

ESR LINEWIDTHS IN SOLUTION: ANOMALOUS BEHAVIOUR IN HYDROGEN-BONDED LIQUIDS, ANISOTROPIC ROTATIONAL DIFFUSION AND NONDIFFUSIONAL MOTIONS†

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ABSTRACT

ESR linewidths have been used to study the dynamics of molecules in liquids. The correlation times characteristic of both the anisotropic g -values modulated by molecular tumbling (τ_θ) and spin-rotational interactions modulated by collision-induced changes in molecular angular momentum (τ_{SR}) are considered. If isotropic rotational diffusion is assumed, a minimum linewidth as a function of temperature is predicted. Furthermore, τ_θ can be set proportional to $r^3\kappa$, where κ depends upon intermolecular torques and forces and r is the translational diffusion radius, and in many cases κ is independent of temperature for a given solvent; similarly, in rotational diffusion theory, $\tau_{SR} = (I/6kT)\tau_\theta^{-1}$ where I is the moment of inertia. The predicted and measured minima in linewidths often differ from each other, and the discrepancy can be attributed either to anisotropic diffusion or, equally well, to the inadequacy of the expression above for τ_{SR} .

Studies have been carried out for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in n -butanol, and in CHCl_3 . If anisotropic rotational diffusion is assumed, the discrepancy in the linewidth minimum can be explained if $(D_{\parallel}/D_{\perp}) \approx 2.2$ in both butanol and CHCl_3 . To correct the relationship between τ_θ and τ_{SR} , one can show on the basis of Ivanov's jump model that $\tau_\theta\tau_{SR} = (I/6kT)\varepsilon_0^2(1 - \lambda_2)^{-1}$ where ε_0 is a mean rotational jump and λ_2 is a function of ε_0 and the spread in jump angles. The value (0.81) of $\varepsilon_0^2(1 - \lambda_2)^{-1}$, required to correct the linewidth minimum, indicates small jumps with a large spread in jump angles.

If $(D_{\parallel}/D_{\perp})$ and $\varepsilon_0^2(1 - \lambda_2)^{-1}$ are taken to be temperature independent, κ appears to be temperature dependent in butanol but not in CHCl_3 ; however, if $\varepsilon_0^2(1 - \lambda_2)^{-1}$ is temperature dependent in butanol, κ could be temperature independent.

INTRODUCTION

The study of magnetic resonance linewidths and spin-relaxation times in liquids yields correlation times for molecular reorientation. These correlation times describe the time dependence of single particle autocorrelation functions of a second rank rotational tensor. Debye¹ described molecular

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reorientation times in terms of the Stokes–Einstein² hydrodynamic theory, and Bloembergen, Purcell and Pound³ applied the theory to magnetic resonance experiments. These hydrodynamic results are strictly valid only for large, spherical particles moving through a homogeneous continuous medium. A number of relations have been suggested and in particular we can write the correlation time τ_θ as⁴:

$$\tau_\theta = \frac{4}{3} \frac{\pi r^3 \eta}{kT} \kappa \quad (1)$$

where η is the coefficient of shear viscosity, T is the absolute temperature, k is the Boltzmann constant, r is the translational diffusion radius of the spherical molecule, and κ is a parameter which accounts for the deviations of the Debye results from the experimental values. The time τ_θ can be obtained from magnetic resonance experiments, η/T can be measured directly, and the radius r can be determined from translational diffusion experiments. The parameter κ for a given solute molecule appears to be independent of η/T for a number of different solvents but can differ from solvent to solvent. This parameter has been recently interpreted in terms of equilibrium ensemble averages as⁵:

$$\kappa = \frac{3}{4} (1/r^2) \langle \mathcal{T}^2 \rangle / \langle \mathcal{F}^2 \rangle \quad (2)$$

where \mathcal{T} is the intermolecular torque, \mathcal{F} is the intermolecular force, r is the hydrodynamic radius of the solute molecule.

In this article we discuss a case where the parameter κ appears to be strongly dependent upon η/T , i.e. $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4^6$ in the strongly hydrogen-bonded solvent, *n*-butanol. We also study this radical in CHCl_3 and find that κ for this system appears to be independent of η/T . We then interpret the data, along with that for other paramagnetic species in alcohols, in several different ways, all of which reflect the dynamical behaviour of the liquid. In particular, we show that κ may actually be constant even in the hydrogen-bonded solvents if the data is analyzed properly.

GENERAL THEORY

The esr linewidth of $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in *n*-butanol was studied as a function of temperature. The free radical has no resolvable hyperfine structure and the spectrum, except at very low temperatures where the simple motional narrowing theory breaks down, consists of a single nearly Lorentzian line. The linewidth, ΔH , is the peak to peak width of the first derivative of the absorption spectrum (see *Table 1*) (see the Appendix for viscosity measurements on butanol).

