Solvent Effects on the ^{14}N Hyperfine Coupling Constants and Spin Exchange Rates for Di-t-butyl Nitroxide and Peroxylamidisulphonate Ions [(O$_3$S)$_2$NO^{2-}]†

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Solvent effects on the ^{14}N hyperfine coupling for solutions of di-t-butyl nitroxide (DTBN) and (O$_3$S)$_2$NO^{2-} (Fremy's salt) are compared. The former is very sensitive, especially towards protic solvents whilst the latter is remarkably insensitive. Similarly, the electronic spectrum for DTBN is very solvent dependent whereas that for Fremy's salt is insensitive to solvent. We have previously established that DTBN forms two hydrogen bonds between the N—O group and water, but only *ca.* one to alcohols. We conclude that the N—O group for Fremy's salt does not readily form hydrogen bonds, all the solvation being at the two —SO$_3^-$ groups. However, in aqueous solutions one weak H-bond may be formed.

Spin exchange rates have been measured for these nitroxides in a range of solvents. Detailed comparison shows that the results for DTBN in water are anomalously low by a factor of *ca.* 2, whilst those for Fremy's salt in water are normal. It is unlikely that this effect is due solely to the presence of the two N—O hydrogen-bonds, since the results for alcoholic solutions correlate well with those for aprotic solvents. The suggestion that hydrophobic interactions are responsible is examined, and strongly supported by studies on the effect of changing the temperature and the addition of t-butyl alcohol.

Solvent effects on the ^{14}N hyperfine coupling for neutral nitroxides have been widely studied. Changes in the widths of the e.s.r. features as a function of environment for dilute solutions have been even more widely studied, and indeed this constitutes a powerful tool for studying solvent and solute dynamics in biological systems. Studies which have been directed specifically towards understanding the role of solvation include those of Jolicoeur and Friedman[1, 2] and of our group.[3, 4] In particular, we established a clear link between line-width changes and ^{14}N coupling constants under a variety of conditions.[3] Our results suggested that for most solvents, at $T \geqslant 25$ °C, broadening was controlled by changes in the spin–rotation correlation time (τ_J) rather than by the tumbling rate (τ_c). The correlation with $A(^{14}N)$ was interpreted in terms of hydrogen bonding, radicals with H-bonds making no contribution to τ_J. Our recent optical studies nicely support this theory, showing that in water, there are two H-bonds per nitroxide and virtually no 'free' nitroxide, which explains why the lines are so narrow. In alcohols the nitroxide is mainly mono-hydrogen bonded but there is some 'free' nitroxide.[5] At low temperatures, line broadening became asymmetric, showing that $(g + A)$-anisotropy was involved. For some systems this was interpreted conventionally in terms of changes in τ_c, but for others, equilibrium between H-bonded and 'free' nitroxide was thought to contribute to the broadening.

One difference between our studies and those of Jolicoeur and Friedman is that they suggested that the broadening observed on cooling aqueous solutions was caused by a surprising increase in τ_J. This was cited as constituting the most direct evidence in

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support of the clathrate theory of solvation, in which water cages are built up around R_2NO molecules such that their rotational freedom is enhanced.[1,2] However, we established that this is an asymmetric broadening caused by $(g+A)$-anisotropy and actually represents a decrease in motional freedom.[3] There is no fall in $A(^{14}N)$ on cooling, or change in the optical spectrum, so H-bonds must remain intact. There is a relationship between the theory of Jolicoeur and Friedman and our results for aqueous acetone in which the $C=O$ stretching band was monitored. For water at 0 °C, the acetone is fully hydrogen-bonded with two bonds to oxygen as for the nitroxides. However, in the solid clathrate the acetone freely rotates, the band changes from Gaussian to Lorentzian, and shifts to the value for solutions in hexane.[6] Thus the change envisaged[1,2] does occur on freezing, but not in fluid solutions.

The effect of adding electrolytes to aqueous or methanolic solutions was again interpreted largely in terms of changes in the strength and number of hydrogen bonds to the N—O group.[4] Thus, for R_2NO molecules, hydrogen-bonding seems to be a vital factor in controlling e.s.r. and optical properties.

