gamma\text{H}_9\text{O}_4^+}{\gamma\text{Ar}^+\cdot\text{OH}\gamma^4\text{H}_2\text{O}} \qquad (3a)$$

of $|1/(p-p_+)|$ against h/W^4 are expected to be linear for very dilute solutions of H_2SO_4. However, this approximation is seldom if ever true in more concentrated acid solutions and this has led to the development of acidity functions which preserve the simple acidity dependence of eqn (3).[10]

It was originally hoped that the acidity function H_0 would provide a single experimental criterion of acidity. Experience has shown, however, that there is nothing unique about H_0 and a series of allied H-functions such as H_+, H_-, H_c *etc.* have been developed with each type of acid–base system requiring its own acidity function.[11]

The above results demonstrate that eqn (3) and (4) are empirical; their validity depends on the particular acidity function behaviour of the protonation equilibrium for phenol radical cations. A number of treatments have been offered in the literature [10, 12-14] in which the activity term in eqn (3*a*) is found to be constant over a range of sulphuric acid concentrations. However, because of the difficulties involved in justifying these results the success of previous approaches was assumed to be fortuitous [15] and it is probable that the same conclusion applies in the present work.

The applicability of eqn (3) and (4) to related acid-base systems was tested in the protonation [11] of phenols to give benzenonium ions as in eqn (5). The positions of equilibrium have been measured [16] at a number of different acid concentrations by



(5)

using the absorbance at λ_{max} of the long wavelength band of the benzenonium ion to estimate the ratios [ArH+]/[Ar]; fig. (2) shows a plot of this ratio against $(h/W^4)^2$. The figure also shows plots of $|1/(p_0-p)|$ against $(W^4/h)^2$ and $|1/(p-p_+)|$ against $(h/W^4)^2$ for the protonation of the 3,5-dihydroxyphenoxyl radical.[17] As expected the plots for the protonation of the radical are linear, but that for carbon protonation is not, although it is almost linear up to 7 mol dm^{-3} H_2SO_4. The difference in the form of these two types of plot is, however, comparable with that

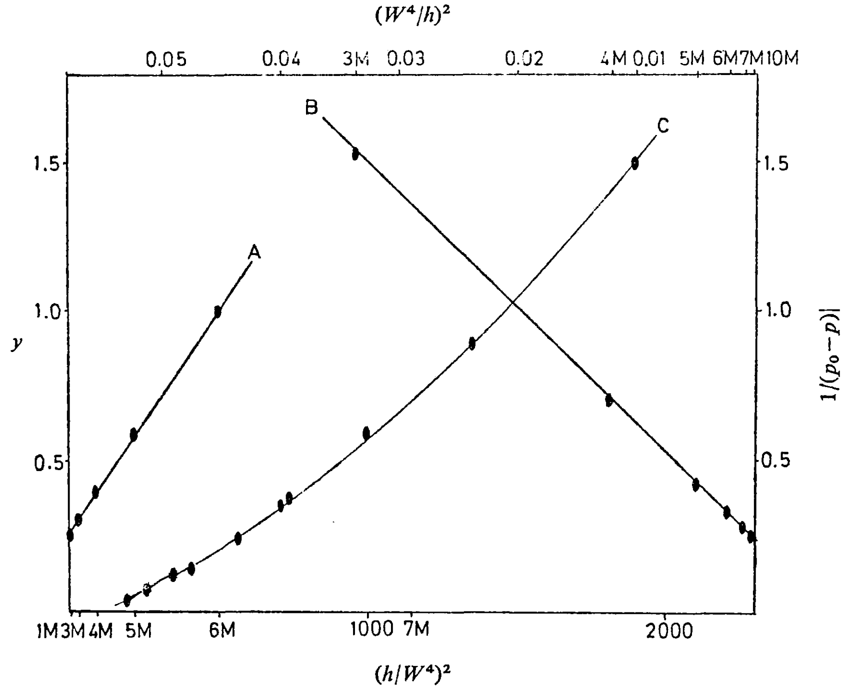


FIG. 2.—Curves A and B are plots of $|1/(p-p_+)|$ against $(h/W^4)^2$ [$y = |1/(p-p_+)|$] and of $|1/(p_0-p)|$ against $(W^4/h)^2$ for radicals from 1,3,5-trihydroxybenzene. Curve C is a plot of [ArH+]/[Ar] against $(h/W^4)^2$ for carbon protonation of 1,3,5-trihydroxybenzene {y = [ArH+]/[Ar], data from ref. (11)} M = mol dm^{-3}.

found previously when the carbon protonation was treated in terms of H_0 or of H_c and also when Ar was changed from alkoxy- to hydroxy-benzene. Some of the latter effects have been ascribed [11, 18] to differences in solvation between the protonated base and the proton plus base.

