Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Alberto Arcioni , Antonietta Tullio & Claudio Zannoni (1996): Order and Dynamics of 9,10-Diphenylanthracene in the Liquid Crystal ZLI-1167. A Fluorescence Depolarization Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 290:1, 255-266

To link to this article: http://dx.doi.org/10.1080/10587259608031911

Mol. Cryst. Liq. Cryst., 1996, Vol. 290, pp. 255–266
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ORDER AND DYNAMICS OF 9,10-DIPHENYLANTHRACENE IN THE LIQUID CRYSTAL ZLI-1167. A FLUORESCENCE DEPOLARIZATION STUDY

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Abstract The behavior of the probe 9,10-diphenylanthracene (DPA) dissolved in the nematic and isotropic phase of the cyanocyclohexyl mesophase mixture ZLI-1167 has been investigated using fluorescence depolarization on the nanosecond time scale. The orientational order parameters and the rotational diffusion coefficients of the fluorescent probe molecule have been determined as a function of temperature together with its fluorescence lifetimes using the Global Target Analysis method with exponential spline interpolating functions. In the isotropic phase of the liquid crystal the probe dynamics approaches the hydrodynamic behavior under slip boundary conditions. A comparison with DPA rotational diffusion times in other systems is provided.

INTRODUCTION

Time-dependent fluorescence depolarization (FD)[1,2] is a powerful tool for the investigation of liquid crystals[3-6] and model membranes.[7-10] Nevertheless its potentialities are not easy to exploit because of the relatively large number of parameters that determine the anisotropy decay as well as the problems associated with the deconvolution of the experimental intensities.[11] Indeed, despite the importance of determining order parameters and dynamics of molecules dissolved in liquid crystals both for fundamental reasons and in view of applications in displays, the number of molecules studied is still very limited. Even more scarce is the number of molecules with similar structures that can help in correlating dynamic behavior to molecular dimensions in a way similar to that allowed by the classical stick (Stokes-Einstein-Debye) or slip boundary condition relations in isotropic fluids.[12-17]

In previous works we have studied two simple polyenes: all-trans 1,6-diphenylhexatriene (DPH)[4] and its longer analogue all-trans 1,8-diphenyloctatetraene (DPO)[18] in the nematic phase of the cyanocyclohexyl mesophase mixture ZLI-1167. Here we provide data for another somewhat related molecule: 9,10-diphenylanthracene (DPA) in the same nematic solvent. The dynamics of DPA has been studied extensively both in simple and complex isotropic solvents and a relation between rotational correlation time and viscosity has been proposed.[16] We shall examine how this compares to our findings in a nematic.

The detailed analysis of fluorescence depolarization data is complicated by deconvolution and by its intrinsic ill-conditioning, implying that often more than one set of parameters can fit the experimental intensities. In an effort to attack these problems, we introduced the "Global Target Analysis" (GTA)[19] procedure for simultaneously analyzing data from experiments at different temperatures. The technique has been generalized,[10] adopting a globalization based on an interpolation with exponential splines,[20] to take into account possible sharp changes occurring in the temperature dependence of the fitting parameters, as is normally the case around first order phase transitions. The use of exponential splines to approximate the parameter temperature dependence whenever a physical law can not be guessed allows the number of fitting variables to be reduced, also improving the reliability of the results. This method is applied here, in conjunction with a theory for the fluorescence depolarization in liquid crystals.[3] The fluorescence intensities were collected in a range of temperatures, both in the nematic and isotropic phases, using the single photon counting technique with a collinear geometry described previously.[4] Data analysis, assuming diffusional reorientation of DPA in an anisotropic potential, yields the probe second rank orientational order parameter $\langle P_2 \rangle$ as well as the rotational diffusion coefficient $D_\perp$ and the fluorescence lifetime τ_F as a function of temperature.

