

ESR Studies of Spin Probes in Anisotropic Media

JACK H. FREED

Department of Chemistry, Cornell University, Ithaca, N. Y. 14853

We wish to summarize some of our recent studies of spin probes in liquid crystalline media. We also wish to indicate some theoretical aspects of spin-dependent phenomena on surfaces and interfaces.

Order Parameters and Equation of State

One of the most useful ways in which magnetic resonance may be applied to anisotropic media is to the determination of the molecular order parameter:

$$S = \frac{1}{2} \langle 3\cos^2\beta - 1 \rangle \quad 1$$

where β is the angle between the preferred spatial direction in the medium, usually referred to as the director and specified by unit vector \hat{n} , and the symmetry axis of the molecule. Actually, this parameter is sufficient only if the molecule is ordered with cylindrical symmetry (either prolate with positive S or oblate with negative S). In general, there is an ordering tensor, which is completely specified once the principal axes of ordering of the molecule relative to the director are known, and the values of S and the "asymmetry parameter" are given.

$$\delta = \frac{\sqrt{6}}{2} \langle \sin^2\beta \cos 2\alpha \rangle \quad 2$$

In eq. 2 α is the azimuthal angle for the projection of the director in the molecular x-y plane. One finds, in the case of nitroxides, that if the principal axes can be chosen on the basis of molecular symmetry, it is then possible to determine S and δ from ESR measurements of the effect of the ordering on hyperfine and g-shifts (1,2). It is, of course, first necessary to accurately measure the hyperfine and g-tensors from rigid-limit spectra preferably in the solvent of interest, since these tensors are generally somewhat solvent-dependent (1,2,3). It was found that, by a proper choice of the molecular z-axis, it is usually possible

to keep δ small relative to S . The ordering tensor may be related to $P_0(\Omega) = P_0(\beta, \alpha)$ the equilibrium distribution by such expressions as:

$$S = \int d\Omega P_0(\Omega) \frac{1}{2} (3\cos^2\beta - 1) \quad 3$$

where

$$P_0(\Omega) = \exp(-U(\Omega)/kT) / \int d\Omega \exp(-U(\Omega)/kT) \quad 4$$

with $U(\Omega)$, the mean restoring potential of the probe in the field of the molecules of the anisotropic solvent. Since the mean torque on the probe is obtained by taking the appropriate gradient of $U(\Omega)$ (1,2,4), one has that it is statistically the potential of mean torque for the spin probe. This potential $U(\Omega)$ can be expanded in a series of spherical harmonics of even rank, since, in liquid crystals \hat{n} and $-\hat{n}$ are equivalent. The leading terms in the expansion are then spherical harmonics of rank 2. So, if we keep only these lowest order terms, and employ the principal axis system of the ordering, then

$$U(\beta, \alpha)/kT = -\lambda \cos^2\beta - \rho \sin^2\beta \cos 2\alpha. \quad 5$$

A non-zero δ then implies a non-zero ρ . Once these potential parameters λ and ρ are measured, then they may be related to theories for the equation of state of the liquid crystal. In the "mean-field" theory of the Maier-Saupe type, one assumes that, for example, $\lambda^{(s)} = S^{(s)} a^{ss}/V^{1/3} T$ (where the superscript implies solvent molecules), where the coefficient a^{ss} which is independent of T and V refers to the strength of the anisotropic potential and $\lambda^{(s)}$ is taken to be proportional to the mean ordering of the surrounding solvent molecules given by $S^{(s)}$. This expression also allows for dependence of the interaction on molar volume V . A simple point of view would be to let $V^{1/3} = r^3 \gamma_s$, so a measurement of γ_s would indicate the nature of the intermolecular forces leading to the orienting potential. The case of $\gamma_s = 2$, implying van der Waals attractions, would correspond to Maier-Saupe Theory. More generally, 3γ would represent some mean radial dependence averaged over the different kinds of interaction forces. In the case of a dilute solution of probe molecules, which are ordered by their interaction with solvent, one should write: $\lambda^{(p)} = S^{(s)} a^{sp}/V^{1/3} T$. Thus, studies of the pressure and temperature variation of the ordering should be useful in testing theories of the equation of state. Interesting thermodynamic derivatives one may hope to measure are $(\partial \ln S^{(1)} / \partial \ln T)_V$ and $(\partial \ln T / \partial \ln V)_{S^{(1)}}$. Actually one obtains the analogous expressions with V replaced by P from pressure-dependent studies. Then one uses P-V-T data to obtain these derivatives. Using the simple mean field theory outlined above, but with $\rho=0$, one finds:

$$\left(\frac{\partial \ln S^{(s)}}{\partial \ln T} \right)_V = \frac{R^s}{1+R^s} \quad 6$$