Dilute solutions of $(O_3S)_2NO^{2-}$ anions have been less studied either by e.s.r. or optically, though there have been studies on solvent and gegen-ion n.m.r. spectra.[7-9] E.s.r. has been used particularly to study ion-pair formation.[10]

Both types of nitroxide have been used to study Heisenberg spin exchange in more concentrated solutions, using e.s.r. line-width increments.[11-19] Unfortunately, spin exchange broadening is always accompanied by dipolar spin–spin broadening. Freed[12] has shown that for solutions of low viscosity, the exchange term dominates, but as the viscosity increases and the temperature falls, the dipolar term becomes increasingly important.

Spin-exchange requires orbital overlap, but this occurs to a minor extent over considerable distances. The theory includes a term involving the life-time (τ_1) of a 'collision complex', which is generally assumed to be short (ca. 10^{-10} s in low viscosity media at room temperature). However, in principle, nitroxides can form diamagnetic dimers, especially in low temperature systems. Such dimerisation is probably not important for DTBN or Fremy's salt, but is thought to occur for diethyl nitroxide on cooling.[20]

The most relevant study to the present work is that of Franks and coworkers.[21] They studied 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) in a range of solvents at room temperature. It was shown that the results do not conform with expectation using the well known equation of Smoluchowsky, based on the Stokes–Einstein theory of diffusion. More important from our viewpoint is that spin exchange was found to be anomalously slow for aqueous solutions, when compared with solvents of similar viscosity.[21] This was discussed in terms of hydrophobic interactions, the postulates of Jolicoeur and Friedman[1,2] being invoked in support of the model proposed.

We had observed this anomaly independently, but the results were not published.[22,23] One aim of the present study was to discover if this anomaly was still present using Fremy's salt, and hence to probe its origin in greater depth.

Experimental

Di-tertiary butyl nitroxide (Eastman) was used without further purification. All solvents used were of the best available grades. Decane was purified by passage through a column of basic aluminium oxide and silica gel. Heptane was stored over 4B molecular sieves for several days prior to use. Toluene was twice distilled and cyanomethane was distilled from fresh P_2O_5 immediately prior to use. Methanol, ethanol and n-propanol were purified by distillation from magnesium activated with iodine, after being refluxed over this mixture for 30 minutes. n-Butanol was purified by shaking with anhydrous sodium carbonate followed by fractionation and t-butanol was purified by fractionation. Water

was either doubly distilled from alkaline permanganate or purified using a Millipore water purifier.

Commercial samples of Fremy's salt (Aldrich) were unsatisfactory, so the salt was prepared by standard procedures. Both the potassium and tetraphenylarsonium salts were prepared, the latter being used in non-aqueous solvent studies.

All solvents were carefully degassed prior to use. Water was degassed by purging with nitrogen for an hour, and all organic solvents were degassed using the freeze-pump-thaw technique. Solutions were made up volumetrically under a nitrogen atmosphere. Stoppered variable temperature aqueous cells were used for e.s.r. studies. Corrections were made for solvent contraction at low temperatures, solvent density data being obtained from standard sources. Viscosity data were obtained from standard sources. The data of Westmeier were used to estimate the viscosities of t-butyl alcohol–water mixtures at 274 K.[24] It is well established that at the onset of Heisenberg spin exchange, the effect of exchange on the proton hyperfine components is important.[12, 25] Exchange narrowing of the proton structure can cause the nitrogen manifold to narrow as the nitroxide concentration is increased. This effect is not significant once the proton lines have been completely exchange narrowed, *i.e.* when the envelope width is much greater than the proton hyperfine splitting constants. Care has been taken in this study to eliminate the effects of proton hyperfine coupling for DTBN by only considering samples which give lines very much broader than the proton hyperfine splitting $A(^1H)$. In aqueous solutions $[A(^1H) \approx 0.05 \text{ G}]$ only lines broader than 0.5 G were used. For other solvents $[A(^1H) \approx 0.1 \text{ G}]$ only lines broader than 1 G were considered.

E.s.r. spectra were recorded on Varian E-3 and E-109 spectrometers, using a V-6040 variable temperature accessory to maintain the temperature to within $\pm 1°$. The spectrometers were calibrated using a standard 10^{-4} mol dm^{-3} solution of DTBN in water. Absorbance measurements were made using Pye Unicam SP1800 and SP340 spectrophotometers.

