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ESR Studies of the Slow Tumbling of
Vanadyl Spin Probes In Nematic Liquid Crystals


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# Abstract

ESR line shapes that are appropriate for slowly tumbling vanadyl spin probes in viscous nematic liquid crystals have been calculated by the stochastic Liouville method. Because of the symmetry possessed by vanadyl, the analysis and interpretation of these line shapes is simplified considerably. Spectral line shapes agreed well with experimental spectra of VOAcAc in the nematic liquid crystal Phase V and BEPC. Deviations from Brownian rotational diffusion were noted. A slowly fluctuating torque analysis yielded good agreement with the experimental spectra.

## Introduction

The application of paramagnetic spin labels in a variety of
experiments has resulted in obtaining a wide range of structural
and dynamical information.[1] In particular, the class of complexes
containing the vanadyl ion $VO^{2+}$ is being used increasingly as a
spin probe.[2] In a recent paper, we have applied the stochastic
Liouville method to calculate ESR line shapes in the slow tumbling
region for vanadyl complexes in an isotropic media.[3] This analysis
allows one to extract quantitative information for the rotational
correlation times $(\tau)$ in the region $10^{-10}$-$10^{-7}$ sec/rad. These slow
tumbling ESR spectra occur when the vanadyl ion is rigidly attached
to a macromolecule (radius 5-50 $\overset{o}{A}$) or when a vanadyl complex is
dissolved in a viscous medium.

Currently, there is much interest in the dynamical properties
of liquid crystals. The purpose of this paper is to study spin
probes in viscous nematic liquid crystals. Because many $VO^{2+}$ com-
plexes have very nearly axially symmetric magnetic parameters which
is the same degree of symmetry possessed by nematic liquid crystals,
the subsequent theoretical analysis is simplified and the results
are easier to interpret than spin probes with less symmetry. Previous
workers recognized this feature of $VO^{2+}$ complexes but have encountered
difficulty in the quantitative interpretation of the ESR line
shapes because of the slow tumbling aspects inherent in viscous
nematic liquid crystals.[4] Our approach is to analyse the ESR
line shapes by the stochastic Liouville method as developed by

PBF for slow tumbling in an anisotropic media.[5]

Vanadyl acetylacetonate (VOAcAc) was chosen as our vanadyl spin probe because it has excellent ESR spectroscopic properties and because it has very nearly axially symmetric magnetic parameters. In addition, our previous detailed work with VOAcAc in a viscous isotropic medium minimized experimental problems. The nematic mixture Phase V from EM Laboratories was the first nematogen studied in this work because it is nematic at low temperatures and has a wide nematic temperature range. A second nematic liquid crystal, butyl-p-(p-ethoxyphenoxycarbonyl)phenyl carbonate (BEPC), which is a single component liquid crystal, was studied, and the results obtained were compared to those for the Phase V mixture.

## Experimental

Degassed samples of nematic liquid crystals doped with vanadyl acetylacetonate (VOAcAc) were prepared by standard vacuum line techniques. VOAcAc was purchased from Alfa Products and recrystallized from acetone. The nematic liquid crystal butyl-p-(p-ethoxyphenoxycarbonyl)phenyl carbonate (BEPC) was obtained from Eastman Kodak and recrystallized from methanol. The nematic mixture Phase V was purchased from EM Laboratories and used without further purification. VOAcAc concentrations ($\sim 5 \times 10^{-4}$ M) were low enough so that contributions to the lineshapes from intermolecular interactions were negligible.

ESR spectra were taken at X band with a Varian (V-4502) spectrometer system. 100 k Hz field modulation was used with low enough modulation amplitude that no distortion in lineshapes was observed. Microwave powers were low enough to preclude saturation effects. Temperature was controlled by a Varian E-257 variable temperature unit and measured with a copper-constantine thermocouple. The temperature gradient over the active region of the cavity was 1-2$^\circ$C. Spectral calibrations were obtained using a Brucker B-NM-12 gaussmeter or from the hyperfine splitting of VOAcAc in toluene at 2$^\circ$C.