where $R^s \equiv (\Delta S^{(s)})^2 a^{ss} / V \gamma_s T$ 6a

with $(\Delta S^{(s)})^2$ the mean square fluctuation in order parameter, and R^s is a quantity that is uniquely predicted by Maier-Saupe theory for a given value of $S^{(s)}$ or $\lambda^{(s)}$. Also:

$$\left(\frac{\partial \ln S^{(p)}}{\partial \ln T} \right)_V = \frac{S^{(s)}}{S^{(p)}} \frac{R^{(p)}}{1+R^{(s)}} \quad 7$$

with $R^{(p)} \equiv (\Delta S^{(p)})^2 a^{sp} / V \gamma_p T$ 7a

Also,

$$\left(\frac{\partial \ln T}{\partial \ln V} \right)_{S^{(s)}} = -\gamma_s \quad 8$$

and $\left(\frac{\partial \ln T}{\partial \ln V} \right)_{S^{(p)}} \equiv -\gamma'_p = -\gamma_p \left[1+R^{(s)} \left(1 - \frac{\gamma_s}{\gamma_p} \right) \right]$ 9

Thus we see that experimental results on $(\partial \ln S^{(i)} / \partial \ln T)_V$ enable tests of the mean-field theories, while those on $(\partial \ln T / \partial \ln V)_{S^{(i)}}$ provide information on the nature of the orienting potentials. The experimental results on $(\ln S^{(i)} / \ln T)_V$ both for $i=s$ from NMR studies on the nematic PAA (5), and for $i=p$ from ESR studies on the weakly-ordered perdeuterated nitroxide spin probe PD-Tempone in the nematic solvent Phase V, are in qualitative agreement with eqs. 6 and 7 respectively, but the predictions are typically about 50% larger in magnitude compared to the experimental results. Since $R^{(s)}$ is predicted to range from about $-3/4$ to -1 in the nematic phase, this is not surprising. Thus, small contributions from other terms in the expansion of $U(\Omega)$ (e.g. the fourth rank spherical harmonics), can readily "explain" such effects (4). The main point is that the thermodynamic measurements of ordering, whether for the pure solvent or the spin probe, compare reasonably well with the single parameter (λ) mean-field theory. Thus, it is reasonable to attach some physical significance to eqs. 8 and 9. The NMR result on PAA gives $\gamma_s = 4$, while recent more approximate results from P-V-T measurements at the isotropic-nematic phase transition give $\gamma_s \approx 3.3-4$ for a range of solvents including MBBA, which is very similar in properties to Phase V (6). Now eq. 9, after allowing for the small corrections in magnitude in $R^{(s)}$ as discussed above, should be moderately well approximated by $\gamma'_p \approx \frac{1}{2} (\gamma_p + \gamma_s)$. The experimental results on PD-Tempone in Phase V have yielded $\gamma'_p \approx 2$. This suggests

that γ_p itself is rather insensitive to changes in the molar volume. This may not be so surprising if we have (1) the weakly aligned spin probe located in a cavity of the liquid crystal; (2) a specific short-range attractive interaction between probe and solvent molecules dominant in $\lambda(P)$; and (3) the size of the cavity is not rendered small relative to the molecular size of PD-Tempone at the pressures achieved. This model is supported and amplified by the spin-relaxation results below. Clearly, it would be of considerable interest to determine γ_p as a function of the size and shape of different probe molecules.

Relaxation and Rotational Reorientation

We now discuss detailed results on ESR relaxation and line-widths: how they are to be analyzed and the microscopic dynamical models they suggest (1-4,7). As long as the concentration of spin probes is low, the line shapes are determined by rotational modulation of the anisotropic interactions in the spin Hamiltonian, in particular the hyperfine and g-tensors; (the nuclear quadrupole interaction exists for nitroxides, but is too small to be of importance except in ENDOR experiments). The important feature of anisotropic media that is different from isotropic media is the existence of the restoring potential $U(\Omega)$, to which the molecular reorientation is subject. The simplest model for molecular reorientation is then Brownian rotational diffusion including $U(\Omega)$ in a rotational Smoluchowski equation. This may be most compactly written in terms of $P(\Omega, t)$, the probability the molecular orientation (relative to a fixed lab frame) is specified by Euler angles Ω at time t , and \hat{N} the vector operator which generates an infinitesimal rotation, by (1,2,8):

$$\frac{\partial P(\Omega, t)}{\partial t} = -\hat{N} \cdot \hat{R} \cdot \left[\hat{N} + \left[\hat{N}U(\Omega) \right] / kT \right] P(\Omega, t) \quad 10$$