Concentrations of DTBN were checked before and after e.s.r. studies using the peak at *ca.* 238 nm and an extinction coefficient of 2140.[26]

Results and Discussion

Results for DTBN

The effects of concentration on linewidths at 274 K are shown in fig. 1 for a range of solvents. Widths are expressed in terms of T_2^{-1}, using eqn (1),

$$T_2^{-1} = (\tfrac{3}{2})^{\frac{1}{2}}\gamma_e(\delta H - \delta H_o) \tag{1}$$

where δH is the width between points of maximum slope, δH_o is the residual width in the absence of spin exchange, γ_e is the gyromagnetic ratio for the unpaired electron and the line shape is taken as Lorentzian. Data were collected only after the onset of broadening as described above and long before the lines began to coalesce.

These results were used to calculate apparent collision rates (k_e) (table 1), using the standard equation for Heisenberg spin exchange

$$T_2^{-1} = k_e[R_2NO] \tag{2}$$

where k_e is the pseudo-second-order rate constant. A computer program was used to perform a least squares analysis. In addition to k_e values, this gave residual widths from the intercepts which are compared with the results for 5×10^{-5} mol dm^{-3} solutions in each solvent. These results are in reasonable agreement. We stress that the values of k_e obtained in this way are not true rate constants, but are useful for comparative purposes.

The Smoluchowsky equation

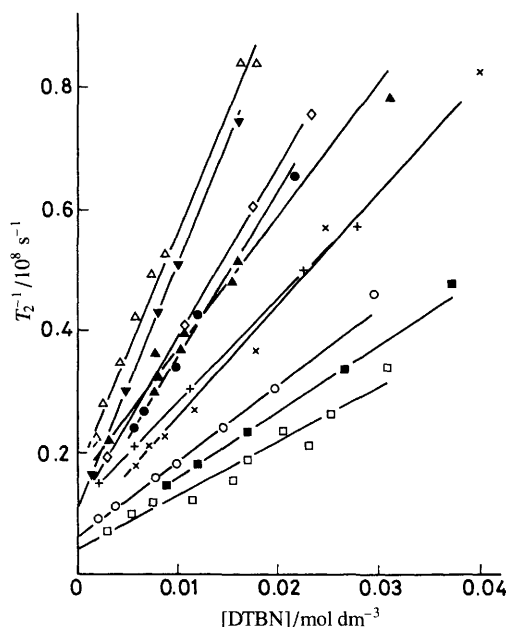$$k_c = (8RT/3000\eta)\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} \tag{3}$$

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Fig. 1. Trends in T_2^{-1} with concentration of DTBN for a range of solvents, ($\triangle$), heptane; ($\blacktriangledown$), MeCN; ($\diamond$), toluene; ($\bullet$), MeOH; ($\blacktriangle$), decane; ($\times$), EtOH; ($+$), dodecane; ($\bigcirc$), n-PrOH; ($\blacksquare$), n-BuOH; ($\square$), H_2O.

Table 1. Summary of the least squares analysis of the results given in fig. 1.

	$k_e{}^a$ /10^9 dm^6 mol^{-1} s^{-1}	residual width^a/G	experimental limiting width/G
methyl cyanide	3.97 ± 0.1	0.67 ± 0.05	0.61
n-heptane	3.89 ± 0.12	1.05 ± 0.06	0.82
toluene	2.75 ± 0.04	0.69 ± 0.02	0.64
methanol	2.69 ± 0.17	0.56 ± 0.12	0.52
n-decane	2.16 ± 0.12	0.98 ± 0.09	0.74
ethanol	1.82 ± 0.11	0.48 ± 0.14	0.58
n-dodecane	1.68 ± 0.04	0.71 ± 0.03	0.72
n-propanol	1.24 ± 0.05	0.36 ± 0.06	0.53
n-butyl alcohol	1.07 ± 0.04	0.31 ± 0.05	0.53
water	0.88 ± 0.05	0.25 ± 0.05	0.33

^{a} From fig. 1.

predicts that in the limit of strong exchange, the rate (k_c) should be a linear function of the ratio of temperature to solvent viscosity (T/η), where k_c is the rate of diffusion controlled collisions. For a nuclear spin $I = 1$ it is generally agreed that p in the relationship between k_c and k_e, $k_e = p k_c$, should take a value of $\frac{1}{3}$.[21, 27, 28]