## Theory

PBF have developed a method for calculating slow tumbling
ESR line shapes in an anisotropic solvent such as a nematic
liquid crystal.[5] This method is based upon the stochastic
Liouville method[6] and is a generalization of the approach of
Nordio and co-workers[7] for the motionally narrowed ESR line
widths of a Brownian particle in liquid crystal. Here, we apply
this general theory to vanadyl spin probes in nematic liquid
crystals. Previous studies have given the appropriate spin
Hamiltonian for VOAcAc.[3,8] In particular, the use of axially
symmetric magnetic tensor parameters has been established. The
motionally narrowed line widths ($\tau < 8 \times 10^{-11}$ sec/rad) calculated
with axially symmetric magnetic parameters differ by less than
0.5% from those calculated with completely asymmetric tensor
values.[8] Also, our slow tumbling study in an isotropic solvent
showed that the use of axially symmetric magnetic parameters gave
excellent agreement with experimental line shapes for slow
tumbling $\tau$ - $8 \times 10^{-11}$-$1 \times 10^{-9}$ sec/rad. Only with the appearance
of features in the ESR line shapes that are characteristic of a
rigid limit line shape does the use of completely asymmetric
parameters improve the fit to experimental line shapes.[3] Because
VOAcAc aligns itself with the VO bond perpendicular to the
director of the nematic liquid crystal, the rotation about the
VO bond should be relatively fast and thus average the x and y axis
magnetic asymmetry.

The rotational diffusion for a molecule undergoing Brownian
rotation in the presence of a cylindrically symmetric restoring

torque $\bar{T}$ is described by[5]

$$\frac{\partial P}{\partial t}(\Omega,t) = R\nabla^2 P(\Omega,t) - \frac{R}{kT\sin\beta} \frac{\partial}{\partial\beta}[\sin\beta(\bar{T})P(\Omega,t)] \qquad (1)$$

where R is rotational diffusion coefficient, $\nabla^2$ is the rotational diffusion operator, and $\beta$ is the angle between the molecular Z-axis (VO bond) and the director. The director is taken to be parallel to the large dc magnetic field. For the axially symmetric VOAcAc, the simple Maier-Saupe type potential[9]

$$U(\beta) = \gamma_2 \cos^2\beta \qquad (2)$$

is suitable and yields

$$\bar{T} = - \frac{\partial U}{\partial\beta} = 2\gamma_2 \sin\beta\cos\beta \qquad (3)$$

Note that for $U(\beta)=0$, Eq.(1) describes the familiar isotropic Brownian rotational diffusion. VOAcAc, an oblate symmetric top molecule, has $\beta_{eq}=\pi/2$ so that $\gamma_2$ is positive.

From Eqs. (1)-(3), the equations for a nematic liquid crystalline solvent may be obtained as in PBF[5] by adding to the left hand side of each equation for the isotropic liquid [Eqs. (A.1)-(A.3) in reference 3].

$$-i \times \frac{\tau^{-1}\lambda^2}{45} c_{0,n}^{L}(j) + i \tau^{-1}\lambda(\frac{1}{3} - \frac{\lambda}{63})\sum_{L'} N(L,L')(-)^n \begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -n & 0 & n \end{pmatrix}$$

$$\times c_{0,n}^{L'}(j) + \frac{4}{105} \tau^{-1}\lambda^2 \sum_{L'} N(L,L')(-)^n \begin{pmatrix} L & 4 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 4 & L' \\ -n & 0 & n \end{pmatrix} c_{0,n}^{L'}(j) \qquad (4)$$

and by changing the right hand side of Eq. (A.1) of reference 3 to be

$$[(2L+1)^{\frac{1}{2}}/I_0] \int_0^{\pi} \mathcal{D}_{0,0}^{L}(0,\beta,0)\exp[\frac{1}{2} \lambda \cos^2\beta]\sin\beta d\beta \qquad (5)$$

where

$$I_0 = \int_0^{\pi} \exp[\frac{1}{2} \lambda \cos^2\beta]\sin\beta d\beta \qquad (6)$$

and $\lambda = -\lambda_2/kT$. The absorption line shape $z''$ is now given by

$$z'' = \text{Im}I_0^{-1} \sum_{j=1}^{8} \sum_{L \text{ even}} (2L+1)^{\frac{1}{2}}[\int_0^{\pi} \mathcal{D}_{0,0}^{L}(\beta)\exp[\frac{1}{2} \lambda \cos^2\beta]\sin\beta d\beta]C_{0,0}^{L}(j)$$

where j refers to the eight allowed transitions.