The dyadic \hat{R} represents the rotational diffusion tensor. One may solve this diffusion equation by various methods and then obtain various expressions for the ESR line widths in the motional narrowing region (2,9,10). The main points to note are that 1) the restricted rotation due to the restoring potential means that the rotational modulation of the spin Hamiltonian $\mathcal{H}_1(\Omega)$ is reduced in magnitude, and 2) the rotational relaxation represented by τ_R for an isotropic liquid, must now be replaced by a collection of correlation times associated with the different orientational components to be relaxed in the spin Hamiltonian. That is, we first expand $\mathcal{H}_1(\Omega)$ in the usual fashion in terms of the generalized spherical Harmonics $\Phi_{LM}^L(\Omega)$:

$$\mathcal{H}_1(\Omega) = \sum_{L,K,M} (-1)^K \Phi_{-KM}^L(\Omega) F_i^{(L,K)} A_i^{(L,M)} \quad 11$$

with $F_i^{(L,K)}$ and $A_i^{(L,K)}$ irreducible tensor components of rank L , where F_i is in molecule-fixed co-ordinates while A is a spin operator in the lab axes. Then the correlation functions:

$$C(KK'; M, M'; \tau) \equiv \langle D_{K, M}^{* (2)}(t) D_{K', M'}^{(2)}(t+\tau) \rangle \\ - \langle D_{KM}^{* (2)}(t) \rangle \langle D_{K', M'}^{(2)}(t+\tau) \rangle \quad 12$$

will exhibit different time dependences for each set of values of the "quantum numbers" K , K' , M , and M' . (Note that $S = \langle D_{00}^{(2)}(\Omega) \rangle$). Such a theoretical analysis has been found, in various studies (12), to give reasonable semi-quantitative agreement with experiment. However, liquid crystalline solvents tend to be somewhat viscous, and large spin probes tend to reorient slowly. Consequently, motional narrowing theory need not apply (1,2,4). This fact has not been adequately appreciated in past work, since the effect of the ordering in reducing the modulation of $\mathcal{H}_i(\Omega)$ yields narrower lines. Nevertheless, the slow motional features manifest themselves in significant shifts of the resonance lines and in lineshape asymmetries. This former effect can lead to significant errors in determination of S as outlined above, if the slow-tumbling contributions are not corrected for. The line-width asymmetry starts to be appreciable at somewhat shorter τ_{1s} , so it can be used as an indicator of slow tumbling in anisotropic media. The slow-tumbling theory of ESR lineshapes in anisotropic media is based upon a generalization of eq. 10 known as the stochastic Liouville equation in which one introduces a probability density matrix that includes simultaneously the spin and orientational degrees of freedom (1,8).

Recent careful studies have now shown the importance of slow-tumbling corrections, but, even more importantly, have demonstrated that the rotational reorientation is not so simply described as given by eq. 10 for Brownian reorientation subject to the potential of mean torque (1-4, 7, 13, 14). This matter has been analyzed theoretically from several points of view (2,3,8). The main point to be made is that molecular probes, which are comparable in size to the solvent molecules, are subject to a range of intermolecular torques affecting the reorientation and these torques are characterized by a wide spectrum of "relaxation times". Brownian motion is the limiting model appropriate when τ_R , the rotational reorientation time of the B particle, is much slower than the "relaxation times" for the intermolecular torques experienced by it, such that the latter are well approximated as relaxing instantaneously. Instead, for particles of molecular dimensions, one must distinguish between forces that are relaxing much faster than, comparable to, and slower than τ_R , since they will tend to play a different role in the reorientational motion. These considerations are particularly important for ordered media such as liquid crystals.

According to our approximate theoretical analysis, fluctuating torques relaxing at a rate that is not slower than τ_R will contribute to a frequency-dependent-diffusion coefficient, e.g. for a simple model wherein the fluctuating torques decay with a single exponential decay constant τ_M , one has:

$$R(\omega) = R_0(1 - i\omega\tau_M) \quad 13$$

where R_0 is the zero-frequency diffusion coefficient. Such a model might approximately account for the reorientation of a probe molecule of comparable size to the surrounding solvent molecules wherein the reorientation of the latter at rates comparable to τ_R , provide the fluctuating torques causing the reorientation of the probe molecule. This is called the "fluctuating torque" model (2,3,4). In the case of an isotropic fluid (i.e. $U(\Omega)=0$), eq.13 leads to a spectral density:

$$J(\omega) \equiv \text{Re} \int_0^\infty e^{-i\omega t} dt C(K;M;t) = \tau_R / [1 + \omega^2 \tau_R^2] \quad 14$$

with $\epsilon \equiv [1 + \tau_M/\tau_R]^2$. Recent observations of anomalous behavior of the non-secular spectral densities (i.e. $\omega = \omega_e$ the electron spin Larmour frequency) for some nitroxide spin probes peroxyamine disulfonate (PADS) and PD-Tempone are amenable to such an interpretation with $\tau_M \sim \tau_R$ (3,15,16). There is also some indication that even for pseudo-secular spectral densities (i.e. ω_n , the nuclear-spin Larmour frequency) such an analysis is appropriate (3). Also, it has been noted (3) that such a model may be appropriate for explaining anomalies in slow-tumbling spectra that had previously (15,16) been attributed to rotational reorientation by jumps of finite angle. The basic point is that the spectral density of eq.14 is similar, but not identical, to typical spectral densities predicted for models of jump diffusion (8).