A plot of k_e against T/η is given in fig. 2. With the marked exception of water at temperatures below *ca.* 345 K, and of certain t-butyl alcohol–water mixtures, the results are reasonably linear. However, a plot in which $k_e \eta$ is compared with η shows clearly that eqn (3) is not obeyed (fig. 3). However, the abnormality of the water data is reinforced.
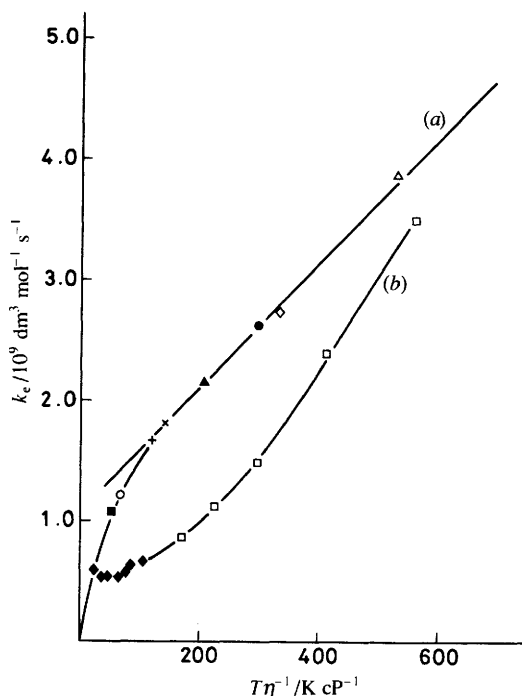
Fig. 2. k_e for DTBN in a range of solvents as a function of T/η. Curve (*a*) symbols as in fig. 1. Curve (*b*), H_2O + t-BuOH mixtures (◆). The water data (□) cover a range of temperatures increasing from left to right. Curve (*a*) has been constrained to pass through zero.

Results for Fremy's Salt Solutions

Our e.s.r. results for dilute solutions (*ca.* 10^{-5} mol dm^{-3}) are listed in table 2, and compared with those for DTBN in fig. 4. Clearly, the large solvent sensitivity of $A(^{14}N)$ for DTBN is almost absent for Fremy's salt. The remarkable lack of solvent dependence for Fremy's salt [$A(^{14}N)$] includes an insensitivity to ion-pairing in the low dielectric solvents. The most stable and most soluble salt in such solvents was [(Ph$_4$As$^+$)$_2$] [(O$_3$S)$_2$NO^{2-}] and, in general, ion-pair formation involves Ph$_4$As$^+$ ions.

There does, however, appear to be a break between the results for aprotic solvents [line (A) in fig. 4] and protic solvents [line (B)]. Since this is very small [$\Delta A(^{14}N) = 0.3$ G] we would hesitate to draw inferences therefrom were it not for the fact that the optical results show a similar break between the two classes of solvent (fig. 5). (We have shown previously that there is a good correlation between the ^{14}N shifts for DTBN and ν_{max} for the optical band in the 23 000 cm^{-1} region.[5])

Within the groups the results for Fremy's salt are scattered, but there is a clear break between protic and aprotic solvents. We think that it is unlikely that these breaks are caused by direct H-bonding to the N—O group. This is because the trends are so small compared with DTBN, which are surely due to H-bonding to the N—O group. We therefore tentatively ascribe the shifts to H-bonding to the —SO$_3^-$ units. These are not expected to be strongly influenced by aprotic media or by ion pairing with the large Ph$_4$As$^+$ cations, but will, of course, be modified by H-bonding. A major drawback to this suggestion is that the values of $A(^{14}N)$ and ν_{max} for water have moved back towards the aprotic region whereas we would expect water to induce a greater shift than the alcohols.[29-31] In view of the great propensity for water to form H-bonds,[31,32] it is possible that this reverse trend is caused by very weak bonding to the N—O group, only for
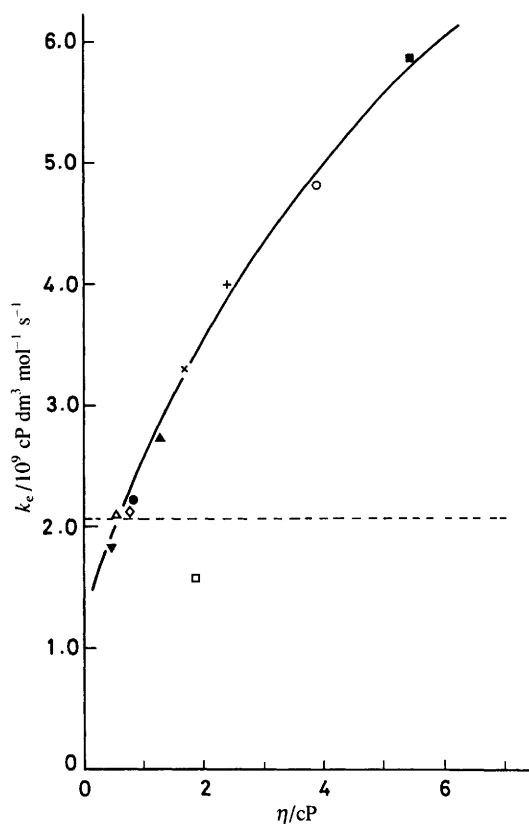
Fig. 3. $k_e \eta$ as a function of η for DTBN in a range of solvents at 20 °C. Symbols as in fig. 1. Note the major deviation for water. The dashed line is that predicted by the Smoluchowsky equation.
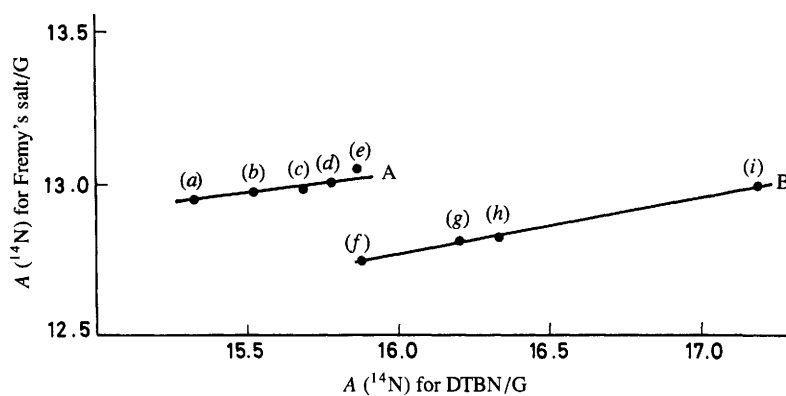