THEORY

Fluorescence depolarization in oriented mesophases has been theoretically described in References 3,19. The relevant equations for a cylindrically symmetric probe in a local uniaxial domain, assuming both the absorption and emission transition moments parallel to the symmetry axis and an experimental setup with parallel geometry (see Reference 4), are:

$$I_{ZZ}(t) = \left[\frac{1}{9} + \frac{4}{9}\langle P_2 \rangle + \frac{4}{9}\phi_{00}(t)\right] F(t) \tag{1}$$

$$I_{ZX}(t) = \left[\frac{1}{9} + \frac{1}{9}\langle P_2 \rangle - \frac{2}{9}\phi_{00}(t)\right] F(t) \tag{2}$$

which give the following form for the polarization anisotropy ratio:

$$r(t) \equiv [I_{ZZ}(t) - I_{ZX}(t)] \,/\, [I_{ZZ}(t) + 2\, I_{ZX}(t)] \tag{3}$$

$$= [\langle P_2 \rangle + 2\,\phi_{00}(t)] \,/\, [1 + 2\langle P_2 \rangle] \tag{4}$$

The reorientational dynamics of the probe is described by the second rank orientational correlation functions $\phi_{qn}(t)$[21]

$$\phi_{qn}(t) = \langle D^{2}_{qn}(\omega_0)\, D^{2*}_{qn}(\omega_t) \rangle \tag{5}$$

where $D^{2}_{qn}(\omega_0), D^{2*}_{qn}(\omega_t)$ are generalized spherical harmonics (Wigner functions) that specify the orientation of the molecule at time 0 and at time t with respect to the laboratory frame. The theoretical intensities on the right hand side of Equations (1) and (2) can be calculated invoking a model for the ordering and the dynamics of the probe. In practice the orientational correlation functions can be calculated using the rotational diffusion model[21,22] with a $P_2 - P_4$ effective orientational potential as suggested by maximum entropy considerations[23,24]

$$-U_{probe}(\beta, T)/kT = a_2(T)\, P_2(\cos\beta) + a_4(T)\, P_4(\cos\beta) \tag{6}$$

where $P_L(\cos\beta)$ are Legendre polynomials, β is the angle between probe symmetry axis and director and $a_2(T)$ and $a_4(T)$ are temperature dependent solute-solvent interaction coefficients. As a special case we can have a pure P_2 potential if just the first item in Equation 6 is present, and this is often a good approximation.[21] Given the potential, the probe order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be calculated as standard Boltzmann averages:

$$\langle P_2 \rangle = \frac{\int_0^{\pi} P_2(\cos\beta) \exp[-U_{probe}(\beta, T)/kT] \sin\beta\, d\beta}{\int_0^{\pi} \exp[-U_{probe}(\beta, T)/kT] \sin\beta\, d\beta} \tag{7}$$

$$\langle P_4 \rangle = \frac{\int_0^{\pi} P_4(\cos\beta) \exp[-U_{probe}(\beta, T)/kT] \sin\beta\, d\beta}{\int_0^{\pi} \exp[-U_{probe}(\beta, T)/kT] \sin\beta\, d\beta} \tag{8}$$

Here we shall assume effective cylindrical symmetry both for the order parameter and the rotational diffusion tensor. Indeed DPA has already been treated as a prolate ellipsoid[15-17] with semiaxes 0.8 and 0.305 nm.

In Figure 1 we show the structure of the fluorescence probe DPA with the axis system employed. Looking at this figure it is actually not obvious that DPA can be assumed to be uniaxial especially if the structure in solution is planar. Thus it is comforting to notice that its biaxiality in ZLI-1167 has recently been measured using ^{13}C NMR[25] and found to be relatively small ($\langle D^{2}_{02} \rangle \leq 0.06$), when referred to the same coordinate system. In any case fluorescence depolarization can only report on the direction corresponding to the orientation of the transition moments that here can be assumed to be parallel to the long axis[16] and thus the order parameters obtained refer to this "para" axis. In addition, since the

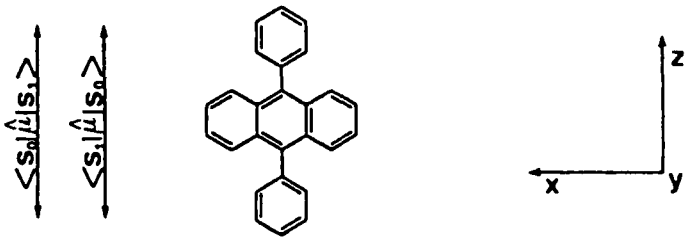

FIGURE 1. The structure of the fluorescence probe DPA together with its transition moments and the axis system employed.

transition moments are parallel to the symmetry axis, they are not modulated by rotational diffusion around it and only the component $D_\perp$ of the rotational diffusion tensor, corresponding to reorientation around an axis perpendicular to the symmetry axis, can be determined.