In the motionally narrowed limit (Redfield limit), the linewidth arises primarily from reorientational averaging of the anisotropic g -tensor and from angular momentum averaging of spin–rotational interactions through collision-induced changes in the angular momentum. If the rotational motion can be described in terms of a spherically symmetric diffusion model⁷, and if the angular momentum correlation time is short compared to that for

ESR LINEWIDTHS IN HYDROGEN-BONDED SOLVENTS

 Table 1. Data for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in butanol. $g_{zz} = 1.994$, $g_{xx} = 2.141$, $g_{yy} = 2.040$.

| Temperature (K) | η (cP) | $\frac{\eta}{T}$ (cP K ⁻¹) | ΔH (G) (experimental) | τ_{20} (s) (from experiment and Figure 1) ($\times 10^{11}$) |
|--------------------|-------------|----------------------------------------|----------------------------------|------------------------------------------------------------------------------|
| 389.3 | 0.40 | 0.00103 | 13.02 \pm 0.101 | 0.985 |
| 381.4 | 0.45 | 0.00118 | 11.70 \pm 0.07 | 1.125 |
| 376.8 | 0.482 | 0.00128 | 11.29 \pm 0.07 | 1.17 |
| 370.6 | 0.55 | 0.00148 | 10.52 \pm 0.14 | 1.26 |
| 363.9 | 0.63 | 0.00173 | 9.3 | 1.51 |
| 363.5 | 0.62 | 0.00171 | 9.503 \pm 0.064 | 1.46 |
| 358.4 | 0.68 | 0.00190 | 8.792 \pm 0.194 | 1.64 |
| 354 | 0.73 | 0.00206 | 8.469 \pm 0.100 | 1.73 |
| 348.5 | 0.82 | 0.00235 | 8.017 \pm 0.100 | 1.88 |
| 343.6 | 0.92 | 0.00268 | 7.598 \pm 0.049 | 2.09 |
| 338.6 | 1.00 | 0.00295 | 7.256 \pm 0.066 | 2.28 |
| 332.8 | 1.12 | 0.00337 | 6.920 \pm 0.036 | 2.52 |
| 328 | 1.25 | 0.00381 | 6.654 \pm 0.017 | 2.85 |
| 320.8 | 1.50 | 0.00486 | 6.475 \pm 0.100 | 3.12 |
| 315.6 | 1.66 | 0.00526 | 6.329 \pm 0.049 | 3.45 |
| 311.2 | 1.82 | 0.00585 | 6.248 \pm 0.043 | 4.2 |
| 305.5 | 2.10 | 0.00687 | 6.356 \pm 0.029 | 5 |
| 296.7 | 2.70 | 0.00910 | 6.61 \pm 0.09 | 5.85 |
| 296 | 2.7 | 0.00912 | 6.606 \pm 0.022 | 5.8 |
| 287.4 | 3.45 | 0.0120 | 7.175 \pm 0.081 | 6.98 |
| 281.6 | 4.00 | 0.0142 | 7.695 \pm 0.017 | 8.18 |
| 273 | 5.20 | 0.0190 | 9.209 \pm 0.065 | 1.09 |
| 268 | 6.10 | 0.0228 | 10.27 \pm 0.06 | 12.5 |
| 262 | 7.50 | 0.0286 | 11.83 \pm 0.06 | 15 |
| 258.4 | 8.40 | 0.0325 | 12.99 \pm 0.06 | 16.5 |
| 251.2 | 10.80 | 0.0430 | 16.06 \pm 0.1 | 20.8 |
| 248.8 | 12.00 | 0.0482 | 16.58 \pm 0.29 | 21.2 |
| 245 | 13.60 | 0.0555 | 18.78 \pm 0.06 | 24.8 |
| 240.7 | 16.00 | 0.0665 | 22.29 \pm 0.46 | 29.3 |
| 240.6 | 16.50 | 0.0686 | 21.25 \pm 0.05 | 28.0 |
| 235.8 | 19.80 | 0.0840 | 25.41 \pm 0.39 | 33.8 |
| 230.5 | 25.00 | 0.1085 | 26.85 \pm 0.15 | 35.8 |
| 230.5 | 25.00 | 0.108 | 27.17 | 36.0 |
| 228.6 | 26.50 | 0.116 | 27.82 | 37.0 |
| 228.5 | 27.30 | 0.1195 | 27.35 \pm 0.05 | 36.6 |
| 223.1 | 34.50 | 0.1546 | 26.85 \pm 0.45 | 35.8 |
| 220.1 | 39.50 | 0.1795 | 25.44 \pm 0.56 | 34 |
| 217.1 | 46 | 0.2119 | 25.3 | 33.9 |
| 213.8 | 54 | 0.2526 | 23.95 \pm 0.04 | 31.8 |
| 208.5 | 71 | 0.3405 | 20.1 | 26.4 |
| 203.5 | 92 | 0.4521 | 19.42 \pm 0.06 | 25.2 |
| 196.1 | 142 | 0.7241 | 15.87 | 27 |
| 190.1 | 205 | 1.0784 | 13.2 \pm 0.2 | 16.8 |
| 185.1 | 290 | 1.5667 | 10.97 | 13.6 |

reorientation^{4, 8}, then we have,

$$\Delta H = \frac{2}{9\sqrt{3}} \frac{\hbar}{g_0\beta} \left[\frac{4\tau_\theta\omega_0^2}{5g_0^2} \{(\Delta g)^2 + 3(\delta g)^2\} \left\{1 + \frac{3}{4}(1 + \omega_0^2\tau_\theta^2)^{-1}\right\} + (\partial g)^2\tau_\theta^{-1} \right]; \quad (3)$$