Fig. 4. Comparison of $A(^{14}N)$ for dilute solutions of DTBN and Fremy's salt in a range of solvents. Line A, aprotic solvents (*a*) CCl$_4$, (*b*) acetone, (*c*) MeCN, (*d*) MeNO$_2$, (*e*) CHCl$_3$; and line B, protic solvents (*f*) t-BuOH, (*g*) MeOH, (*h*) glycol, (*i*) H$_2$O.

Table 2. Information on DTNB and Fremy's salt

solvent	peak position[a]		E_T	
	/nm	/cm^{-1}	/kJ mol^{-1}	/Kcal mol^{-1}
	DTBN			
acetic anhydride	451	22 173	265.25	63.46
toluene	459	21 786	260.63	62.35
CCl$_4$	457.5	21 858	261.49	62.56
DMF	453	22 075	264.08	63.18
DMA	454.5	22 002	263.21	62.97
Et$_2$NH	457	21 882	261.77	62.62
HMPA	457	21 882	261.77	62.62
acetone	454	22 026	263.5	63.04
DMSO	452.5	22 099	264.38	63.25
NMF	444	22 523	269.44	64.46
t-BuOH	444	22 523	269.44	64.46
MeOH	438	22 831	273.13	65.34
H$_2$O	421	23 753	284.16	67.98
MeCN	450	22 222	265.84	63.60
EtOH	441	22 676	271.27	64.897
IPA	443	22 573	270.05	64.60
cyclohexane/hex	462.5	21 622	258.66	61.88
dodecane	462.5	21 622	258.66	61.88
ethanediol	435.5	22 962	274.7	65.72
formamide	435.5	22 962	274.7	65.72
NMA (30.6 °C)	448	22 321	267.03	63.88
	Fremy's salt			
acetone	537	18 622		
MeOH	538.5	18 570		
CH$_3$OD	540	18 519		
H$_2$O	542	18 484		
MeOH–DMSO	544	18 382		
MeCN	547.5	18 265		
DMF	548.5	18 231		
nitromethane	549.0	18 215		
DMSO	550	18 181		
DMA	550	18 181		
DMSO–CH$_2$Cl$_2$	552	18 116		

[a] 25 °C.

aqueous solutions. Thus, H-bonding to —SO$_3^-$ groups causes a shift to low $A(^{14}N)$ values, and this is balanced, for water, by a comparable shift to high $A(^{14}N)$ values, as expected if bonding to >NO were significant.