The behaviour of the radicals in table 2 and in previous work which obey eqn (4) is complicated by the clear implication that two protonating species are involved in the formation of the radical cations. The possibility of simple diprotonation of the phenoxyl radicals under the experimental conditions is sufficiently unlikely to be neglected, so that alternative explanations must be considered. It is highly probable that the radical cations are solvated, presumably by $H_9O_4^+$, because in the solutions containing a high concentration of radical ion there is little " free " water. In phenoxyl radicals with *m*- or *p*-oxygen substituents relative to the site of protonation, solvent-radical complexes involving two $H_9O_4^+$ species may be found; when such a complex is sufficiently long-lived, the e.s.r. parameters would vary with $(h/W^4)^2$. Such complexes could not be formed from monohydric phenoxyls and since $Ar^{+\cdot}OH$ and $H_9O_4^+$ are of comparable size they would not be formed from phenoxyls with *o*-oxygen substituents. Evidence for significant solvation of the radicals has come from a study of the protonation of 3,5-dimethoxyphenoxyl [17] and it has been demonstrated that, in a number of other systems,[19, 20] hydrogen bonding of radicals causes changes in the *g*-factors (and other e.s.r. parameters) of the magnitude shown in tables 1 and 2. This means that the formation of " free " phenol radical cations is not necessarily implied by the variations used in this work to calculate the dissociation constants.

D. M. H. thanks the S.R.C. for a research grant.

[1] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1978, **74**, 432.
[2] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1976, **72**, 1221.
[3] W. T. Dixon, W. E. J. Foster and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.
[4] A. J. Dobbs, *Electron Spin Resonance* (Specialist Periodical Report, Chemical Society, London, 1974), vol. 2, p. 281.
[5] F. Dallacker and A. Weiner, *Annalen*, 1969, **725**, 99.
[6] W. T. Dixon, M. Moghimi and D. Murphy, *J.C.S. Faraday II*, 1974, **70**, 1713.
[7] P. R. Wells, *Linear Free Energy Relationships* (Academic Press, London, 1968).
[8] G. B. Barlin and D. D. Perrin, *Quart. Rev.*, 1966, **20**, 75.
[9] J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 295.
[10] C. H. Rochester, *Acidity Functions* (Academic Press, London, 1970).
[11] A. J. Kresge, H. J. Chen, L. E. Hukka and J. E. Kouba, *J. Amer. Chem. Soc.*, 1971, **93**, 6174.
[12] K. N. Bascombe and R. P. Bell, *Disc. Faraday Soc.*, 1957, **24**, 158.
[13] R. P. Bell, *The Proton in Chemistry* (Chapman and Hall, London, 2nd edn, 1973).
[14] J. C. D. Brand, *J. Chem. Soc.*, 1950, 997.
[15] N. C. Deno and R. W. Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244.
[16] A. J. Kresge and H. J. Chen, *Analyt. Chem.*, 1969, **41**, 74.
[17] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1977, **73**, 1475.
[18] A. J. Kresge, G. W. Barry, K. R. Charles and Y. Chiang, *J. Amer. Chem. Soc.*, 1962, **84**, 4343.
[19] T. Kawamura, S. Matsunami and T. Yonezawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 1111.
[20] T. Yonezawa, T. Kawamura, M. Ushio and Y. Nakao, *Bull. Chem. Soc. Japan*, 1970, **43**, 1023.

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The Electron Spin Resonance Spectra of Semiquinones obtained from Some Naturally Occurring Methoxybenzoquinones

By **Dolores M. Holton** and **David Murphy,*** Department of Chemistry, Bedford College, Regent's Park, London NW1 4NS

Radical anions of methoxyquinones and related compounds were generated in a static system in alkaline media. The unpaired electron distribution in these radicals could not be satisfactorily verified by simplified SCF calculations. It is shown that a simple relationship exists between splittings in the semiquinones and corresponding splittings in the closely related alkyl aryl ether radical cations. This relationship correlates very closely with the excess charge effect which has been examined quantitatively for aromatic hydrocarbon radical ions, indicating that the same effect is operative in the oxygenated radicals, in which the splittings of the cations are *ca.* 20% greater than corresponding splittings in the anions. These correlations, together with observed smooth variations of splitting patterns with substitution have permitted unambiguous assignment of the coupling constants of radicals such as the fumigatin anion or the 1,2-methylenedioxynaphthalene cation, without recourse to new computation.

ABOUT 90 benzoquinones have been obtained from natural sources,[1] most of them distributed among *ca.* 20 families of flowering plants and of fungi. Due to the ease of formation of semiquinone radicals from both the quinones and the corresponding reduced forms, e.s.r. spectroscopy has become an important tool for the characterisation of these compounds. A wide range of *o*-, *m*- and *p*-semiquinones has been studied in this way,[2,3] and the techniques established have been extended to radicals related to pyridines,[4] naphthalenes,[5] coumarins,[6,7] and tropolones.[8,9] However, the formation of semiquinone radicals is only the first step in the autoxidation of a dihydric phenol or, indirectly, of quinones in alkaline media,[10] and e.s.r. has been usefully employed in the study of products formed by further oxidation, dimerisation, and degradation of the parent structures. It was the aim of the present investigation to extend e.s.r. studies of this type to the important group of fungal metabolites such as fumigatin (2-hydroxy-3-methoxy-6-methyl-*p*-benzoquinone) and the antibiotic aurantiogliocladin (2,3-dimethoxy-5,6-dimethyl-*p*-benzoquinone) and to other quinones related to the tetrahydroxybenzenes.