For anisotropic media, the "fluctuating torque" model with eq.13 may also be applied to eq.10 (or more precisely its Fourier-Laplace transform). Because $U(\Omega) \neq 0$, the spectral densities are more complex than given by eq.14. In fact, it becomes necessary to recognize the tensorial properties of $R(\omega)$ as well as τ_M^{-1} . In an "anisotropic diffusion" model, the principal axes of diffusion are fixed in the molecular co-ordinate frame (2,4). This is a model which is also appropriate for isotropic media. In an "anisotropic viscosity" model the principal axes of R (as well as τ_M^{-1}) would be fixed in a lab frame, e.g. with respect to the macroscopic director (2,4). One can, furthermore, introduce a "localized anisotropic viscosity" model in which there is ordering on a microscopic scale (i.e. a local director), but it is randomly distributed macroscopically.

Experimental results on the weakly ordered PD-Tempone spin probe have been found to exhibit rather large anomalies in the incipient slow-tumbling region ($\tau_R \gtrsim 10^{-9}$ sec.), where the ESR

lines are beginning to lose their Lorentzian shape. These anomalies could be successfully accounted for by a fluctuating torque model in which τ_M is highly anisotropic when referred to the lab frame (i.e. the torques inducing reorientation about the axis parallel to the director are very slow). But, for a variety of aspects (not the least of which is the fact that ϵ would have to be very large (ca. 20) implying $\tau_M > \tau_R$), which are inconsistent with the basic "fluctuating torque" model, this mechanism does not appear to be an adequate explanation. (A simple "anisotropic viscosity" model may successfully be applied to predict the observations, but it too would lead to physically untenable predictions).

Combined studies of the pressure dependence as well as the temperature dependence of the ESR lineshapes have been useful in demonstrating that this anomaly (in which the two outer lines of the ^{14}N hyperfine triplet are significantly broader than predicted from simple theory for $\tau_R \sim 10^{-9}$ sec.) is mainly dependent on $\tau_R(T,P)$ and nearly independent of the particular combination of T and P. This is good evidence that the anomaly is associated with the viscous modes, as is τ_R itself (2,4).

We now turn to the models appropriate when there are important fluctuating components of the anisotropic interactions which relax significantly slower than τ_R . In this case, it is necessary to augment the potential of mean torque $U(\Omega)$ by an additional component $U'(\Omega,t)$ which is slowly varying in time, but with a time average $\langle U'(\Omega) \rangle = 0$. In this "slowly relaxing local structure" (SRLS) model, each spin probe sees a net local potential given by $U(\Omega) + U'(\Omega,t)$ which remains essentially constant during the time-scale, τ_R , required for it to reorient. Then, over a longer time-scale, the local reorienting potential $U'(\Omega,t)$ relaxes. An approximate analysis of ESR lineshapes using this model does appear to have the correct features for explaining the observed anomalies, but a full treatment would be very complex (2,4). This analysis yields rough estimates of the order parameter relative to the local structure of $S_1^2 \sim 1/16$ and $\tau_X/\tau_R \sim 10$, where τ_X is the relaxation-time of the local structure. (Again, one can bring in anisotropies in τ_X^{-1}). This SRLS mechanism is one that may also be applied to macroscopically isotropic media, which however, on a microscopic level display considerable structure. A very approximate analysis (2,4) for the isotropic spectral densities analogous to eq.14 yields

$$j_0(\omega) = [D_0(\omega) + S_1^2 \tau_X / (1 + \omega^2 \tau_X^2)] \quad 15a$$

$$j_2(\omega) = D_2(\omega) \quad 15b$$

where $j_0(\omega)$ is the spectral density for the $K=0$ (cf. eqs.11-12) terms and $j_2(\omega)$ for the $K=2$ terms. For $\omega^2 \tau_R^2 \ll 1$, one may approximate $D_0(\omega)$ and $D_2(\omega)$ by:

$$D_0(\omega=0) = [1 + 0.27S_1 - 2.87S_1^2 + 1.522S_1^3] \tau_R \quad 16a$$

$$D_2(\omega=0) = [1 + 0.052S_1 + 0.264S_1^2 + 0.177S_1^3] \tau_R \quad 16b$$

provided S_1 is positive and $\lambda > 0.8$; while

$$D_0(\omega=0) = [1 - 0.180S_1 - 3.11S_1^2 - 6.34S_1^3] \tau_R \quad 17a$$

$$D_2(\omega=0) = [1 - 0.134S_1 - 0.601S_1^2 - 2.654S_1^3] \tau_R \quad 17b$$

provided S_1 is negative and $\lambda < -0.4$. One effect of the results expressed by eqs. 15 is to cause the $j_0(\omega)$ and $j_2(\omega)$ spectral densities to be different, just as though there were anisotropic diffusion. It is the more complex frequency dependence, as well as $\tau_X/\tau_R \gg 1$, that enables eqs. 15 to have features which are consistent with the anomalous experimental observations.