For anisotropic viscosity,

$$i \ \tau_L^{-1}C_{0,n}^{L}(j) = i[\tau_L^{-1}\frac{L(L+1)}{6} + (\tau_{11}^{-1}-\tau_{\perp}^{-1})\frac{n^2}{6}]C_{0,n}^{L}(j) \qquad (7)$$

in Eqs. (A.1)-(A.3) of reference 3 and $\tau^{-1} = \tau_{\perp}^{-1}$ in Eq. (4) above. $\tau_{11}$ is the rotational correlation time about an axis parallel to the director and $\tau_{\perp}$ refers to an axis perpendicular to the director.

The equilibrium distribution $P_0(\Omega)$ is given by

$$P_0(\Omega) = \exp(\lambda \cos^2\beta)/4\pi^2 \int_0^{\pi} \exp(\lambda \cos^2\beta)\sin\beta d\beta \qquad (8)$$

The order parameter S is then

$$S = \langle P_2(\beta) \rangle = \int P_2(\beta)P_0(\Omega) \ d\Omega \qquad (9)$$

where

$$P_2(\beta) = \frac{1}{2}(3 \cos^2\beta - 1) \qquad (10)$$

Because VOAcAc is a much smaller molecule than the liquid crystal solvent molecules, the above diffusion equation for a Brownian particle may be expected to be modified for inertial effects.[10] One worthwhile modification to these equations involved the local solvent structure inducing a slowly flucuating torque on our spin probe.[11-13]

The resulting equations explicitly contain inertial effects to lowest order and correspond to a model in which this torque flucuates between two values with a lifetime of $\tau_m$. These added equations are of the form[12]

$$[(\omega-\omega_v)- i\, m\, \tau_m^{-1}]c^L_{0,n,p,m} + [L(L+1)\frac{kT}{I}]^{\frac{1}{2}} [\sqrt{p+1}\; c^L_{0,n,p+1,m} +$$

$$\sqrt{p}\times c^L_{0,n,p-1,m}] + [\frac{kT}{I}\frac{6\tau}{\tau_m}]^{\frac{1}{2}} [\sqrt{p}\sqrt{m+1}\; c^L_{0,n,p-1,m+1} +$$

$$\sqrt{p+1}\sqrt{m}\; c^L_{0,n,p+1,m-1}] = \delta_{p,0}\,\delta_{m,0} \tag{11}$$

where m=0, 1 and p=0, 1. I is the moment of inertia of the spin probe. Also

$$\tau_m = \tau_{L,n}(\sqrt{\xi_{L,n}} -1) \tag{12}$$

## Results and Discussion

In order to simulate slow tumbling spectra, one must know the components of the g and A tensors which occur in the spin Hamiltonian. These values may vary slightly with solvent. The $A_{||}$ and $g_{||}$ components are readily determined from a rigid limit spectrum. This spectrum was obtained by slowly cooling the liquid crystal sample through the nematic range with the dc magnetic field turned off and then taking the spectrum at $77^\circ K$. The $A_\perp$ and $g_\perp$ values may then be obtained from the isotropic $a_0$ and $g_0$ values gotten from the liquid crystal samples above the nematic-isotropic clearing point transition temperature. Our values for the magnetic parameters were essentially the same as those obtained in toluene.[3,8] For Phase V, $A_{||}$ = -184 G, $A_\perp$ = -68 G, $g_{||}$ = 1.943, $g_\perp$ = 1.982. For BEPC, $A_{||}$ = -185 G, $A_\perp$ = -68G, $g_{||}$ = 1.943, and $g_\perp$ = 1.982.

Experimental ESR spectra were obtained for the nematic range $72^\circ$ to $-29^\circ C$ for Phase V and $82^\circ$ to $37^\circ C$ for BEPC. All spectra contained very asymmetric line shapes indicative of the slow tumbling region. In fact, the isotropic spectra taken just above the nematic-isotropic clearing point were obviously in the slow tumbling region. Although there was considerable supercooling below the nematic-solid freezing point, no discontinuities were observed in the ESR spectra or in their subsequent analysis.

Simulated spectra corresponding to a Brownian particle in a liquid crystal solvent were calculated from Eq.(7) and Eqs. (A.1)-(A.3) of reference 3 modified by Eq.(B.3) of reference 3 for non-secular effects and by Eqs.(4) and (5) for an anisotropic solvent.