RESULTS

Radicals were generated by autoxidation of the corresponding dihydric phenols in aqueous sodium hydroxide solution.[10] Well resolved e.s.r. spectra were generally observed (Figure 1), and the parameters obtained are given in the Table.

Assignment of Coupling Constants.—Simple graphical procedures [11,12] have been developed, which can be used to assign definite patterns of unpaired electron distribution to the various modes of oxygen substitution. As these spin distributions are not perturbed significantly by other substituents, it has sometimes been feasible for e.s.r. parameters to be used analytically.[7,13] The patterns obtained in this way are then verified by calculations based on simple MO theory.[11,14,15] The assignment of the many small splittings given in the Table, especially those due to methoxy-groups, presents an interesting and severe test of these graphical methods.

In some cases there is a smooth variation of the splitting pattern with substitution, as in radicals (A)—(C), where the trends of the coupling constants are clearly shown. It is unfortunate that in other instances in which there is serious ambiguity, the McLachlan semiempirical SCF procedure, which has proved highly satisfactory elsewhere,[14,15] fails to predict many splittings with acceptable accuracy.

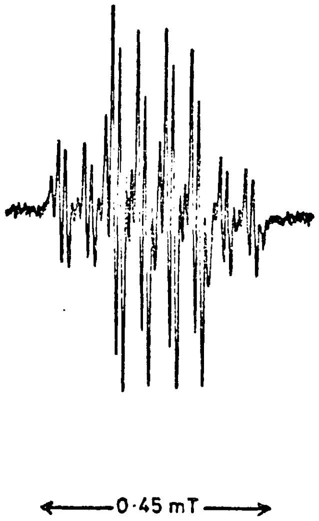
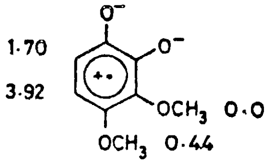


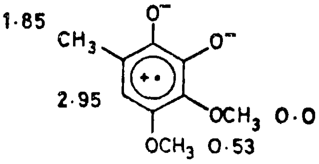
FIGURE 1 E.s.r. spectrum of 3,4,5-trimethoxy-*o*-benzosemiquinone

Many values are reproduced only by using different parameters for each radical, a process which is virtually meaningless for diagnostic purposes.

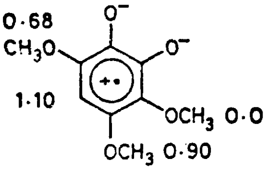
A simple relationship between corresponding splittings in phenoxyl radicals and phenol radical cations has been used to assign coupling constants in ambiguous cases,[12] and it can be seen that corresponding splittings in semiquinones and ether radical cations [15,16] are similarly related [(A)—(D), (E) and (F)]. This similarity has been reported previously,[16] and is a clear indication of virtually identical spin distributions in the corresponding anions and cations. It follows then, since it has been demonstrated that the splittings in the ether radical cations can be successfully predicted using SCF theory,[15] that this method provides a convincing assignment of many of the splittings in the Table. Alternatively, where the spin distribution of a semiquinone is well established, assignments in the corresponding cation can be made with reasonable certainty.



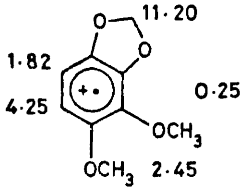
(A)



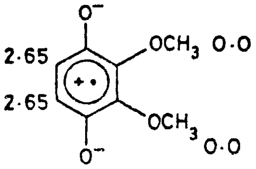
(B)



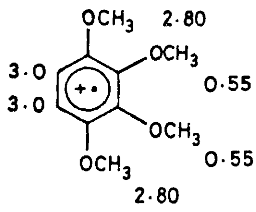
(C)



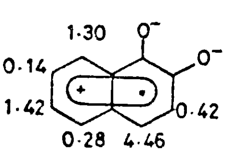
(D)



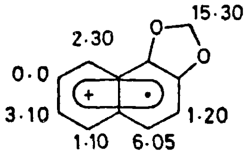
(E)



(F)



(G)



(H)

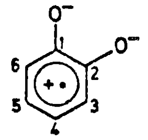
An interesting and slightly more complex example is provided by radicals (G) and (H). Here the splittings for the radical cation from 1,2-methylenedioxynaphthalene,[17] a potent synergist for carbamate insecticides, are assigned by comparison with 1,2-naphthosemiquinone.[5] Radical (H) is the first species of this type in the naphthalene series which has been examined by e.s.r. spectroscopy.

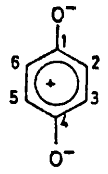
Excess Charge Effects.—It is important to note that the relationship discussed in the previous section is strictly only applicable to the *ratios* of the splittings in the various radicals, [*e.g.* in radical (A), $a_5/a_6 = 2.30$; in radical (D), $a_5/a_6 = 2.33$]. In each case, the *magnitude* of the splittings of the cations exceeds that of the anions by *ca.* 20%. In the case of the aromatic hydrocarbon radical ions, this effect has been examined quantitatively,[18,19] and a reasonable explanation of the experimental observations has been provided in terms of the total charge on the radicals. Qualitatively, the effect is due to the 'contraction' of the carbon $2p_z$ orbitals in the positively charged ions.[20] If the spin distribution in corresponding pairs of semiquinones and ether radical cation is indeed nearly identical,[16] a similar effect could account for the difference in the magnitudes of the splittings in these species.

