AN EXPLANATION OF ANOMALOUS RESULTS IN THE NMR RELAXATION
OF A PROBE IN LIQUID CRYSTALLINE MEDIA

H.A. LOPES CARDOZO, J. BULTHUIS

Chemical Laboratory of the Free University, Amsterdam, The Netherlands

and

J.H. FREED * and W.M.M.J. BOVÉE

Department of Applied Physics, Delft University of Technology, Delft, The Netherlands

The methyl-^{13}C and the ^{14}N longitudinal relaxation times in acetonitrile, dissolved in a thermotropic liquid crystal are analyzed with a slowly relaxing local structure model. This model gives rise to a frequency dependent relaxation mechanism which explains the relatively short ^{14}N relaxation time compared to the methyl-^{13}C relaxation time.

1. Introduction

In a previous paper [1], the results were given of an NMR relaxation study of acetonitrile dissolved in a nematic liquid crystal (Merck's Licrystal V). The longitudinal relaxation time of the methyl-^{13}C was measured by an inversion-recovery pulse sequence under proton decoupling. The ^{14}N T_1 was abstracted from the proton decoupled cyano-^{13}C line, which is substantially broadened due to the scalar relaxation mechanism.

In order to abstract the correlation times for rotational diffusion perpendicular to, and around the symmetry axis, from the measured relaxation times, the equations derived by Woessner [2,3] for NMR relaxation in the case of anisotropic rotational diffusion were modified in a simple manner, to allow for preferential orientation. In view of the relatively small degree of ordering ($S_{zz} \approx 0.1$), it was assumed that the classical model of rotational diffusion for an isotropic liquid was also valid for a small molecule as acetonitrile in a nematic liquid.

Using a value of 3.6 MHz for the quadrupole coupling constant e^2qQ/h of ^{14}N as measured in a lyotropic liquid crystal [4], the methyl-^{13}C T_1 and the cyano-^{14}N T_1 appeared to be incompatible. Real values of $\tau_\perp$ and $\tau_\parallel$ could only be obtained by increasing the ^{14}N quadrupole coupling constant by an undue amount (a factor of two at least). No such discrepancies were found in relaxation time measurements on acetonitrile in normal liquids [3,5–7].

It was pointed out that the discrepancy might be lifted by taking into account correlations between reorientational motions of acetonitrile and the liquid crystal molecules.

In the present communication it will be shown that it is possible to explain the observed anomalies by the theory of Polnaszek and Freed [8]. These authors presented a model, extended by Freed [9], in which the surrounding solvent molecules may be regarded as providing a local structure which relaxes on a slower timescale than the probe molecule. This slowly relaxing local structure (SRLS) model can give rise to frequency dependent spectral densities, which can explain the relatively short ^{14}N T_1 compared to the ^{13}C T_1.

2. Analysis

Although acetonitrile is a small molecule with a weak ordering, fluctuations in director orientation [9,10] also can give rise to non-negligible frequency dependent relaxation contributions. They cannot, however, explain the large discrepancies between the experimental relaxation times and we shall ignore them here for the sake of simplicity but they should be included in a more rigorous treatment. Application of the SRLS model leads to the following spectral density functions (eq. (5.5) of ref. [9])

$$J_{KM}(\omega) = \frac{\kappa(K,M)\tau_R}{1 + \omega^2\tau_R^2} + \tfrac{1}{5}[5\kappa(0,M)]^2\delta_{K,0}\langle|S_1|^2\rangle\left[\frac{\tau_x}{1 + \omega^2\tau_x^2} - \frac{\tau_R'}{1 + \omega^2(\tau_R')^2}\right]. \tag{1}$$

S_1 is the local order parameter, τ_x the correlation time for the slowly relaxing local structure, K represents irreducible tensor components in the molecular frame and M in the laboratory frame. Eq. (1) is written under the condition of axial symmetric local ordering. More general expressions are given by Lin and Freed [11]. The cross-terms in τ_R' may usually be neglected as by definition $(\tau_R')^{-1} = \tau_R^{-1} + \tau_x^{-1}$ and $\tau_R^{-1} \gg \tau_x^{-1}$. It should be noted that there are other small cross-terms of the same order of magnitude as these in τ_R', which, formally, should be included in eq. (1). We assume that the parallel reorientation is much faster than the perpendicular one (i.e. $D_\| > D_\perp$). Then the relaxation of the methyl-^{13}C is dominated by the perpendicular reorientation, and we can neglect terms in eq. (1) with $K \neq 0$. This is rigorously true for the ^{14}N relaxation because of the axial symmetry of the electric field gradient at the ^{14}N nucleus. Thus, in the following $\tau_R = \tau_\perp$. It is further assumed that the extreme narrowing condition $\omega^2\tau_\perp^2 \ll 1$ is applicable. As shown by Lin and Freed [11], it is not necessary to distinguish ‘between different jump models in analysing motional narrowing results for weakly ordered probe molecules [+]. Therefore, although the SRLS contribution to eq. (1) is derived for the strong jump model, the values for the parameters $\kappa(K,M)$ may be taken from a computation for the case of brownian diffusion of a molecule experiencing a reorienting potential (see table 2 of ref. [9]; in the present case refined values given in ref. [11] were used). If, for example, $S_{zz} = 0.1$ (which is about the ordering parameter at 22°C) $\kappa(0,0) = 0.2419$, $\kappa(0,1) = 0.2162$, and $\kappa(0,2) = 0.1600$. For these specific values the longitudinal relaxation times of ^{14}N and methyl-^{13}C can be written as follows