ω_0 is the Zeeman frequency (s^{-1}), β is the Bohr magneton,

$$g_0 = \left(\frac{1}{3}\right)(g_{xx} + g_{yy} + g_{zz}), \quad (4)$$

$$\Delta g = g_{zz} - \left(\frac{1}{2}\right)(g_{xx} + g_{yy}), \quad (5)$$

$$\delta g = \left(\frac{1}{2}\right)(g_{xx} - g_{yy}), \quad (6)$$

$$\partial g = [(g_{zz} - 2.00231)^2 + (g_{yy} - 2.00231)^2 + (g_{xx} - 2.00231)^2]^{\frac{1}{2}} \quad (7)$$

where g_{xx} , g_{yy} , g_{zz} are components of the diagonalized g -tensor in the molecular coordinate system. In obtaining equation 7 we have assumed that the spin-rotational correlation time, $\tau_{\text{SR}}^{(\alpha)}$, about the α -principal molecular axis is given by the Hubbard expression^{4, 8-10}

$$\tau_{\text{SR}}^{(\alpha)} = \frac{I_\alpha}{6kT} \tau_\theta^{-1} \quad (8)$$

where k is the Boltzmann constant and I_α is a moment of inertia about the α -axis. It is usually assumed that this expression is valid provided

$$\tau_\theta \gg \tau_{\text{SR}}^{(\alpha)}, \quad (9)$$

a condition satisfied in the experiments described here. However, in a later section we shall discuss the validity of equation 8.

For the $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ molecule in butanol we determined the g -tensor from measurements in the butanol glass at 77 K:

$$g_{xx} = 2.141$$

$$g_{yy} = 2.040$$

$$g_{zz} = 1.994.$$

We assumed that these values were unchanged in the liquid. For the radical in CHCl_3 we assumed the g -tensor determined by Maki *et al*⁶. for this radical in a CHCl_3 -DMF glass:

$$g_{xx} = 2.140$$

$$g_{yy} = 2.043$$

$$g_{zz} = 1.996.$$

The experiments were carried out at $\omega_0 = 5 \times 10^{10} \text{ s}^{-1}$.

Equation 3 can be used to calculate ΔH as a function of τ_θ ; the width ΔH has a minimum when plotted as a function of τ_θ , (see *Figure 1*), a result compatible with the experimental observation that ΔH has a minimum when given as a function of η/T . Whereas the theoretical minimum in butanol is $\Delta H_{\text{min}} = 6.89 \text{ G}$ at $\tau_\theta = 4.6 \times 10^{-11} \text{ s}$, the observed minimum is 6.25 G at $T = 311 \text{ K}$. Although one can always attribute the excess of observed width over theoretical width to unknown relaxation mechanisms or to sample impurities, one must question equation 3 itself in trying to account for the

ESR LINewidthS IN HYDROGEN-BONDED SOLVENTS

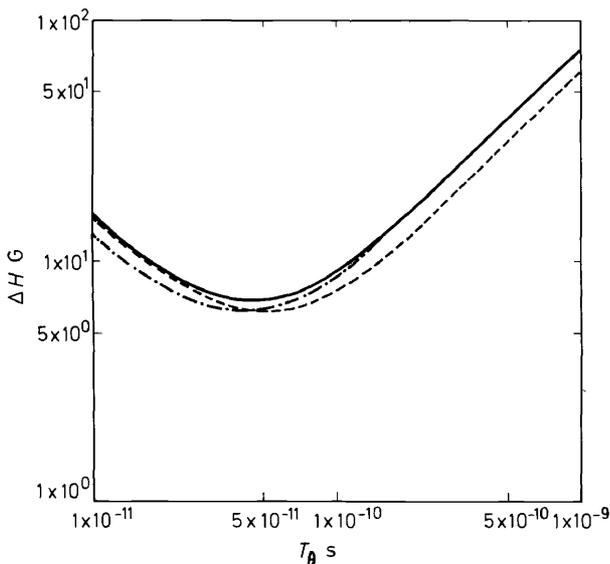


Figure 1. ----- ΔH (peak to peak width of the derivative spectrum) versus τ_{20} for n-butanol. ΔH was calculated according to equation 10 with $x = 0.180$; the components of the g -tensor are those given in Section II. ——— ΔH versus τ_{θ} for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in n-butanol calculated according to equation 3. - - - - - ΔH versus τ_{θ} for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in n-butanol calculated according to spin-rotation correction with $\epsilon_0(1 - \lambda_2)^{-1} = 0.81$.

excess of the theoretical width over that observed. A more careful analysis indicates that the assumption of isotropic rotational diffusion, implicit in equation 3, need not be applicable; furthermore, the assumption, implicit in the derivation of equation 3, that the spin-rotational correlation time, τ_{SR} , is proportional to τ_{θ}^{-1} (i.e. equation 8), may be invalid. In the next section we will consider anisotropic diffusion and in a later section we will study τ_{SR} .