Figure 2 shows a plot of the splittings of semiquinones from derivatives of 1,2-, 1,4-, 1,2,3-, 1,2,4-, 1,2,3,4-, 1,2,4,5-, and 1,2,3,4,5-polyhydroxybenzenes against corresponding values for the related ether radical cations.[15,16] All suitably related pairs of anion and cation radicals for which e.s.r. spectra have been observed in this and in earlier work [11,15,16] are given in Figure 2. For comparison, values for a number of aromatic radical ions [18] have been included. Within experimental error a straight line relationship is obtained embracing both sets of data. This plot is good evidence that the effect in the oxygenated radicals is identical to that in the hydrocarbons, and that the same explanation for it probably applies to all of the radicals. The agreement is particularly encouraging due to the assumptions made in

TABLE 1

E.s.r. parameters ($a/10^{-4}$ ~~x~~) for semiquinones from derivatives of tetra- and penta-hydroxybenzenes

(i) Substituents in 	Coupling constats (±0.05) a_3	a_4	a_5	a_6
(A) 3,4-$(OCH_3)_2$	a_{OCH_3} 0.0	a_{OCH_3} 0.44	3.92	1.70
(B) 3,4-$(OCH_3)_2$, 6-CH_3	a_{OCH_3} 0.0	a_{OCH_3} 0.53	2.95	a_{CH_3} 1.85
3,6-$(OCH_3)_2$, 4-CH_3	a_{OOH_3} 0.0	a_{CH_3} 5.61	1.70	a_{OCH_3} 0.61
4,5-$(OCH_3)_2$	0.32	a_{OCH_3} 1.10	a_{OCH_3} 1.10	0.32
4,5-(OCH_2O)	0.33	a_{CH_2} 4.22	a_{CH_2} 4.22	0.33
3,4,5-$(OCH_3)_3$	a_{OCH_3} 0.0	a_{OCH_3} 0.10	a_{OCH_3} 1.20	0.60
(C) 3,4,6-$(OCH_3)_3$	a_{OCH_3} 0.0	a_{OCH_3} 0.90	1.10	a_{OCH_3} 0.68
3,5-$(OCH_3)_2$	a_{OCH_3} 0.75	1.70	a_{OCH_3} 1.00	0.95

(ii) Substituents in 	a_2	a_3	a_5	a_6
(E) 2,3-$(OCH_3)_2$	a_{OCH_3} 0.0	a_{OCH_3} 0.0	2.65	2.65
2,3-(OCH_2O)	a_{CH_2} 0.18	a_{CH_2} 0.18	2.63	2.63
2,3-$(OCH_3)_2$, 5-CH_3	a_{OCH_3} 0.0	a_{OCH_3} 0.0	a_{CH_3} 2.45	1.98
2,3-$(OCH_3)_2$, 5,6-$(CH_3)_2$	a_{OCH_3} 0.0	a_{OCH_3} 0.0	a_{CH_3} 2.15	a_{CH_3} 2.15
(J) 2-O⁻, 3-OCH_3, 6-CH_3		a_{OCH_3} 0.0	4.0	a_{CH_3} 1.18
2,6-$(OCH_3)_2$	a_{OOH_3} 0.81	1.45	1.45	a_{OCH_3} 0.81

grouping together apparently different classes of radical in this way.

The existence of this systematic relationship greatly strengthens the validity of this approach to the assignment of splitting patterns in both semiquinones and the corresponding radical cations. The method permits the splitting pattern in anions such as that from fumigatin (J) or the 4-*O*-methyl ether (C) to be written down, using only data from related radical cations [15] which have been previously confirmed by computation.

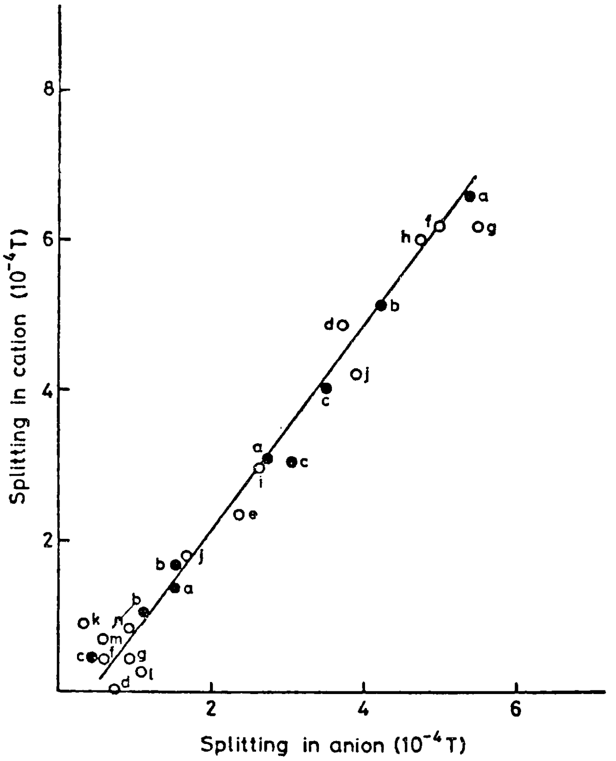
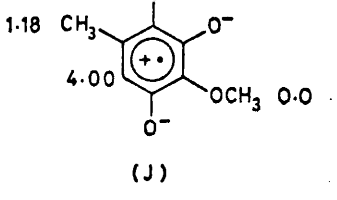