In order to check this conclusion, trends in $A(^{14}N)$ for Fremy's salt were studied as a function of the mole fraction of dimethylsulphoxide (DMSO) in water+DMSO mixtures (fig. 6). There is a rapid fall in $A(^{14}N)$ as DMSO is added, with a minimum at 12.86 G, which is close to the value for methanol solutions. This result is nicely accommodated if we postulate that DMSO readily removes water (OH) groups from the weakly bonded N—O site, causing a shift to low values, and subsequently dehydrates the —SO$_3^-$ groups, causing a reverse shift.

We tentatively conclude that the N—O group of Fremy's salt is not H-bonded in alcoholic solution, but forms one weak H-bond in water.
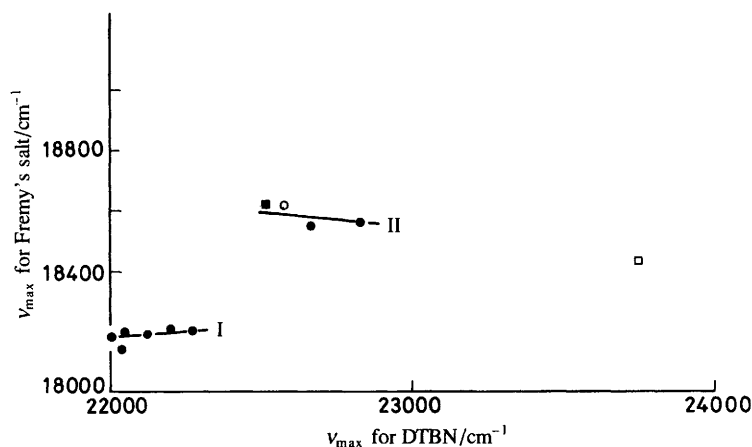
Fig. 5. Comparison between ν_{max} for Fremy's salt and DTBN in a range of solvents. Curve I covers a range of 7 aprotic solvents, and Curve II a range of alcohols. ($\square$) is for aqueous solutions.
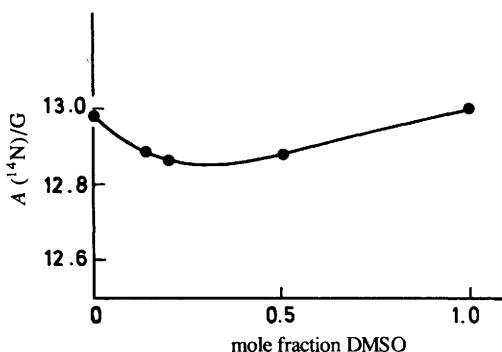

Fig. 6. Trend in $A(^{14}N)$ for Fremy's salt in $H_2O + DMSO$ solutions as a function of the mole fraction of DMSO.

Spin Exchange for Fremy's Salt

The results are summarised in fig. 7–9, which can be compared with fig. 1–3, respectively, for DTBN. In this case, there is no residual coupling to protons, so the line-width differences for very dilute solutions must be associated with either spin–rotation effects or $g - A$ anisotropy (see above). Fig. 8 shows that there is again a linear dependence on T/η, but in this case water is not anomalous. Fig. 9 shows that $k_e \eta$ is still strongly solvent dependent, but confirms that water behaves normally.

Spin Exchange: Conclusions

The major conclusions from both studies are (i) that although solutions in non-viscous solvents behave approximately in the way predicted by Smoluchowsky's equation those with high viscosity exhibit apparent rates which are considerably greater than expected, and (ii) that aqueous solutions of dialkyl nitroxides in water have anomalously low rates whereas Fremy's salt behaves normally in water.