ANISOTROPIC DIFFUSION

Although we should consider totally anisotropic rotational diffusion, and the diffusion tensor and the g -tensor need not necessarily be diagonal in the same coordinate system, the accuracy of the experimental data does not warrant the use of so many adjustable parameters. Therefore, we will assume axially symmetric anisotropic rotational diffusion for which the unique principal axis lies along the molecular z -axis, i.e. the axis along which g_{zz} is specified. In this case, equation 3 can be rewritten as^{9, 11}

$$\Delta H = \frac{2}{9\sqrt{3}} \frac{\hbar}{g_0\beta} \sum_m \left[\frac{4\tau_{2m}\omega_0^2}{5g_0^2} \{(\Delta g)^2\delta_{m0} + 3(\delta g)^2\delta_{m2}\} \right. \\ \left. \times \left\{ 1 + \frac{3}{4}(1 + \omega_0^2\tau_{2m}^2)^{-1} \right\} + \partial g^2\tau_{2m}^{-1}\delta_{m0} \right. \\ \left. + \frac{3}{2}(g_{zz} - 2.0023)^2 (\tau_{22}^{-1} - \tau_{20}^{-1}) \right] \quad (10)$$

where $m = 0, 2$;

$$\tau_{2m}^{-1} = 6D_{\perp} + m^2(D_{\parallel} - D_{\perp}); \quad (11)$$

and D_{\parallel} and D_{\perp} are the elements of the rotational diffusion tensor along and perpendicular to the molecular z -axis, respectively.

We can now calculate ΔH as a function of the two parameters, τ_{20} and x , where x is the dimensionless variable

$$x = \frac{\tau_{20}}{\tau_{22}}. \quad (12)$$

We find that the minimum calculated value of ΔH can be made to agree with the observed value only for unique values of x and τ_{20} , i.e. $\tau_{20} = 5.2 \times 10^{-11}$ s and $x = 1.80$. This value of x is equivalent to the statement that $D_{\parallel} = 2.2 D_{\perp}$, which means that rotational diffusion is twice as fast about the molecular z -axis as about the other two axes, a result that is quite reasonable for a planar radical with the molecular z -axis perpendicular to the plane. It should be reemphasized that we cannot be sure that the rotational diffusion is axially symmetric, but it should also be noted that the value of the minimum in ΔH is a sensitive function of the ratio x . Furthermore, different results would be obtained if D_{\parallel} were along either the x or y molecular axes, but it seems reasonable in this nearly planar molecule to assume that the unique axis of the diffusion tensor is normal to the plane.

We have assumed that the ratio x is independent of temperature and viscosity, a result which follows if the Stokes-Einstein relation holds for both τ_{20} and τ_{22} . (In recent work Freed *et al.*^{11a} have obtained consistent results in their analysis of the esr spectra of $(\text{SO}_3)_2\text{NO}^{2-}$ in solution by assuming that x is temperature independent.) We have then used equation 10 to calculate ΔH as a function of τ_{20} with $x = 1.80$ (Figure 1). Clearly, the variation of ΔH with changes in τ_{20} is very slight near the minimum, and great uncertainty

Table 2. Data for $(n\text{-C}_4\text{H}_9)_4\text{N} \cdot \text{NiS}_4\text{C}_4(\text{CN})_4$ in CHCl_3 . $g_{xx} = 2.140$, $g_{yy} = 2.043$, $g_{zz} = 1.996$.

| Temperature (K) | η (cP) | $\frac{\eta}{T}$ (cP K ⁻¹) | ΔH (G) (experimental) | τ_{20} (s) (from experiment and Figure 1) ($\times 10^{11}$) |
|-----------------|-------------|----------------------------------------|-------------------------------|---------------------------------------------------------------------|
| 310.4 | 0.485 | 0.00156 | 6.899 ± 0.066 | 2.36 |
| 306.6 | 0.505 | 0.00165 | 6.801 ± 0.1 | 2.43 |
| 300.8 | 0.528 | 0.00176 | 6.459 ± 0.082 | 2.80 |
| 298.6 | 0.542 | 0.00182 | 6.508 ± 0.1 | 2.72 |
| 286 | 0.615 | 0.00215 | 6.151 ± 0.031 | 3.25 |
| 279.9 | 0.655 | 0.00234 | 6.10 ± 0.05 | 3.50 |
| 268.8 | 0.74 | 0.00275 | 6.117 ± 0.040 | 3.4 |
| 264.1 | 0.782 | 0.00297 | 6.052 ± 0.032 | 4.49 |
| 258.5 | 0.84 | 0.00325 | 6.329 ± 0.016 | 5.0 |
| 251.2 | 0.92 | 0.00366 | 6.557 ± 0.016 | 5.9 |
| 244.8 | 1.01 | 0.00413 | 6.909 ± 0.055 | 6.3 |
| 239.8 | 1.09 | 0.00452 | 7.306 ± 0.022 | 7.25 |
| 233.6 | 1.19 | 0.00509 | 7.919 ± 0.033 | 8.5 |

exists in determining τ_{20} from the measured values of ΔH about this minimum. It is interesting to note that at the minimum, the nonsecular contribution to the linewidth, i.e. those terms with the factor $(1 + \omega_0^2 \tau_{2m}^2)^{-1}$, account for 5.6 per cent of the width, and the spin rotational contribution, i.e. those terms with the factor τ_{2m}^{-1} , accounts for 45 per cent of the width.