FIGURE 2 Graphical relationship between corresponding coupling constants in radical cations and radical anions. ●, Aromatic hydrocarbon radical ions (from ref. 18); a, anthracene; b, tetracene; c, perylene. ○, semiquinones and related radical cations (from this work and from refs. 11, 15, and 16). Substituents: d, 1,2-(OCH$_3$)$_2$, 1,2-(O$^-$)$_2$; e, 1,4-(OCH$_3$)$_2$, 1,4-(O$^-$)$_2$; f, 1,2-(OCH$_2$O)-4-OCH$_3$, 1,2,4-(O$^-$)$_3$; g, 1,2,3-(OCH$_3$)$_3$, 1,2,3,-(O$^-$)$_3$; h, 1,2-(OCH$_2$O)-3-OCH$_3$, 1,2-(O$^-$)$_2$-3-OCH$_3$; i, 1,2,3,4-(OCH$_3$)$_4$, 1,4-(O$^-$)$_2$-2,3-(OCH$_3$)$_2$; j, 1,2-(OCH$_2$O)-3,4-(OCH$_3$)$_2$, 1,2-(O$^-$)$_2$-3,4-(OCH$_3$)$_2$; k, 1,2,4,5-(OCH$_3$)$_4$, 1,2-(O$^-$)$_2$-4,5-(OCH$_3$)$_2$; l, 1,2-(OCH$_2$O)-3,4,6-(OCH$_3$)$_3$, 1,2-(O$^-$)$_2$-3,4,6-(OCH$_3$)$_3$; m, 1,2-(OCH$_2$O)-3,4,5-(OCH$_3$)$_3$, 1,2-(O$^-$)$_2$-3,4,5-(OCH$_3$)$_3$. (All splittings due to aromatic C-H protons are included)



(J)

EXPERIMENTAL

E.s.r. Spectra.—Spectra of semiquinone anions were obtained in a static system [3] following autoxidation [5] of dihydric phenols in aqueous alkaline solution (pH 8—12). Where the dihydroxy-compounds were very susceptible to aerial oxidation, the corresponding quinones were reduced using alkaline dithionite immediately prior to the autoxidation; autoxidation of the quinones in aqueous alkali did not result in generation of semiquinone radicals as has been observed with less highly substituted substrates.[10] Spectra from 3,4-dimethoxy-1,2-methylenedioxybenzene [21] and 1,2-methylenedioxynaphthalene [17] were obtained by oxidation of the ethers (10^{-2} mol dm^{-3}) in $H_2SO_4.4H_2O$ using 10^{-2} mol dm^{-3} cerium(IV) sulphate in $H_2SO_4.4H_2O$ in a flow system as described previously.[16] Unresolved second-order effects were manifested in the broadening of the centre lines in the spectra of the methlenedioxy-compounds.

Materials.—1,2-Dihydroxy-3,4-dimethoxybenzene,[21] 1,2-dihydroxy-3,4-dimethoxy-6-methylbenzene,[22] 1,2-dihydroxy-3,4,5-trimethoxybenzene,[23] 1,2-dihydroxy-4,5-methylenedioxybenzene,[24] 1,4-dihydroxy-2,3-dimethoxybenzene,[25] and 1,2,4-trihydroxy-3-methoxy-6-methylbenzene [22] were prepared as in the cited literature. 1,2-Dihydroxy-3,6-dimethoxy-4-methylbenzene was obtained by hydrazine hydrate–potassium hydroxide reduction of the corresponding aldehyde.[25] 1,2-Dihydroxy-3,5-dimethoxybenzene was prepared by alkaline hydrogen peroxide oxidation of commercial 2′-hydroxy-4′,6′-dimethoxyacetophenone. 1,2-Dihydroxy-4,5-dimethoxybenzene and 1,4-dihydroxy-2,3-dimethoxy-5,6-dimethylbenzene were obtained by alkaline sodium dithionite reduction of the corresponding commercial quinones. The other precursors were commercial materials. All compounds used were purified by the usual methods, and had physical constants which agreed well with those of the literature.

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REFERENCES

[1] R. H. Thomson, ' Naturally Occurring Quinones,' Academic Press, London, 1971.

[2] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 408, 4302; 1965, 1488.

[3] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 1964, **8**, 101.

[4] P. Ashworth, *Biochem. J.*, 1974, **141**, 577.

[5] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1974, 739.

[6] P. Ashworth, *Tetrahedron Letters*, 1975, 1435.