$$1/T_1(^{14}N) = \tfrac{3}{2}\pi^2(e^2qQ/h)^2\left[0.856\,\tau_\perp + 0.2337\langle|S_1|^2\rangle\frac{\tau_x}{1 + \omega_N^2\tau_x^2} + 0.5120\langle|S_1|^2\rangle\frac{\tau_x}{1 + 4\omega_N^2\tau_x^2}\right], \tag{2}$$

$$1/T_1(^{13}C) = \tfrac{1}{9}(\tfrac{9}{2}\gamma_C^2\gamma_H^2\hbar^2)\left[0.6169\,\tau_\perp + 0.0975\langle|S_1|^2\rangle\frac{\tau_x}{1 + (\omega_H - \omega_C)^2\tau_x^2} + 0.2337\langle|S_1|^2\rangle\frac{\tau_x}{1 + \omega_C^2\tau_x^2}\right.$$

$$\left. + 0.1875\langle|S_1|^2\rangle\frac{\tau_x}{1 + (\omega_H + \omega_C)^2\tau_x^2}\right]. \tag{3}$$

Eqs. (2) and (3) differ from the well known result for an isotropic liquid in two respects. First there is the contribution from the slowly relaxing local structure model. Secondly, due to the preferential orientation, the coefficients of $\tau_\perp$ in eqs. (2) and (3), deviate from the values 1 and 2/3 respectively, in the case of rotational diffusion in an isotropic liquid under the condition of motional narrowing. The factor 1/9 at the r.h.s. of eq. (3) is the value of $[\tfrac{1}{2}(3\cos^2\theta - 1)]^2$, θ being the angle between the C—H bond and the molecular symmetry axis, for a tetrahedral configuration.

It is clear that no unique value can be obtained for $\tau_\perp$ from eqs. (2) and (3) as we have only two equations

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[+] An inertial model is not considered here, a dramatic effect is not likely [12] and, moreover, an inertial model cannot explain the observed discrepancies.

Table 1 [a]

Temp. (°C)	$T_1(^{13}C)$ (s)	$10^4 T_1(^{14}N)$ (s)	S_{zz}	$\langle|S_1|^2\rangle$	$10^{12}\tau_\perp$ (s)	$10^9\tau_x$ (s)
36	6.2	1.37	0.077	0.023	4.35	1.91
29.5	5.6	1.04	0.089	0.021	5.95	2.93
22	4.8	0.80	0.099	0.021	8.96	4.02
13	3.6	0.54	0.108	0.024	16.54	5.60
6.5	3.0	0.39	0.114	0.026	26.43	8.39
0.5	2.4	0.28	0.120	0.033	37.90	11.12
−4.5	2.1	0.19	0.124	0.049	50.27	20.31

[a] The values of $T_1(^{13}C)$, $T_1(^{14}N)$ and S_{zz} are abstracted from table 1, table 2 and fig. 2 of ref. [1], respectively.

with three unknowns. The assumption, however, that $\langle|S_1|^2\rangle$ does not change greatly with temperature and the consideration that $\tau_\perp$ should have a temperature dependence very similar to that of τ_x are extra conditions which restrict the number of possible solutions.

The values in table 1 were obtained by imposing on $\tau_\perp$ an Arrhenius type behaviour, resulting in an activation energy of 10.3 kcal/mole close to the value of 9.6 found by Polnaszek and Freed [8] for PD-Tempone dissolved in Licrystal phase V. It is expected that $\langle|S_1|^2\rangle$ will increase somewhat at lower temperatures. The values of τ_x and $\langle|S_1|^2\rangle$ appear reasonable in the framework of the SRLS model and are in good agreement with the values of τ_x ($2 \times 10^{-9} < \tau_x < 2.5 \times 10^{-8}$) and $\langle|S_1|^2\rangle$ ($0.1 < \langle|S_1|^2\rangle < 0.01$) obtained by Polnaszek and Freed [8] and by Hwang et al. [13] in their analyses of the anomalous ESR results for spin probes dissolved in liquid crystals.

The results of the calculations show that it is possible to explain the observed ^{14}N and methyl-^{13}C longitudinal relaxation times in acetonitrile, dissolved in a nematic liquid crystal by invoking the slowly relaxing local structure model. In view of the approximations to be made and the number of parameters involved, the theory can only be applied in a qualitative way. We hope to obtain further evidence for the applicability of the SRLS model from experiments at different field strengths ‡.

‡ Preliminary results on a 180 MHz NMR spectrometer (Bruker WH-180) show a substantial increase in the cyano-^{13}C line width, indicating a lengthening of the ^{14}N longitudinal relaxation time at this higher frequency, in agreement with the SRLS model.

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