We can next use *Figure 1* and the experimentally determined linewidths in *Table 1* to obtain τ_{20} as a function of η/T , and we can combine these results with equation 1 to determine $r^3\kappa$ as a function of (η/T) , provided we associate τ_{20} with τ_θ . We have not measured the translational diffusion constant, and could not, therefore, determine r directly or its dependence on (η/T) . Instead, we also used the methods outlined above to determine $r^3\kappa$ for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in CHCl_3 , a weakly hydrogen-bonded solvent, and we assumed that $\kappa = 1$ in the high temperature limit for this solvent. The data in this solvent are given in *Table 2*; the ΔH versus τ_{20} curve is very similar to that in *Figure 1* provided the appropriate g -values are used. The value of x is equal to 2.0 in CHCl_3 . We found by this method that $r^3 = 64.6 \text{ \AA}^3$ and in CHCl_3 , κ is essentially independent of (η/T) (*Figure 2*).

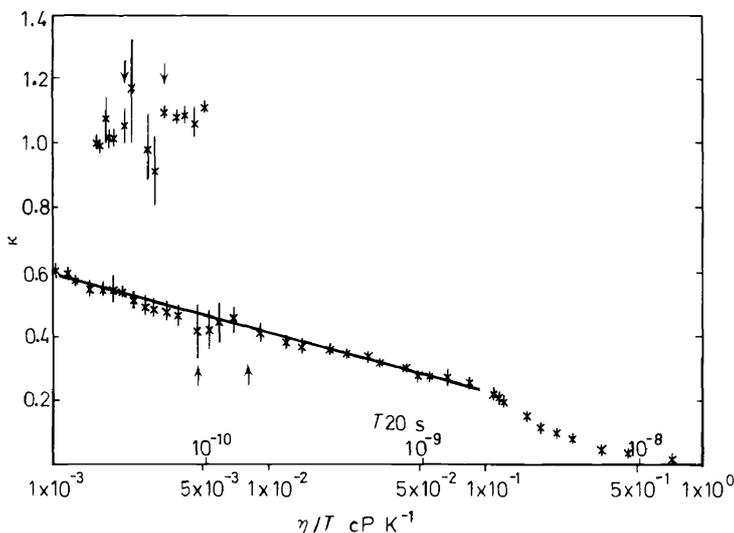


Figure 2. κ versus η/T for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$ in both butanol and CHCl_3 . $r^3 = 64.6 \text{ \AA}^3$. $x = 1.80$. The components of the g -tensor are those given in *Table 2*.

The values of $r^3\kappa$ in butanol can then be combined with the value of r^3 determined in CHCl_3 to yield values of κ as a function of η/T in butanol. The relative κ values are more significant than are the absolute values. In *Figure 2*, κ is plotted as a function of (η/T) and it is seen that in butanol it varies very markedly. Note that because the molecule and the diffusion tensor are not spherically symmetric, the hydrodynamic radii cannot be simply related to the molecular radius⁹.

In the Redfield limit, equations 10 and 3 are valid, but at high viscosity they

no longer apply. Elsewhere¹² we have shown that the Redfield limit applies provided

$$2\tau_{\theta} \left(\frac{\omega_0}{g_0} \right) \sqrt{[(\Delta g)^2 + 3(\delta g)^2]/45} < 0.45, \quad (13)$$

at which point the line deviates markedly from a simple Lorentzian. Thus, in the present case, equation 10 should be applicable provided $\tau_{20} < 4.2 \times 10^{-10}$ s. The graph in *Figure 2* indicates that for $\tau_{20} < 4.2 \times 10^{-10}$ s, the variation of κ in butanol is nearly linear in $\log(\eta/T)$. We can plot the straight line

$$\kappa = -0.19 \log \eta/T + 0.0402 \quad (14)$$

through the data. The deviations from this line at $\tau_{20} > 4 \times 10^{-10}$ s can be attributed to the breakdown of Redfield theory.^{12, 13}

DISCUSSION OF ANISOTROPIC DIFFUSION

In this study, we have shown that in order to fit the butanol data to the theoretical expression in equation 10, we could set the rotational diffusion anisotropy coefficient, $x = 1.80$. We have assumed that x is independent of η/T , and we have neglected the possible small effect of unresolved hyperfine lines. The solutions were sufficiently dilute (2.82×10^{-4} M and 4.4×10^{-4} M) so that intermolecular spin interactions could be neglected. In the analysis we have assumed that even in liquid solution, the elements of the g -tensor are those determined from measurements made in the glass at 77 K. There are small shifts in the isotropic g -value but whether or not there are significant changes in g_{xx} , g_{yy} and g_{zz} , we do not know. Of course, if they do change appreciably, our entire analysis is open to question, particularly since the calculated widths are sensitive to the values of $(g_{xx} - g_{yy})$. In CHCl_3 , $x = 2.0$.

In CHCl_3 the parameter κ is independent of (η/T) as it appears to be for radicals in many non-hydrogen-bonded or weakly hydrogen-bonded solvents.⁴ However, in butanol the parameter κ appears to vary strongly with (η/T) ; in fact, at high temperature (small τ_{20}), the variation appears to be linear in $\log \eta/T$. For $\tau_{20} > 4.2 \times 10^{-10}$ s, the variation of κ with η/T becomes more rapid, but the theory of line shapes indicates that the simple formulas, equations 3 and 8, do not hold in this region^{12, 13}. Thus we might attribute the high temperature variation of κ , as described in equation 14, to the breakdown of the Stokes-Einstein-Debye relationship for τ_{20} as a function of η/T ; and the additional variation at low temperatures to the breakdown of spin relaxation theories valid only in the Redfield limit¹².