EXPERIMENTAL

DPA was purchased from Aldrich and used without further purification. We have employed as solvent for DPA the liquid-crystalline mesophase ZLI-1167 (a ternary mixture of propyl, pentyl and heptyl cyano-cyclohexyls i.e. trans, trans-4'-alkyl bicyclohexyl-4-carbonitriles) obtained from Merck, with a nematic range between 305 and 356 K.[26] This liquid crystal is particularly convenient for our studies, since it does not absorb in the wavelength region of the experiment.[4,18]

We used a concentration of 1×10^{-4} g DPA/g ZLI-1167. The sample was held in a flat quartz cell with 110 μm spacing, thermostated by an oil circulation. The inner surface of the cell was coated with polyvinylformal and then rubbed to achieve homogeneous alignment of the liquid crystal molecules parallel to the rubbing direction. Preliminary linear dichroism (LD) experiments were performed measuring at various temperatures the difference $(OD_{\parallel} - OD_{\perp})$ between the sample optical density parallel and perpendicular to the alignment direction (see Figure 2). The preferential orientation of the absorption transition moment of DPA was then confirmed to be parallel to the nematic director. Time-dependent fluorescence depolarization experiments were performed using a single photon counting apparatus equipped with a nanosecond flash-lamp.[4] Intensities were determined in a range of temperatures from 35 °C to 100 °C within the aligned and isotropic phases. The flash-lamp was filled with N_2 at a pressure of 1 atm and operated at a 25 kHz repetition rate with an electrode gap of 0.85 mm. The fluorescence probe molecules were

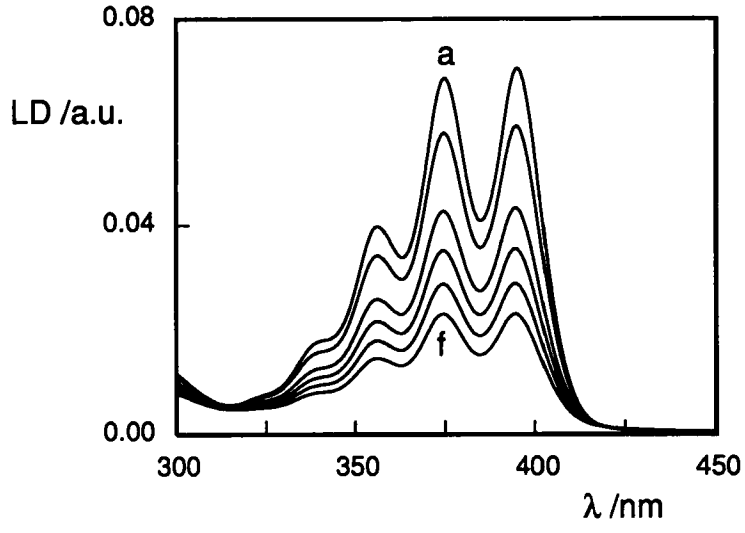

FIGURE 2. The linear dichroism (LD) spectrum of the probe DPA in the ZLI-1167 liquid crystal at various temperatures. Curves from **a** to **f** correspond respectively to T = 33 °C, 50 °C, 70 °C, 77 °C, 81 °C and 83 °C.

excited at 358 nm and observed at 430 nm with a transparency (see-through) geometry.[4] At every temperature the excitation polarizer was kept vertical and the emission polarizer periodically rotated collecting alternatively the parallel (I_{ZZ}) and the perpendicular (I_{ZX}) intensity. Tipically decay curves were measured over 700 channels with a width of 0.11 ns and a maximum peak height of $\approx 2 \times 10^4$ counts for the sum $I_{ZZ} + 2\,I_{ZX}$.