[7] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Perkin II*, 1975, 101.

[8] G. A. Russel, C. M. Tanger, and Y. Kosugi, *J. Org. Chem.*, 1978, **43**, 3278.

[9] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1974, 1430.

[10] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[11] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Faraday II*, 1974, **70**, 1713.

[12] W. T. Dixon and D. Murphy, *J.C.S. Faraday II*, 1975, **71**, 1221.

[13] W. T. Dixon, W. E. J. Foster, and D. Murphy, *J.C.S. Perkin II*, 1978, 729.

[14] W. T. Dixon, P. M. Kok, and D. Murphy, *J.C.S. Faraday II*, 1977, **73**, 709.

[15] D. M. Holton and D. Murphy, *J.C.S. Faraday II*, 1979, **75**, 1185.

[16] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1976, 1823.

[17] R. L. Metcalf, T. R. Fukuto, C. Wilkinson, M. H. Fahy, S. Abd El-Aziz, and E. R. Metcalf, *J. Agric. Food. Chem.*, 1966, **14**, 555.

[18] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, 1963, **6**, 273.

[19] J. R. Bolton, *J. Chem. Phys.*, 1965, **43**, 309.

[20] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803.

[21] W. Baker, E. H. T. Jukes, and C. A. Subrahmanyam, *J. Chem. Soc.*, 1934, 1681.

[22] W. Baker and H. Raisrick, *J. Chem. Soc.*, 1941, 670.

[23] W. Baker, *J. Chem. Soc.*, 1941, 662.

[24] F. Dallacker and A. Weiner, *Annalen*, 1969, **729**, 99.

[25] W. Baker and R. I. Savage, *J. Chem. Soc.*, 1938, 1602.

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Effects of Near Degeneracy in the Frontier Orbitals on the Electron Spin Resonance Spectra of Radicals Related to 1,2,3-Trihydroxy-benzene (Pyrogallol)

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2,3-Methylenedioxyphenoxyl was generated in solutions containing 0–9 mol dm^{-3} sulphuric acid. Large variations in the e.s.r. spectra, due to progressive formation of the phenol radical cation with increasing acid concentration, are shown to be caused by a difference in the symmetry properties of the odd electron orbital in the neutral and charged species. Near degeneracy of the pair of frontier orbitals of the system which are symmetrical and antisymmetrical with respect to a plane bisecting C(2) and C(5) in the substrate causes this effect, which may also confirm the tentative assignment of coupling constants for 3-hydroxy-*o*-benzosemiquinone made by Carrington and Smith.

In the course of an extensive study of the protonation of phenoxyl radicals,[1-4] the equilibrium

$$\mathrm{Ar\dot{O}} \underset{-\mathrm{H}^+}{\overset{+\mathrm{H}^+}{\rightleftharpoons}} \mathrm{Ar\overset{+}{\dot{O}}H} \qquad (1)$$

has been followed by varying the acidity of the solutions. Proton exchange was always fast[5] over the range studied so that e.s.r. spectra obtained were completely averaged and no hyperfine interactions with hydroxylic protons could be observed. Each of the e.s.r. parameters was therefore made up of contributions proportional to the concentrations of the participitating species, so that a plot of the e.s.r. parameters against a function of the acid strength gave curves from which the K_a and pK_a for the radical cations could easily be calculated.[1,3,4] In general, there was a simple relationship between corresponding splittings in phenoxyl radicals and phenol radical cations, with relatively small changes (±10%) in the splittings on protonation,[1] so that the change in the *g*-factor was the most useful quantity for following the equilibria. In this paper an exceptional example, 2,3-methylenedioxyphenol, will be discussed since in this case the change in the magnitude and in the sign of the splittings on protonation prove that there must be a substantial change in the symmetry of the unpaired electron orbital.

EXPERIMENTAL

E.s.r. spectra were obtained by the oxidation of 5×10^{-3} mol dm^{-3} solutions of 2,3-methylenedioxyphenol with 5×10^{-3} mol dm^{-3} cerium(IV) sulphate, both in aqueous sulphuric acid, in the flow system described previously.[6] The sulphuric acid + water mixtures were made up by weight fraction, using commercial 98% H_2SO_4. *g*-Values were measured using Fremy's salt ($g = 2.0055$)[7] as an external standard and the temperature of the solutions was 22.5 ± 0.5 °C. 2,3-Methylenedioxyphenol, m.p. 65 °C, was prepared from commercial 2,3,4-trihydroxybenzoic acid by the method of Baker and Savage.[8]