(i) It is not our concern to consider the validity of Smoluchowsky's equation. The problem was addressed by Ablett *et al.*,[21] but there is one aspect that they decided to
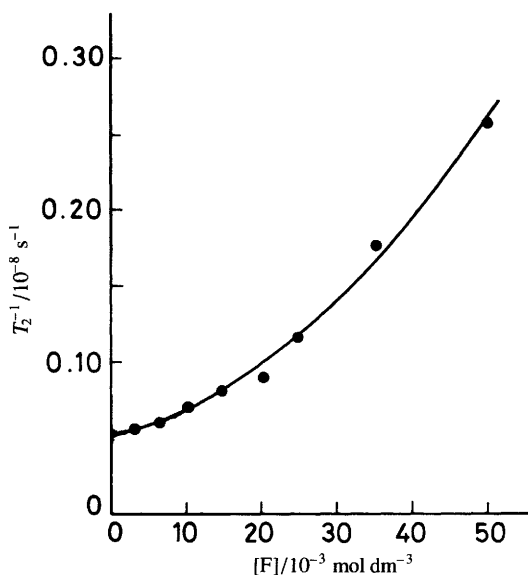
Fig. 7. Values for T_2^{-1} for a range of aqueous solutions of Fremy's salt (F) as a function of concentration. (Based on the $M_I = 0$ feature.)
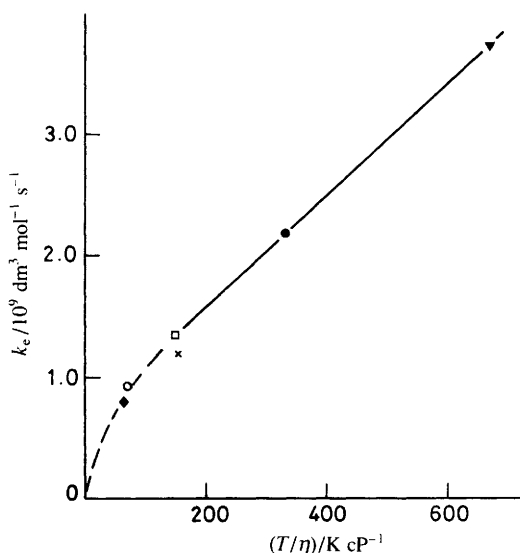

Fig. 8. k_e for Fremy's salt in a range of solvents as a function of T/η. Symbols as in fig. 1 and 2.

neglect, which in our view must play some part in the behaviour of solutions with high viscosity, namely, dipolar broadening. As was pointed out,[21] this is not expected to be important for non-viscous solutions, but, according to the equations developed by Abragam[33] and Freed[12] it should contribute almost as much as spin exchange to the linewidth for the more viscous solutions. This arises because the radicals spend more time close enough to have a significant zero field splitting for the triplet-state encounters, but too far apart for significant spin exchange broadening.

(ii) Two possible explanations need to be considered for the low value of k_e for DTBN in water, namely hydrogen-bonding and hydrophobic type solvation. The former was
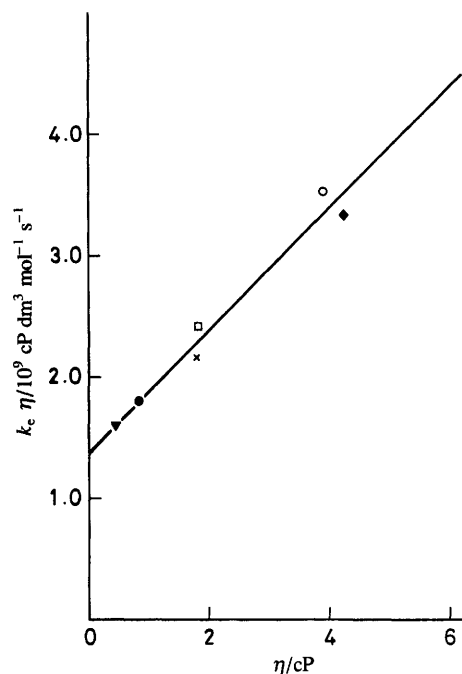
Fig. 9. $k_e \eta$ as a function of η for Fremy's salt in a range of solvents. Symbols as in fig. 1 and 2.

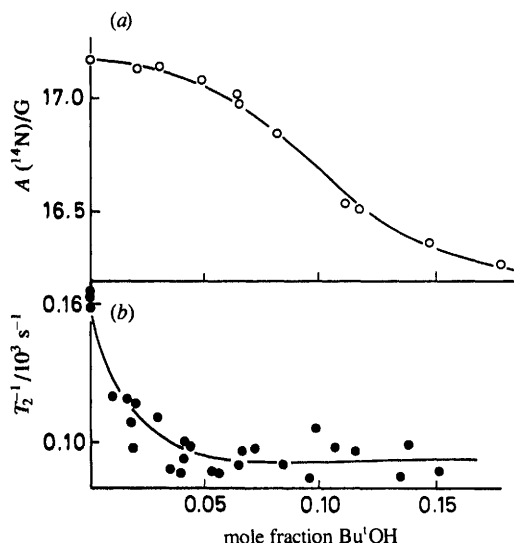**Fig. 10.** Effects of adding t-BuOH to an aqueous solution of DTBN on (a) $A(^{14}N)$ and (b) T_2^{-1}, the exchange governed line-width. [DTBN] = 1.7×10^{-2} mol dm^{-3}.

not considered previously,[21] but cannot be ignored since aqueous solutions of DTBN are unique in forming two hydrogen bonds to the nitroxide oxygen.[5] It might be that such bonding could shield the two >NO groups from intimate contact. However, it seems to us that whilst this may be a contributing factor, it cannot account for the unique effect of water since the nitroxides are predominantly mono-hydrogen bonded in methanol,[5] but there is no indication of abnormality for this solvent.