DATA ANALYSIS

Fluorescence anisotropy decays for a probe performing rotational diffusion in an oriented mesophase are given in general by a rather large number of exponentials. Experimental fluorescence intensities were first deconvoluted analyzing data for each temperature independently in terms of the microscopic parameters using the Individual Target Analysis (ITA) procedure, described in Reference 11, with a modified Gauss-Newton-Marquardt non linear least-squares fitting. We emphasize that the aim of this type of analysis is not to perform a fit of the intensities to a sum of free exponential decays but rather to choose a model potential and fit the smaller number of parameters that determine the model. Assuming a pure P_2 potential each measurement in the nematic and isotropic phase was individually analyzed and the relative reduced chi-square χ_r^2 was minimized in terms of (i) probe order parameter $\langle P_2 \rangle$ and (ii) probe rotational diffusional coefficient $D_\perp$.

Results from ITA were used as starting points for the Global Target Analysis.[4,10,19] This was found to be an important practical point, because a good selection of starting parameters significantly reduces the computing time required to reach the minimum of the global chi-square. Globalization is based on the consideration that in our problem we have a set of parameters, the maximum entropy coefficients $a_2(T)$, $a_4(T)$, as well as $D_\perp(T)$, that are linked by a continuity relation and can be assumed to be smooth, except at a phase transition, where they can change quite rapidly. Even if we do not know *a priori* a linking relation, the constraint of them lying on a continuous curve may be strong enough to allow searching for a global fit rather than a local, possibly over-optimistic one. In other words we trade a solution which corresponds to the very minimum χ_r^2 at a certain temperature, which however could be a non-physical one, with an overall optimal solution for all the temperatures at the same time.

The problem of finding an interpolating relation that is flexible enough to accommodate every possible variation of the parameters, without pre-determining the results, was tackled in Reference 10 with the use of exponential splines, assuming that the temperature variation of the parameters $a_2(T)$, $D_\perp(T)$ and $\tau_F(T)$ can be interpolated by this kind of functions and fitting the position of the spline knots. In this way it is possible to substantially limit the number of parameters involved in the fit and to extend the analysis across the phase transition even if drastic changes occur for some parameters. We adopted a four-knot spline for $a_2(T)$ while for $D_\perp(T)$ and $\tau_F(T)$ we have used a three-knot spline. The other parameters involved (see Reference 4), i.e. time-shift, scale and scattering factors were fitted individually at each temperature. The correction factor accounting for the different sensitivity of the detection system to the vertical and horizontal polarization was determined according to the procedure proposed in Reference 27 and was 1.13. This value was used both in the individual and global analyses.

RESULTS AND DISCUSSION

Individual Target Analyses

A preliminary deconvolution was performed at every temperature on the total intensity $I_{ZZ} + 2I_{ZX}$ to achieve information on the fluorescence lifetimes τ_F of DPA. The kinetics of the probe decay was found to be monoexponential in the whole temperature range, with a lifetime ranging from 7.4 to 7.5 ns.

Afterwards the experimental intensities were analyzed, with the model mentioned previously, over 400 channels, obtaining χ_r^2 values ranging from 1.03 to 1.24. The results found for the fluorescence lifetime τ_F, the second-rank order parameter $\langle P_2 \rangle$ and the rotational diffusion coefficient $D_\perp$ for the probe DPA are plotted as a function of temperature in Figures 3A, 3B and 3C.