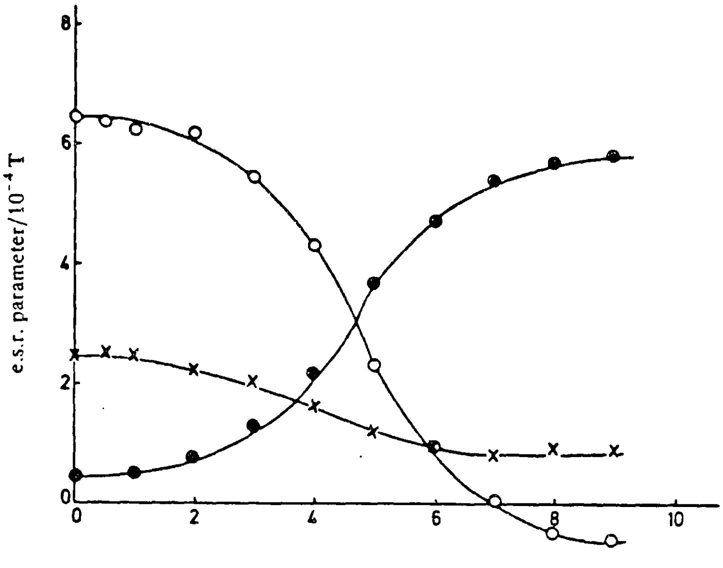
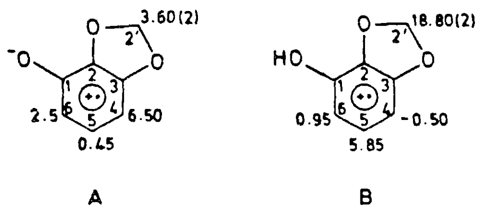


FIG. 1.—Plot of e.s.r. parameter against concentration of H_2SO_4 for radical A. ○, a_4; ●, a_5; ×, a_6.

RESULTS

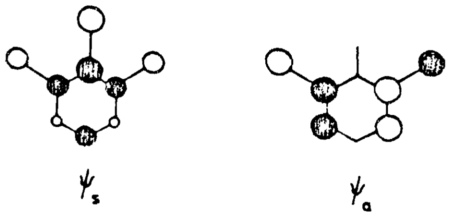
The e.s.r. parameters of 2,3-methylenedioxyphenol were measured over the range 0–9 mol dm^{-3} sulphuric acid and the values of the three aromatic proton splittings are given in fig. 1. The coupling constants for 2,3-methylenedioxyphenoxyl (A) and the 2,3-methylenedioxyphenol radical cation (B) are given in scheme 1.



SCHEME 1.—E.s.r. parameters ($a/10^{-4}$ T) for radicals A (g = 2.004 63) and B (g = 2.003 91)

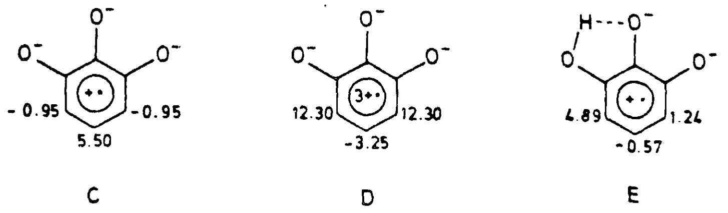
DISCUSSION

The curves presented in fig. 1 clearly reveal a significant difference in the symmetries of the unpaired electron orbitals in radicals A and B. The spin distribution in radical B, which has been confirmed by SCF theory,[9,10] shows that the odd electron occupies an orbital which closely resembles the symmetrical orbital ψ_s (scheme 2); this is the normal situation for radicals related to 1,2,3-trihydroxybenzene.[11,12] In the case of radical A the spin distribution, which is not predicted by the SCF calculations,[10,11] reveals a contribution from the antisymmetrical orbital ψ_a (scheme 2).



SCHEME 2.—Symmetrical (ψ_s) and antisymmetrical (ψ_a) orbitals for 1,2,3-trisubstituted benzenes. Sign and approximate relative magnitude of coefficients from SCF calculations.

In order to examine the implications of this assumption, McLachlan's simplified SCF procedure[9] has been used to calculate the m.o. energy levels for radical C, the pyrogallosemiquinone anion,[11,12] (scheme 3), and the energy levels and orbital symmetries are given in table 1. It can be seen that although ψ_s and ψ_a, one of which is occupied by the odd electron in these radicals, are not degenerate, their energies are very close. Indeed, it has proved possible to obtain e.s.r. spectra of mixtures of two radicals (C and D, scheme 3) obtained by one and three electron oxidation, respectively, of 1,2,3-trihydroxybenzene.[13] The two sets of coupling constants for these radicals effectively give the shapes of ψ_s and ψ_a. Other experiments have shown[11] that in cases where there is near degeneracy, some substituents can have the effect of reversing the order of some of the orbitals. This is due, in the case of a methyl substituent for example, to the high coulomb energy of the hydrogen group orbital of π symmetry.[14] It is likely then that the combination of substituents in



SCHEME 3.—E.s.r. parameters ($a/10^{-4}$ T) for radicals from 1,2,3-trihydroxybenzene.