It is interesting to note that the Pincus-deGennes model of spin relaxation by director fluctuations (17,18) can be applied to ESR relaxation (2) just as it has been to NMR relaxation (19). It is also, in a sense, a slowly relaxing structure mechanism. The important differences with the above SRLS model are the Pincus-deGennes model (1) is a hydrodynamic one based upon long-range ordering and not a local structure, and (2) includes only small fluctuations of the director orientation about its mean orientation. Feature 2) results in the prediction (2) that its ESR contribution is opposite in sign (as well as much too small in magnitude for a weakly ordered probe) to "explain" our observed anomalies.

Recent analyses on a highly ordered cholestane nitroxide spin-probe have exhibited the importance of applying a slow tumbling analysis (1,13,14). Also, a spin-relaxation theory which recognizes the statistical interdependence of rotational reorientation and director fluctuations (or of the former and SRLS) has recently been developed (29).

It should be clear, then, that interesting microscopic features of molecular motions in anisotropic media manifest themselves in ESR spectra, and it is still a challenge to unravel the intricate details of observed spectral anomalies.

Many of the general features applied to anisotropic fluids, as discussed above, would be applicable for studying rotational reorientation of molecules on surfaces and at interfaces. That is, one could determine an ordering tensor as given by eqs. 1 and 2 with the director usually normal to the surface. However, the director will no longer obey the symmetry relation $\hat{n} = -\hat{n}$. Thus, the expansion of $U(\Omega)$ in spherical harmonics would have to include odd rank terms. In particular, one should add to the $L=2$ terms, such as given by eq. 5, the $L=1$ term proportional to $\cos\beta$. Rotational diffusion would still be described by eq. 10;

the correlation functions defined by eq.12 would still be appropriate for motional narrowing, although their detailed form is altered; and the SLE equation for slow tumbling would have to include the new $U(\Omega)$. It remains to be seen what particular features of the microscopic motions will manifest themselves in careful ESR studies.

Phase Transitions

In the pressure-dependent study of PD-Tempone in Phase V solvent, the nematic-solid phase transition was also studied (4). It was found that in frozen solution, PD-Tempone undergoes rapid isotropic rotational reorientation with values of τ_R about the same on either side of the phase transition. This suggests that the probe is located in a cavity, and its structure is very similar, whether above or below the phase transition. However, as the pressure is increased, τ_R actually becomes shorter! This is taken to imply that increasing the pressure freezes out residual movement of solvent molecules into the cavity, and the motion of the spin probe becomes less hindered in the cavity. Also, we may note that a large relaxation anomaly, of the type discussed above, is observed in the solid phase, and it is suppressed as the pressure is increased. This is consistent with our model of the probe in a cavity in the solid and with the SRLS mechanism.

The isotropic-nematic phase transition of nematic solvent MBBA with PD-Tempone probe has been studied with careful temperature control (7). The ESR linewidths are fitted to the usual expression: $\delta = A + BM + CM^2$, where M is the ^{14}N nuclear-spin z-component quantum number. The parameters B and C are observed to behave anomalously as the phase transition at temperature T_c is approached from either side. In fact they appear to diverge. The non-anomalous, or background contributions to B and C (i.e. B_0 and C_0) may be analyzed in the usual manner to show that τ_R is again nearly the same on either side of the phase transition. The anomalous contributions to B and C (i.e. ΔB and ΔC) are found to be fit by the form:

Isotropic Phase:

$$\begin{aligned} \Delta B &= (0.034)(T-T^*)^{-0.6 \pm 0.2} & 18a \\ \Delta C &= (0.041)(T-T^*)^{-0.5 \pm 0.1} & 18b \end{aligned}$$

Nematic Phase

$$\begin{aligned} \Delta B &= (0.051)(T^+-T)^{-0.5 \pm 0.1} & 19a \\ \Delta C &= (0.077)(T^+-T)^{-0.5 \pm 0.1} & 19b \end{aligned}$$

These results have been successfully analyzed in terms of Landau-deGennes mean-field theory (21,22) for the weak first order

transition, as applied to ESR relaxation (1). In this theory, the free energy of orientation (F') of the liquid crystal is expanded in a power series in the nematic order parameter Q ; i.e.