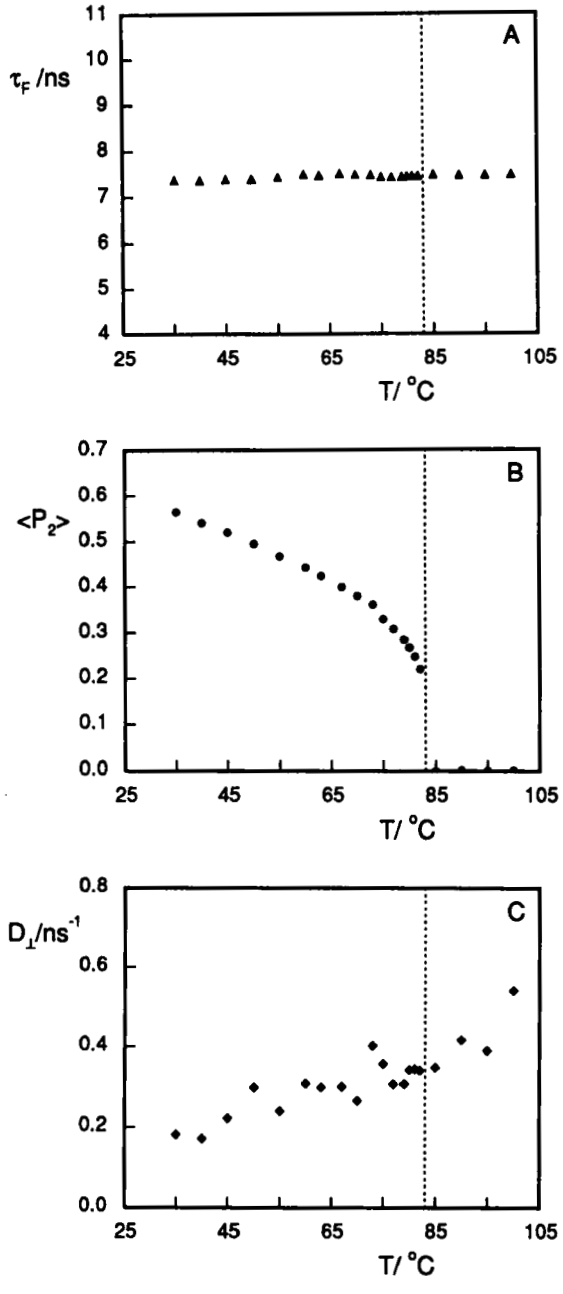

FIGURE 3. Results of the individual target analyses with a pure P_2 potential for DPA in ZLI-1167. We show the fluorescence lifetime τ_F (A), the second-rank order parameter $\langle P_2 \rangle$ (B) and the rotational diffusion coefficient $D_\perp$ (C) as a function of temperature. The vertical dotted line indicates the nematic-isotropic temperature.

Global Target Analysis

The GTA procedure with exponential splines, carried out on all the intensities at the same time (i.e. considering about 16,000 experimental points) and using a simple P_2 trial potential gave a global χ^2_r of 1.45. In Figures 4A, 4B and 4C we show the relative results obtained for the fluorescence lifetime τ_F, the second-rank order parameter $\langle P_2 \rangle$ and the rotational diffusion coefficient $D_\perp$ for the probe DPA as a function of temperature. We see that the sharp change in the temperature variation of the order parameter $\langle P_2 \rangle$ at the phase transition can be well fitted by the exponential spline interpolation. Moreover the rotational probe mobility increases regularly with temperature, as shown by the behavior of the diffusion coefficient.

Rotational dynamics

We now compare the values of the rotational diffusion time $\tau_R = 1 / (6 D_\perp)$ of DPA in the range of temperatures corresponding to the isotropic phase of the liquid crystal with the predictions of the generalized Stokes-Einstein-Debye (SED) theory.[12-17] According to this theory the rotational diffusion time τ_R of a solute in a certain solvent can be written as

$$\tau_R = f C \frac{V \eta}{k_B T} \tag{9}$$

where V is the van der Waals volume of the solute molecule, η is the solvent's shear viscosity, f is a factor dependent on solute's molecular shape, C is a hydrodynamic boundary conditions factor and k_B is the Boltzmann constant. The best way of comparing this kind of results is probably that of examining the ratio $\gamma = \tau_R / (\eta / T)$ which eliminates the direct dependence on temperature and viscosity. Thus γ should be a constant for a certain solute-solvent system. Using our experimental rotational diffusion times and interpolating the viscosity values reported in Reference 28 for the isotropic phase of the ZLI-1167 liquid crystal we obtained a mean value for γ

$$\gamma_{DPA} \equiv \frac{\tau_{R,DPA}}{\eta / T} = 2.1996 \times 10^4 \text{ ps cP}^{-1} \text{ K} \tag{10}$$

Adopting the molecular dimensions reported in Reference 16 and the usual relations for stick boundary conditions[12-14] we then calculated the van der Waals volume V and the shape factor f for the prolate ellipsoid DPA (see Table I), obtaining for $\gamma^{stick} \equiv \tau_R^{stick} / (\eta / T) = f V / k_B$ a value of 4.5463×10^4 ps cP^{-1} K (cf. Table I). For slip boundary conditions no analytical formula is available, but a good approximation of $\gamma^{slip} \equiv \tau_R^{slip} / (\eta / T) = C \gamma^{stick}$ can be obtained once the factor C, which corresponds to the ratio between the friction coefficient with slip and that with stick boundary conditions, is