The parameter κ , as defined in equation 2, relates intermolecular torques to intermolecular forces. At high temperatures the hydrogen bonding in butanol is less important than at low temperatures, and for anisotropic solute and solvent molecules, κ should be relatively large. At low temperatures, one would expect the translational motion of the solute radical to be greatly impeded by the strongly hydrogen-bonded solvent network, but the rotational motion of the large solute molecule would be less affected because it already exists in a cavity in which the network has been broken and in which it can rotate relatively freely. Thus κ should decrease at low temperatures as

observed. In the following sections, however, we shall argue that κ may be constant. In this connection it is interesting to note that in paramagnetic molecules with nuclear hyperfine interactions, the reorientation time can be determined independently of the spin rotational effects and a corresponding κ can be determined.¹⁴ Vanadyl acetylacetonate has been studied in various solvents and the κ values appear to be temperature independent¹⁴ even in butanol.¹⁶ (Some recent preliminary data seems to indicate that there may be some decrease of κ with decreasing temperature¹⁵.) Note also that the κ determined for ClO₂ in n-butanol¹⁰, a κ which is related to spin-rotational interactions, seems to vary with (η/T) whereas in 'normal' solvents this is not the case⁴. Furthermore for ClO₂ in tris(butyl) phosphate, a very viscous solvent, the κ obtained for spin-rotations differs from that obtained for reorientation^{16a}.

Throughout it has been assumed that κ is a scalar but in reality it is a tensorial molecular property. Thus for an ellipsoidal molecule, κ should have two values if diagonalized in the same frame in which the rotational diffusion tensor is diagonal. Thus τ_{20} and τ_{22} depend upon $r_{20}^3\kappa_{20}$ and $r_{22}^3\kappa_{22}$ respectively, where r_{2n} and κ_{2n} are the appropriate hydrodynamic radii and κ_{2n} ¹⁰. † Since we are primarily interested in the temperature variation of κ , and not its absolute value, our results are not altered in any fundamental way by the anisotropy of $r_{2n}^3\kappa_{2n}$.

SPIN-ROTATIONAL CORRECTIONS

The discrepancy between the minimum ΔH obtained by means of equation 3 and that observed experimentally can alternatively be explained on the basis of a correction introduced in the relationship between spin-rotational correlation times and reorientation correlation times, i.e. corrections to equation 8. If we assume that the rotating molecule is trapped, i.e. it oscillates over a small angle, for a time τ and is then released by solvent fluctuations¹⁷ so that free rotation can occur for a very short time τ_f , ($\tau_f \ll \tau$), then the step model of Ivanov¹⁸ can be applied. The reorientation correlation time, τ_θ , for a second rank tensor is, according to Ivanov,

$$\tau_\theta = \tau(1 - \lambda_2)^{-1} \quad (15)$$

where λ_2 is a function of the mean rotational jump angle, ε_0 , and of the width σ , of the distribution of jump angles. For a rectangular distribution of jump angles,

$$\lambda_2 = \frac{4}{5\sigma} \left[\cos \varepsilon_0 \sin \frac{\sigma}{2} + \frac{1}{2} \cos 2\varepsilon_0 \sin \sigma + \frac{\sigma}{4} \right]. \quad (16)$$

† For an ellipsoidal molecule⁹ with principal axes of length $x = y = 2b$ and $z = 2a$,

$$r_{20} = \left[\frac{4(a^2 - b^2)b}{3(2a - b^2S)} \right]^{\frac{1}{3}}, \quad r_{22} = \left[\frac{4(a^4 - b^4)}{3(2a^2 - b^2)S - 2a} \right]^{\frac{1}{3}}$$

$$S = \int_0^\infty \frac{dr}{(a^2 - r)^{\frac{1}{2}}(b^2 - r)}$$

If we now assume that

$$\tau_{\text{SR}} = \tau_f(\tau_f/\tau) \quad (17)$$

for $\tau \gg \tau_f$, and

$$\varepsilon_0 = \sqrt{\left(\frac{6kT}{I}\right)} \tau_f, \quad (18)$$

where I is a mean moment of inertia, it readily follows that

$$\tau_{\text{SR}} = \frac{I}{6kT} \tau_\theta^{-1} [\varepsilon_0^2(1 - \lambda_2)^{-1}]. \quad (19)$$

This equation differs from equation 8 by the factor $\varepsilon_0^2(1 - \lambda_2)^{-1}$, and it is interesting to study this factor in various limits. For 'small jumps'

$$\lim_{\varepsilon_0 \rightarrow 0} \varepsilon_0^2(1 - \lambda_2)^{-1} \rightarrow [1 - \frac{1}{12}(\sigma/\varepsilon_0)^2] < 1, \quad (20)$$

and τ_{SR} is smaller than predicted by equation 8. If the width of the distribution of jumps is very small, then $\sigma \ll \varepsilon_0$, and τ_{SR} is given by equation 8. On the other hand for appreciable or large 'jumps', and narrow distributions of jumps, i.e. $\varepsilon^4 \gtrsim \sigma^2$, the quantity $\varepsilon_0^2(1 - \lambda_2)^{-1} > 1$, and τ_{SR} is larger than predicted by equation 8.