Another argument against the H-bonding theory can be found in our results for DTBN in aqueous t-butyl alcohol (TBA) (fig. 10). There is a marked decrease in T_2^{-1} in the 0–0.5 mole fraction (TBA) range. However, in this region $A(^{14}N)$ is almost invariant, and the width change follows the increase in viscosity. In contrast, in the mole fraction range 0.05–0.15 there is no significant change in T_2^{-1} despite the fact that $A(^{14}N)$ rapidly decreases in this range. This change corresponds to loss of one H-bond so it should have induced a major change in T_2^{-1} had H-bonding been the cause of the anomaly.

We therefore agree with Ablett *et al.*[21] that the anomaly lies in the interaction between water and the hydrophobic Me_3C— groups. Our interpretation differs, however, in that we consider that the NO group is di-hydrogen bonded, whereas Ablett *et al.*[21] use the model of Jolicoeur and Friedman[1,2] in which the $(Me_3C)_2NO$ molecules are completely enclathrated, with no H-bonding.

To test the concept that partial cage structures tend to keep the nitroxide molecules apart, we have studied the effect of increasing the temperature on k_e (fig. 2). The results show that the anomaly for aqueous solutions is steadily reduced on heating, becoming zero at *ca.* 345 K. This is the behaviour we expect since clathrate cages are known to 'melt' very rapidly on heating,[34] whereas the hydrogen bonding is not greatly modified.[3]

These conclusions can be compared with those used to interpret e.s.r. results for m-dinitrobenzene anions in water,[35] which seem to us to constitute good evidence for partial enclathration in fluid aqueous solution. The spectra establish that the anions are completely asymmetric in water, the unpaired electron interacting with only one nitro-group. This requires that solvation of the $—NO_2^-$ unit has a remarkably long lifetime ($\tau \approx 4.5 \times 10^{-8}$ s at 0 °C) before switching to the other $—NO_2$ group. This effect was rapidly reduced on heating, and in methanol the anions showed two equivalent $—NO_2$ groups, the lifetime of the asymmetric solvates being reduced to *ca.* 10^{-9} s. We can only explain this large difference using a partial cage model which tends to fix the asymmetry [see (I)].

For DTBN, we suggest that the incipient cages tend to block contact between the molecules. This effect may well be reinforced by H-bonding at the N—O group, the two modes of solvation acting sinergistically, as for the m-dinitrobenzene anions.

(I)
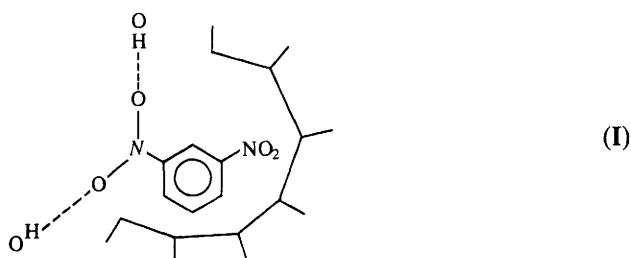
The results obtained with added TBA are in accord with the model. For a variety of reasons it is thought that TBA is solvated in a similar manner by water at low temperatures.[36] It does not affect cage formation for DTBN in the 0–0.5 mole fraction region (fig. 10) which is just the region in which cages are thought to be important for TBA. At higher concentrations pairing or clustering occurs, but cages are still favoured. In this range the fall in $A(^{14}N)$ for DTBN suggests loss of one H-bond, but there is still no clear loss of the water 'anomaly'.

Infrared Studies

In our studies of DTBN using optical spectroscopy, attempts were made to monitor changes in the N—O stretch frequency using infrared and resonance Raman

spectroscopy.[5] However, for some reason this feature is relatively insensitive to solvent changes and attempts to obtain quanitative information failed. Similar attempts with Fremy's salt have shown that in this case also the N—O group is insensitive. This was expected, but the results cannot be taken to support our other studies in view of the results for DTBN.

We also attempted to use the S—O bands to monitor solvation at the —SO_3^- groups, but these again proved to be relatively insensitive to changes in solvent so the study was abandoned.

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