Spectra were simulated by varying essentially only two parameters: $\tau$, the rotational correlation time, and $\lambda$, which is proportional to the orienting potential. In general, the effect of increasing /$\lambda$/($\lambda$ is negative for VOAcAc)is to decrease the separation between hyperfine lines and to decrease the line widths. An increase in $\tau$ will generally broaden lines,decrease line separation (in the slow tumbling region) and increase asymmetry in the lines. Although the simulated spectra were in reasonable agreement, chere were significant and consistent descrepancies between calculated and experimental spectra. The calculated high-field "hyperfine lines" are more narrow than observed experimentally while the low-field lines were too broad. When Eq.(8) for anisotropic viscosity was incorporated into the above equations, the simulated spectra were in very good agreement with the experimental spectra. The spectra were in this case fit by varying three parameters $\tau_{||}$ , $\tau_{\perp}$, and $\lambda$.

It was noted that as the temperature was lowered the ratio of $\tau_{\perp}/\tau_{||}$ increased. Also, the best fits indicated that $\tau_{||}$ was becoming shorter with decreasing temperature. Because these results seemed implausible, the flucuating torque approach was tried. This analysis, although approximate, attempts to account for the small size of spin probe relative to the liquid crystal molecular size. Here we now incorporate Eqs.(12) and (13) into the above Brownian rotation equations. Very good fits were obtained by letting $\xi_{L,0}=2$ and $\xi_{L,n}=10(n\neq0)$ and varying two parameters, $\tau$ and $\lambda$. See Table I.

TABLE Ia

Ordering Parameter (S) and Rotational Correlation Time ($\tau$)
as a Function of Temperature for Phase V

| Temp($^{\circ}$C) | $S^{a,b}$ | $\tau^{a}$ ($\times 10^{-9}$ sec/rad) |
|---|---|---|
| 69 | -0.11 | .11 |
| 55 | -.14 | .20 |
| 41 | -.18 | .38 |
| 34 | -.22 | .74 |
| 20 | -.26 | 1.4 |
| 6 | -.29 | 2.3 |
| -9 | -.33 | 4.7 |
| -26 | -.36 | 9.2 |

a) Obtained from simulated spectra using flucuating torque
analysis with $\xi_{L,0}=2$ and $\xi_{L,n}=10$ ($n\neq0$).

b) Calculated numerically from Eq. (10).

## Table Ib

Ordering Parameter (S) and Rotational Correlation
Time ($\tau$) as a Function of Temperature for BEPC

| Temp (°C) | $S^{a,b}$ | $\tau^a$ ($\times 10^{-9}$ sec/rad) |
|-----------|-----------|-------------------------------------|
| 81 | -.16 | 0.18 |
| 75 | -.18 | 0.25 |
| 65 | -.20 | 0.34 |
| 56 | -.22 | 0.57 |
| 46 | -.25 | 0.91 |
| 38 | -.28 | 1.2 |

a.  BEPC liquid crystal. Obtained from simulated spectra using fluctuating torque analysis with $\xi_{L,0}=2$ and $\xi_{L,n}=10$ ($n \neq 0$).

b.  Calculated numerically from Eq. (10).

## Conclusion

The stochastic Liouville method as developed by PBF has been applied to the calculation of slowly tumbling ESR line shapes for vanadyl complexes in nematic liquid crystals. Quantitative information about the ordering and rotational diffusion was obtained for VOAcAc in Phase V for the nematic temperature range 69°C ($S = -0.11$, $\tau = 1.1 \times 10^{-10} \frac{sec}{rad}$) to -26°C ($S = -.36$, $\tau = 9.2 \times 10^{-9} \frac{sec}{rad}$). For BEPC, the nematic temperature range 81°C to 38°C corresponded to values ($S = -0.16$, $\tau = 1.8 \times 10^{-10} \frac{sec}{rad}$) and ($S = -0.28$, $\tau = 1.2 \times 10^{-9} \frac{sec}{rad}$) respectively. Deviations from Brownian rotational diffusion was noticed and unquestionably arose from the relatively small size of the vanadyl probe. Application of a flucuating torque model approximated this effect and improved the fits to experimental spectra.

The success of this approach encourages us to investigate larger $VO^{2+}$ probes (which would more nearly minic the liquid crystal itself) as well as to pursue the study of the highly viscous smectic liquid crystals.

Also, the quantitative analysis of the spin probe ordering (and rotational motion) would allow one to monitor the ordering of liquid crystal subjected to both static and alternating electric fields.

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