$F' = \frac{1}{2} \bar{A} Q^2 - \frac{1}{3} \bar{B} Q^3 + \frac{1}{4} \bar{C} Q^4$. One then minimizes the free energy to obtain the values of Q in the nematic phase (Q_N) as well as the location of T_c . One then allows for small fluctuations of Q about the mean values of $Q=0$ in the isotropic phase and Q_N in the nematic phase by including in the free energy a term:

$\int L(\nabla Q)^2 d^3r$, where L is a force constant for distortions and $\nabla Q(\vec{r})$ is the gradient of Q . One then studies small fluctuations in F' (or $\Delta F'$) by Fourier analyzing $Q(\vec{r})$, and keeping only lowest order terms in Fourier components Q_q in the isotropic phase (and ΔQ_q the FT of $\Delta Q \equiv Q - Q_N$ in the nematic phase). Thus we have:

$$\Delta F' = \frac{1}{2} V \sum_q (\bar{A} + L q^2) |Q_q|^2 \quad \text{isotropic phase} \quad 20a$$

$$\Delta F' = \frac{1}{2} V \sum_q (\bar{A} + L_N q^2) |\Delta Q_q|^2 \quad \text{nematic phase} \quad 20b$$

where $\bar{A} = \bar{A} - \frac{2BQ}{3} + 3CQ_N^2$ and V is the sample volume. It is then assumed that $\bar{A} = \frac{1}{3}(T - T^*)$. One then determines that the relaxation times, τ_q for the q^{th} mode are given by:

$$\tau_q^{-1} = L(\xi^{-2} + q^2)/\nu \quad \text{isotropic} \quad 21a$$

$$\tau_q^{-1} = L_N(\bar{\xi}^{-2} + q^2)/\nu_N \quad \text{nematic} \quad 21b$$

where $\xi^2 \equiv L/a(T - T^*)$ and $\bar{\xi}^2 \equiv L_N/A = L_N/3a(T^+ - T)$ (with $T^+ \equiv T_c + \frac{1}{3}(T_c - T^*)$ and the approximation applies only near T_c). The quantities ξ and $\bar{\xi}$ are the coherence lengths of the order fluctuations in the isotropic and nematic phases respectively, and ν and ν_N are the respective viscosities. One then obtains for the ESR linewidth contributions for the weakly ordered spin probe:

$$AB = 5B_0 \tau_R^{-1} K_{0,0}(0) \quad 22$$

$$AC = C_0 \tau_R^{-1} [8K_{0,0}(0) - 3K_{0,1}(u_N)] \quad 23$$

where

$$K_{0,M}(\omega) = \frac{kTv\xi(S(D))^2}{\sqrt{2} k_B L^2(S(S))^2} (1 + [1 + (\omega/\omega_\xi)^2]^{1/2})^{-1/2} \quad 24$$

and $\omega_\xi \equiv L/\nu\xi^2$. Below T_c , one replaces ξ everywhere by $\bar{\xi}$ in eq. 24. Eq. 24 predicts $K_{0,M}(0) = \xi$ or $\bar{\xi}$, and we have $\xi = (T - T^*)^{-1/2}$ and $\bar{\xi} = (T^+ - T)^{-1/2}$ from their derivations. This is in exact agreement with our observations of eqs. 18 and 19. We also find experimentally that $T_c - T^* = 1^\circ$ and $T^+ - T_c = 0.5^\circ$ also in agreement with prediction. The magnitude of AB (and AC) in the isotropic phase

can be predicted from eqs. 22-24 and values of the experimental parameters measured by Stinson and Litster (23) in the isotropic phase. The agreement with our experimental results is again very good. (Stinson and Litster measured α , L and ν by light scattering).

Thus the ESR observations about the isotropic-nematic phase transition display a symmetry for spin-relaxation due to critical fluctuations, and the characteristic features are predicted rather well by simple mean-field theory combined with a motional-narrowing relaxation theory. It is significant to note that light scattering and NMR studies only successfully deal with order fluctuations above T_c and could not demonstrate this symmetry about T_c . The two above examples should clearly demonstrate the utility of ESR studies of phase transitions in the anisotropic media.