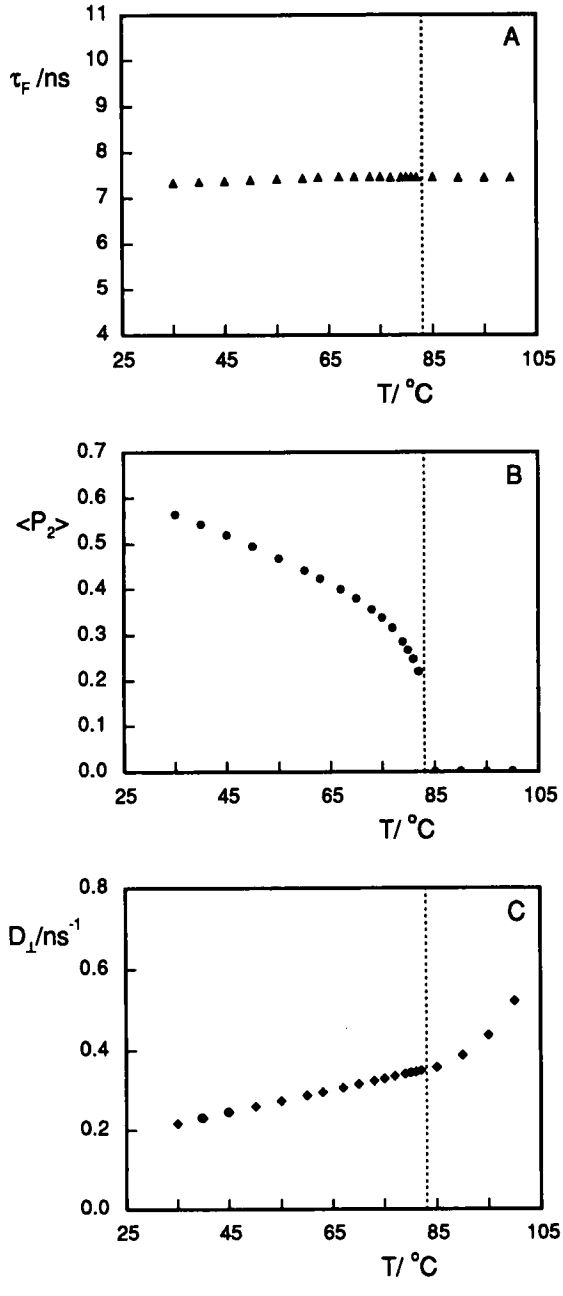

FIGURE 4. Results of the global target analysis with a pure P_2 potential for DPA in ZLI-1167. We show the fluorescence lifetime τ_F (A), the second-rank order parameter $\langle P_2 \rangle$ (B) and the rotational diffusion coefficient $D_\perp$ (C) as a function of temperature. Global $\chi_r^2 = 1.45$. The vertical dotted line indicates the nematic-isotropic temperature.

known by interpolating the numerical values calculated by Hu and Zwanzig[29]. In this way we obtained for γ^{slip} a value of 1.7571×10^4 ps cP^{-1} K (cf. Table I).

TABLE I Hydrodynamic parameters for DPA, DPH and DPO fluorescence probes

	a /nm	b /nm	V /nm^3	f	τ_R^{stick} / (η / T) / 10^4 ps cP^{-1} K	τ_R^{slip} / (η / T) / 10^4 ps cP^{-1} K
DPA	0.8	0.305	0.312	1.996	4.5463	1.7571
DPH	0.7	0.282	0.233	1.878	3.1944	1.1364
DPO	0.82	0.276	0.261	2.317	4.4136	2.0027

It is interesting to note that the experimental γ value for this system falls in the range between the two hydrodynamic limits, even though very close to the slip one. This indicates that DPA dynamics in the isotropic phase of this liquid crystal approaches the hydrodynamic behavior under slip boundary conditions, as could be expected for a nonpolar solute in a solvent of relatively low polarity.

We have also compared in Figure 5 our results with those obtained for DPA in simple solvents.