Although Ivanov's expression was derived for spherical molecules, we will assume that for asymmetric molecules, $\tau_{\text{SR}}^{(\alpha)}$ and I_α can replace τ_{SR} and I in equation 19, where α represents the α th molecular axis, but that τ_θ and $\varepsilon_0^2(1 - \lambda_2)^{-1}$ are spherically symmetric. (This approximation is compatible with the assumption that κ in equations 1 and 2 is a scalar^{4, 5}). It follows that equation 3 should be altered by replacing ∂g^2 by $\partial g^2 \varepsilon_0^2(1 - \lambda_2)^{-1}$. The calculated minimum value of ΔH for (n-C₄H₉)₄N·NiS₄C₄(CN)₄ in butanol can then be made to agree with the observed value if $\varepsilon_0^2(1 - \lambda_2)^{-1} = 0.81$ and $\tau_\theta = 4 \times 10^{-11}$ s. For the same radical in CHCl₃, $\varepsilon_0^2(1 - \lambda_2)^{-1}$ has the same value. If $\varepsilon_0^2(1 - \lambda_2)^{-1}$ is assumed independent of temperature, the ΔH versus τ_θ curve can be plotted as shown in *Figure 1*, and the same results, as described above in the anisotropic rotational diffusion calculations, are obtained for the dependence of κ upon (η/T) .

If the interpretation given above is responsible for the observed decrease in the minimum value of ΔH over that predicted by equation 3, then since $\varepsilon_0^2(1 - \lambda_2)^{-1} < 1$, equation 20 must be applicable. This implies that reorientation takes place by small jumps, and since $\varepsilon_0^2(1 - \lambda_2)^{-1} = 0.81$, the width of the rectangular distribution of jumps is $\sigma = 1.5 \varepsilon_0$, i.e. the range of angular jumps ε is $0.25 \varepsilon_0 < \varepsilon < 1.75 \varepsilon_0$.

The analysis above depends upon the assumption that τ_{SR} is given by equation 19. In this approximation τ_{SR} is equal to the correlation time for angular momentum, although τ_{SR} also involves a reorientation contribution; for small ε_0 the approximation should be valid^{4, 5}. The treatment above is in many ways similar to that proposed by Brown, Gutowsky and Shimomura¹⁹.

CONCLUSION

For $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NuS}_4\text{C}_4(\text{CN})_4$, the observed decrease in the minimum ΔH , below that predicted by the simple theory in equation 3, can be accounted for either by an anisotropy in the rotational diffusion ($D_{\parallel} \approx 2D_{\perp}$) or by an appreciable spread in the rotational jumps ($\sigma \approx 1.5\epsilon_0$). In *n*-butanol, a hydrogen-bonded solvent, κ appears to decrease with decreasing temperature but in CHCl_3 , κ appears to be constant; thus a modified Debye law apparently holds in CHCl_3 but not in *n*-butanol.

Recent work by Loewenstein *et al.*²⁰ on the spherical molecules $\text{K}_3\text{W}(\text{CN})_8$ and $\text{K}_4\text{Mo}(\text{CN})_8$ also indicates that the simple theory in equation 3 does not hold in hydrogen-bonded solvents. Although the problem is complicated by unresolved N-hyperfine structure, it appears that the minimum ΔH is larger than that predicted by equation 3, and that κ decreases with decreasing temperature as it does in the present work. Since the molecule is a spherical top, the rotational diffusion is probably isotropic and the increase in the minimum may be due to the $\epsilon_0^2(1 - \lambda_2)^{-1}$ factor; if this is so, $\epsilon_0^2(1 - \lambda_2)^{-1} > 1$, and rather big rotational jumps must take place. Of course, the increase in the minimum ΔH may be due to other relaxation mechanisms²¹. (Note that in the present work the observed minimum is less than that predicted on the basis of equation 3).

Angerman and Jordan¹⁶ in their studies of vanadyl acetylacetonate in alcohols analyzed the spectra in terms of the linewidth formula¹⁴

$$\Delta H = \alpha' + \alpha'' + \beta I_z + \gamma I_z^2 \quad (21)$$

where I_z is the quantum number of the vanadyl spin along the applied field. They measured β and γ as functions of temperature and from these they were able to measure τ_θ and to determine that κ is independent of temperature. With these values of τ_θ (or κ), they were able to calculate α' and thus determine the residual width, α'' . If this residual width is attributed to spin-rotational relaxation^{8, 14}, and if the Hubbard relation, equation 8, holds, then α'' is given by the δg^2 terms of equation 3. Jordan *et al.* found that α'' was larger than the predicted value and the discrepancy increased with decreasing temperature. It seems unlikely that the discrepancy in α'' is due to other relaxation mechanisms because most other possible relaxation mechanisms would become less important at lower temperatures²¹. It can also be seen from the data of Angerman and Jordan that the minimum ΔH predicted by equation 3 is greater than that observed. All these data can be rationalized by assuming that κ is constant²² and, hence, the Debye law holds, provided the spin rotational contributions require a temperature dependent $\epsilon_0^2(1 - \lambda_2)^{-1}$ factor. Near the minimum in ΔH , it is seen that $\epsilon_0^2(1 - \lambda_2)^{-1} < 1$ for vanadyl acetylacetonate as well as for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$; as the temperature decreases, $\epsilon_0^2(1 - \lambda_2)^{-1}$ increases, and the value of α'' increases over that expected on the basis of equation 3.