Spin Exchange and Chemically-Induced Spin Polarization in Two Dimensions

Translational diffusion may be monitored by spin probes as a function of the concentration of the probes. This has been extensively studied in isotropic liquids (24,25) and some work has been performed in liquid crystals (13,26). In these works, one monitors the translational diffusion by the concentration-dependent line broadening due to the Heisenberg spin-exchange of colliding spin probes in solution. It is interesting to speculate on the nature of such phenomena if radicals are confined to translate on a two dimensional surface. From the point of view of radical-radical interactions on surfaces, one may ask the related questions about spin-dependent reaction kinetics on surfaces and the associated magnetic resonance phenomena of CIDNP and CIDEP which have been amply studied in three dimensions (27,28). Deutch (29) has pointed out that such phenomena should be qualitatively different in two vs. three dimensions, mainly because the re-encounter probability of two radicals which have initially separated is always unity for two dimensions, but less than unity in three dimensions. A recent study (30) focuses on the two dimensional aspects from the point of view of the Pedersen-Freed theory (28). In this theory, the stochastic Liouville equation (SLE), which simultaneously includes the spin and diffusive dynamics, is solved by finite difference methods subject to an initial condition (usually that the radicals are initially in contact or slightly separated). The results then show the accumulated spin-dependent effects after the radical pair have had the opportunity to re-encounter many times (and possibly react). This is referred to as the "complete collision". One then obtains (1) the probability of spin exchange per collision (ΔP), (2) the fractional probability of reaction per collision if there are no spin-dependent selection rules (A), (3) the probability per collision of conversion of non-reactive triplets to singlets which immediately react (\mathcal{F}^*), and (4) the polarization of radical A

from the radical-pair mechanism per collision (P_a). However, in two dimensions, because the re-encounter probability is always unity, the "collision" is never complete as $t \rightarrow \infty$, unless other processes act to interfere (e.g. radical scavenging, radical T_1 , or radicals leaving the surface). Thus a finite time scale is brought on by these other processes. It has been pointed out that a finite time scale can be replaced by a finite outer radial collecting (or absorbing) wall boundary at r_N in these problems (28). It is convenient to solve for finite r_N and then transform to the equivalent time representation. We summarize approximate expressions obtained from the numerical solutions.

The re-encounter probability (t_f) for finite r_N is given by:

$$t_f = 1 - \ln\left(\frac{r_I}{d}\right) / \ln\left(\frac{r_N}{d}\right) \quad 25$$

where r_I is the initial radical separation and d the encounter distance. (The next set of results are quoted for $r_I=d$). The quantity Λ obeys:

$$\Lambda = k\tau_1 \ln\left(\frac{r_N}{d}\right) / \left[1 + k\tau_1 \ln\left(\frac{r_N}{d}\right)\right] \quad 26$$

where k is the first order rate constant for irreversible disappearance of singlet radical pairs when in contact with a "sphere of influence" from d to Δr_k , and $\tau_1 = d\Delta r_k/D$ is a characteristic lifetime of the encounter pair with D the relative diffusion coefficient. (One recovers the 3D result by replacing $\ln(\frac{r_N}{d})$ in eq.26 by unity). Thus as $r_N \rightarrow \infty$, $\Lambda \rightarrow 1$ as it should, since there will be many re-encounters to guarantee reaction for finite k .

Then \mathcal{F}^* approximately obeys:

$$\mathcal{F}^* = \frac{\frac{1}{40} \left(\frac{r_N}{d}\right)^4 \left(\frac{Qd^2}{D}\right)^2}{1 + \frac{1}{40} \left(\frac{r_N}{d}\right)^4 \frac{Qd^2}{D} 1.8 \left[\ln\left(\frac{r_N}{d}\right)\right]^{-1} \left[1 + \ln\left(\frac{r_N}{d}\right) \left(\frac{Qd}{D}\right)^{0.2}\right]} \quad 27$$

where $2Q$ is the difference in Larmor frequencies of the two interacting radicals. As r_N gets large (and/or for large $\frac{Qd^2}{D}$) eq.27 goes as

$$\mathcal{F}^* = \left(\frac{Qd^2}{D}\right)^{0.2} \ln\left(\frac{r_N}{d}\right) / \left[1 + \ln\left(\frac{r_N}{d}\right) \left(\frac{Qd}{D}\right)^{0.2}\right] \quad 28$$

which increases with $\ln r_N$ until $\mathcal{F}^* = 1$, its maximum value. (Eqs. 27 and 28 neglect the relatively small effects of the exchange interactions (30)). For typical values of the parameters eq. 28 is usually appropriate. Note that CIDNP polarizations are typically closely related to the product, \mathcal{F}^* (28). Eq.27 is different in its Q dependence from the Q^2 power-law typically

found in 3D. This Q dependence suggests that in 2D the mechanism does not require the time period between successive encounters for the spin-dependent evolution due to having $Q \neq 0$. Instead the relevant spin-dependent evolution occurs while the radicals are in contact during each encounter.