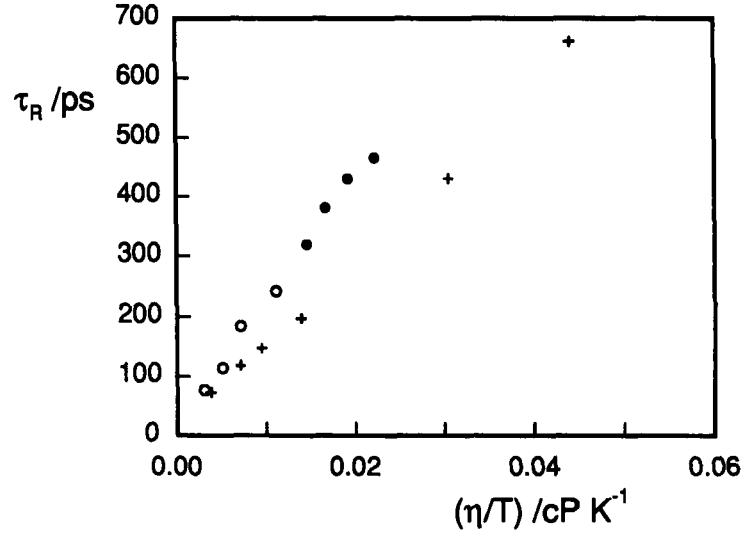

FIGURE 5. Rotational diffusion time τ_R (•) for DPA in the isotropic phase of the ZLI-1167 liquid crystal as a function of η / T. We also show results from Ben-Amotz *et al.*[16] for DPA in *n*-alkanes (o) and *n*-alcohols (+).

In this figure we have plotted our values for the rotational diffusion time τ_R (●) as a function of η / T and compared them with results from Ben-Amotz *et al.*[16] for DPA in *n*-alkanes (o) and *n*-alcohols (+). It is comforting to see that the values determined here show the same linear behavior as reported for *n*-alkane solvents. Moreover, if we consider the ratio τ_R / τ_R^{stick}, the value of 0.48 that we obtain is in good agreement with the value of 0.53 reported in Reference 16 for DPA in *n*-alkanes. Both systems thus seem to show the same slip dynamical behavior, probably because of the weak interactions between solute and solvent that take place in both cases.

We now turn to the comparison between DPA and the two other fluorescence probe DPH and DPO. In the isotropic phase the reorientation of the more voluminous probe DPA is significantly faster than that of DPO and similar to that of the shorter DPH molecule. This is possibly due to the fact that the motion of DPA is more of a slip type. In turn this could be rationalized considering that DPA is not rigid and that its tumbling could be coupled to a change of internal torsional angle, so as to reduce the volume of solvent that has to be displaced on reorientation. The effect of different hydrodynamic boundary conditions in the nematic phase is more difficult to take into account because of the lack of simple analytical formulations, but this torsional-slip mechanism could help in explaining the faster reorientation of DPA compared to DPO.

CONCLUSIONS

We have studied the fluorescence probe DPA in a nematic mesophase by means of the fluorescence depolarization technique. We have shown that the Global Target Analysis approach can be used to extract information about the temperature dependence of the lifetime, the second-rank order parameter and the rotational diffusion coefficient for the fluorescence probe molecule. In particular the exponential spline interpolation was confirmed to be extremely useful in analyzing the system across the nematic-isotropic phase transition. The biaxiality of the probe can be assumed to be small, in agreement with independent ^{13}C NMR findings. The dynamic behavior of DPA in the isotropic phase of the liquid crystal approximates the predictions of the slip boundary conditions hydrodynamic limit, as expected in the absence of strong solute-solvent interactions. The rotational diffusion times obtained are in good agreement with results for the same probe dissolved in *n*-alkane solvents. A comparison of the rotational times for DPA, DPH and DPO suggests the importance of rotational torsional coupling for DPA both in the isotropic and the nematic phase. We believe that a systematic study of simple fluorescence probes with well defined shapes can be very important in establishing a relation between molecular dimensions and reorientation times both in the nematic and the isotropic phase.

ACKNOWLEDGMENTS

We are grateful to MURST, CNR and EC HCM (CT930282) for support for this work. We also thank Dr. R. Tarroni for useful discussions.

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