In the paragraph above, if $(\alpha' + \alpha'')$ for vanadyl acetate were analyzed as it was for $(n\text{-C}_4\text{H}_9)_4\text{N}\cdot\text{NiS}_4\text{C}_4(\text{CN})_4$, and the values of τ_θ and κ were not determined from the hyperfine measurements, i.e. from β and γ , we would find that κ decreased with decreasing temperature. Therefore, we might speculate that κ , in fact, is constant in all the experiments described here:

($n\text{-C}_4\text{H}_9$)₄N·NiS₄C₄(CN)₄, vanadyl acetylacetonate and K₃W(CN)₈; that near the minimum ΔH , the factor $\epsilon_0^2(1 - \lambda_2)^{-1}$ that alters the spin-rotational contribution is less than unity for ($n\text{-C}_4\text{H}_9$)₄N·NiS₄C₄(CN)₄ and vanadyl acetylacetonate, but greater for K₃W(CN)₈; that in hydrogen-bonded solvents $\epsilon_0^2(1 - \lambda_2)^{-1}$ decreases with increasing temperature, i.e. ϵ_0 decreases with increasing temperature. This interpretation is compatible with that of Gutowsky *et al.*¹⁹ and with the activation energy results of Loewenstein *et al.*²⁰

The results of Burlamacchi and Romanelli^{16a} could also be explained on the basis of equation 19.

As a final word of caution note that in the study of ($n\text{-C}_4\text{H}_9$)₄N·NiS₄C₄(CN)₄ in butanol and CHCl₃, the deviations from equation 3 could be explained equally well in terms of either anisotropic diffusion or in terms of isotropic 'Ivanov jumps'.

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APPENDIX

n-Butanol viscosity data are available²³ to temperatures as low as -51°C ; we have measured the viscosity at -80.0°C and found a value of 170 ± 5 cP. This value lies on the extrapolated $\log \eta$ versus T^{-1} curve obtained from existing data and this curve was, therefore, used to determine viscosities at the temperatures indicated in *Table 1*.

The viscosity measurement at -80.0°C was carried out by measuring the time required for a fixed volume of *n*-butanol to flow through a vertical capillary tube. The system was kept dry by the insertion of CaSO₄ between it and the air. The temperature was controlled in a well-stirred dry-ice-acetone bath.

REFERENCES

- ¹ P. Debye, *Polar Molecules*. Dover Publications (1929).
- ² A. Einstein, *Ann. Physik*, **17**, 549 (1905); **19**, 371 (1906).
- ³ N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
- ⁴ R. McClung and D. Kivelson, *J. Chem. Phys.* **49**, 3380 (1968).
- ⁵ D. Kivelson, M. G. Kivelson and I. Oppenheim, *J. Chem. Phys.* **52**, 1810 (1970).
- ⁶ A. Maki, *J. Am. Chem. Soc.* **85**, 2029 (1963).
- ⁷ D. Kivelson, *J. Chem. Phys.* **33**, 1049 (1960).
J. Freed and G. Fraenkel, *J. Chem. Phys.* **39**, 326 (1963).
- ⁸ P. Atkins and D. Kivelson, *J. Chem. Phys.* **44**, 169 (1966).
P. Atkins, *Molec. Phys.* **12**, 201 (1967).
- ⁹ R. McClung, Thesis (1967).
- ¹⁰ P. S. Hubbard, *Phys. Rev.* **131**, 1155 (1963).
- ¹¹ J. H. Freed, *J. Chem. Phys.* **41**, 2077 (1964).
- ^a S. A. Goldman, G. V. Bruno, C. F. Polnaszek and J. H. Freed, to be submitted.
- ¹² R. Huang and D. Kivelson, to be submitted.
- ¹³ H. Sillescu and D. Kivelson, *J. Chem. Phys.* **48**, 3493 (1968).

ESR LINEWIDTHS IN HYDROGEN-BONDED SOLVENTS

- ¹⁴ R. Wilson and D. Kivelson, *J. Chem. Phys.* **44**, 154 (1966).
- ¹⁵ J. Hwang, Private communication.
- ¹⁶ N. S. Angerman and R. B. Jordan, *J. Chem. Phys.* **54**, 837 (1971).
- ^a L. Burlamacchi and M. Romanelli, *Chem. Phys. Lett.* **10**, 59 (1971).
- ¹⁷ S. H. Glarum and J. H. Marshall, *J. Chem. Phys.* **46**, 55 (1967).
- J. E. Anderson, *J. Chem. Phys.* **47**, 4879 (1967).
- P. W. Atkins, A. Loewenstein and Y. Margalit, *Mol. Phys.* **17**, 329 (1969).
- ¹⁸ E. N. Ivanov, *Soviet Physics JETP* **18**, 1041 (1964).
- ¹⁹ R. J. C. Brown, H. S. Gutowski and K. Shimomura, *J. Chem. Phys.* **38**, 76 (1963).
- ²⁰ R. Poupko, H. Gilboa, B. Silver and A. Loewenstein, *Ber. Bunsen-Ges.* **75**, 279 (1971).
- ²¹ D. Kivelson, *J. Chem. Phys.* **45**, 1324 (1966).
- P. W. Atkins, *Molec. Phys.* **13**, 37 (1967).
- ²² K. Eiseenthal has measured reorientation directly for large molecules in alcohols and has found α constant (Private communication).
- ²³ T. Tonomura, *Bull. Chem. Soc. Japan* **6**, 124 (1931).