TABLE 1.—CALCULATED[a] M.O. ENERGY LEVELS FOR RADICAL C

level	energy	symmetry
1	$\alpha + 3.3096\beta$	S
2	$\alpha + 2.6701\beta$	A
3	$\alpha + 2.5060\beta$	S
4	$\alpha + 1.6182\beta$	S
5 (ψ_a)	$\alpha + 0.5959\beta$	A
6 (ψ_s)	$\alpha + 0.5804\beta$	S
7	$\alpha - 0.9387\beta$	S
8	$\alpha - 1.1535\beta$	A
9	$\alpha - 1.9880\beta$	S

[a] Parameters from ref (10); $\alpha_o = \alpha_c + 1.6\beta$, $\beta_{co} = 1.3\beta$

radical A has fortuitously equalised the energies of ψ_a and ψ_s so that mixing can occur. If this is so, in the (unsymmetrical) radical A, the molecular orbitals will be linear combinations:

$$\psi_1 = \lambda\psi_a + \mu\psi_s,$$
$$\psi_2 = \mu\psi_a - \lambda\psi_s$$
$$(\lambda^2 + \mu^2 = 1)$$

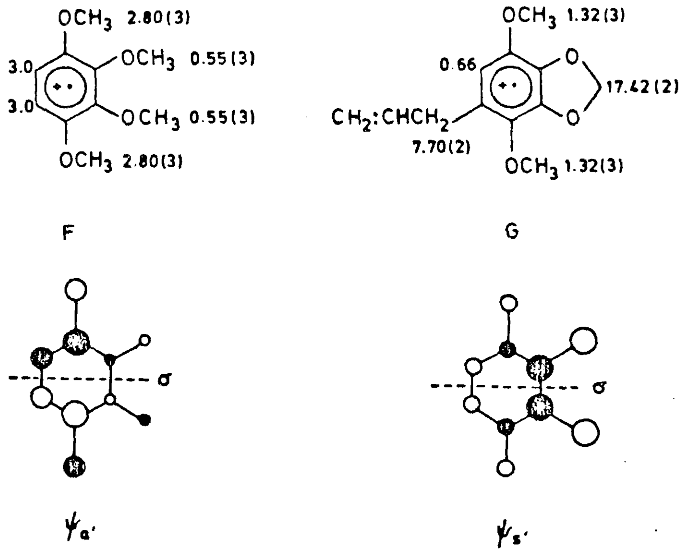
and the corresponding spin populations, uncorrected for spin polarisation, at an atom would be:

$$c_1^2 = (\lambda c_a + \mu c_s)^2$$
$$c_2^2 = (\mu c_a - \lambda c_s)^2.$$

However, values for λ and μ could not be found using the observed couplings for radicals A, C and D, indicating that the system is not in a pure state. Instead, the data is consistent with the system being in a mixed state; 40% of the molecules having the unpaired electron in ψ_a and 60% in ψ_s, so that the effective spin population is a simple average. In the absence of reliable estimates of the orbital coefficients for ψ_s and ψ_a for radical A, the presence of a pure state cannot be ruled out, but a realistic prediction cannot be made without further supporting data.

It is very interesting to note that this analysis applies equally to singly protonated pyrogallo-semiquinone (E), in which case the tentative assignments made by Carrington and Smith[12] are shown to be correct.

The magnitude of the redistribution of spin density on protonation of radical A is reminiscent of the situation in radicals related to 1,2,3,4-tetrahydroxybenzene.[11] With one exception, the splitting pattern in that system, confirmed by calculation, is as in radical F (scheme 4) in which the unpaired electron orbital $\psi_{a'}$ is antisymmetrical



SCHEME 4.—E.s.r. parameters[11] ($a/10^{-4}$ T) and coefficients of odd electron orbitals for radicals F and G. σ, symmetry plane. Sign and approximate relative magnitude of coefficient from SCF calculations.

with respect to the symmetry plane σ. In the exceptional example (radical G), which has a large splitting lying on that nodal plane, perturbation of the orbitals by the various alkyl substituents has led to a change in the order so that the unpaired electron occupies an orbital, $\psi_{s'}$, which is symmetrical with respect to the plane σ.

CONCLUSION

The implication of these results is that great care must be exercised when assigning e.s.r. parameters of systems where there are nearly degenerate orbitals of differing symmetry into which the unpaired electron might go. Apparently small perturbations can cause large changes in spin distribution and it is in these situations that SCF calculations are notoriously sensitive to small changes in parameterisation and are consequently unreliable.

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[1] W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1976, **72**, 1121.
[2] W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1977, **73**, 1475.
[3] W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1978, **74**, 432.
[4] D. M. Holton and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1979, **75**, 1637.
[5] W. T. Dixon and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1976, 72, 135.
[6] W. T. Dixon, W. E. J. Foster and D. Murphy, *J. Chem. Soc., Perkin Trans.* 2, 1973, 2124.
[7] J. Q. Adams, S. W. Nicksic and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.
[8] W. Baker and R. I. Savage, *J. Chem. Soc.*, 1938, 1602.
[9] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[10] W. T. Dixon, P. M. Kok and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1977, **73**, 709.
[11] D. M. Holton and D. Murphy, *J. Chem. Soc., Faraday Trans.* 2, 1979, **75**, 1185.
[12] A. Carrington and I. C. P. Smith, *Mol. Phys.*, 1964, **8**, 101.
[13] W. T. Dixon and D. Murphy, *J. Chem. Soc., Perkin Trans.* 2, 1975, 850.
[14] W. T. Dixon, *J. Chem. Soc., Faraday Trans.* 2, 1977, **73**, 67.

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