For CIDEP, a contact exchange model yields:

$$P_a = \frac{\frac{1}{2} \left(\frac{r_N}{d}\right)^2 \left(\frac{Qd^2}{D}\right)^1}{1 + b \left(\frac{r_N}{d}\right)^2 \left(\frac{Qd^2}{D}\right)^\epsilon} \left(\frac{2J_0\tau_1}{1 + \frac{13}{4} \ln\left(\frac{r_N}{d}\right) (2J_0\tau_1)^2} \right) \quad 29$$

with $\epsilon = 1.2$ and $b = 3/2$ for $2J_0\tau_1 \ll 1$ and $\epsilon = 0.85$ and $b = 1/5$ for $2J_0\tau_1 > 1$. Here J is the magnitude of the exchange interaction of infinitesimal range Δr_j and $\tau_1 = d\Delta r_j/2D$. Again, the Q-dependence indicates the importance of the spin dependent evolution during each encounter. For finite range of exchange interaction (i.e. $J(r) = J_0 e^{-\lambda(r-d)}$) one has $\tau_1(\lambda) \frac{d}{D} \left(1 + \frac{1}{2d\lambda}\right)$ with a similar, but not identical, form to eq.29. In particular, for $2J_0\tau_1(\lambda) > 1$ (and/or large r_N),

$$P_a = \frac{\frac{3}{8} \left(\frac{r_N}{10d}\right)^{3.3} \left(\frac{Qd^2}{D}\right)^1 (2J_0\tau_1(\lambda))^{-0.02}}{1 + \frac{1}{8} \left[\ln\left(\frac{r_N}{d}\right)\right]^{2.75} \left(\frac{r_N}{10d}\right)^{3.3} \left(\frac{Qd^2}{D}\right)^{0.85} \left(\frac{d^2}{\tau_1(\lambda)D}\right)^{\frac{1}{2}}} \quad 30$$

For Heisenberg-spin exchange, a contact exchange model yields:

$$\Delta P(d_t) = \left(\ln\left(\frac{r_N}{d}\right)\right)^2 (2J_0\tau_1)^2 / \left[1 + \left(\ln\left(\frac{r_N}{d}\right)\right)^2 4(J_0^2 + Q^2)\tau_1^2\right]$$

31

This is like the 3D result, which is recovered by letting $\ln\left(\frac{r_N}{d}\right) \rightarrow 1$. For finite exchange range, one has the possibility of d values of $\Delta P(d_t)$ greater than unity as in 3D (28):

$$\Delta P(d_t) = 1 + \left[\ln(1 + J_0 d^2/D)\right] 3 / \left[\ln\left(\frac{r_N}{d}\right)\right]^2 \lambda d$$

$$\text{for } J_0^2 \tau_1^2 \left(\lambda \ln \frac{r_N}{d}\right)^2 \gtrsim .001$$

32

which becomes the 3D result if $\frac{1}{3} \left[\ln\left(\frac{r_N}{d}\right)\right]^2 \rightarrow 1$.

Lastly, we can replace the dependence upon r_N in the above expressions with that on s , the Laplace transform of time by using:

$$s^{-1} = \left[\ln\left(\frac{r_N}{d}\right) - \frac{1}{2} \right] (r_N)^2 / 4D. \quad 33$$

Then, these results are rigorously for radical pairs which are scavenged or "collected" by a (pseudo) first-order rate process with rate constant s . More approximately then, they correspond to the values at time $t \sim s^{-1}$. The generally weak dependence of these equations on r_N (e.g. the validity of eq. 28, etc.) hence on s , suggests that the approximate point of view is entirely satisfactory. Then we can approximately replace s by $k_r + T_1^{-1}$ in eq.33 (where k_r would take care of radical scavenging, rate of leaving the surface, etc.) for use in the previous expressions. When desired, however, the SLE equation may be solved, explicitly including the disruptive effects.

In some applications, in particular that of Heisenberg spin exchange, the radicals are initially randomly distributed. Thus, one must first determine the steady-state rate for new bimolecular collisions of radical-pairs, ($2k_2$, cf. 28). While in 3D this is a well-defined quantity, it is not quite true for 2D, since the rate always has some time-dependence (31). Thus, in this case the actual rate (for unit concentrations) of spin exchange at time t (or times $t \rightarrow \infty$) would be obtained from the convolution $\int_0^t \Delta P(t-\tau) k(\tau) d\tau$ or alternatively from its Laplace transform: $\Delta P(s)k(s)$ using eq.33 and eq.31 or 32 for ΔP . Similar comments apply for CIDEP ($P_g(s)$) and CIDNP ($=A(s)F^*(s)$) due to random initial encounters.

In addition, we note that for magnetic resonance in 2D, spin relaxation by modulation of intermolecular dipolar interactions is an important concentration-dependent mechanism (32). It is expected to be sensitive to the structure (i.e. the pair correlation function) appropriate for the fluid or surface (33), just as are the other mechanisms we have discussed (28).

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