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Dynamics of Partially Oriented L-Phenylalanine- d_8 in the CsPFO/H₂O Lyotropic System via ^2H NMR Relaxation Studies

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Dynamics of the L-phenylalanine- d_8 has been here investigated by analyzing the ^2H NMR spin–lattice relaxation times of this selectively deuterium enriched amino acid diluted in the cesium pentadecafluorooctanoate/water (CsPFO/H₂O) lyotropic system both in the nematic (N^+D) and in the lamellar (L_D) phases. Information on the internal and overall molecular motions as well as on collective motions has been achieved by a global fitting procedure. The dynamic processes affecting this probe molecule reflect its particular conformational and interaction properties with respect to the lyotropic environment. The best reproduction of the experimental data is obtained by assuming free internal reorientations of the benzylic moiety, which results in diffusion constants of the same order of magnitude of the overall molecular spinning motion. Moreover, the contribution of collective motions (order director fluctuations and layer undulations) is estimated to be greater than that commonly observed by other techniques in lyotropic systems.

1. Introduction

Among liquid crystalline mesophases, those formed from *amphiphiles* (i.e., surfactants) dissolved in solvents, typically water, are known as lyotropic liquid crystalline (LLC) phases.^{1,2} These LLC phases formed by surfactants may exhibit a rich polymorphism of structures and aggregates, such as micellar or lamellar ones, whose features depend on temperature, pressure, and surfactant concentration. The interest in these systems lies mainly in their many possible applications: surfactant-based LLCs show the same interesting applications of their thermotropic analogues for display and sensing technologies, but thanks to their variety of mesophases they also have other interesting and distinctive uses, such as nanoarchitecturing and biosensing for specific devices.^{3,4} Many of these LLC applications are linked to the presence, not compulsory to induce a general mesophasic behavior, of host molecules (“guest solutes”). Due to the presence of different components, these possibly dissolved “guests” show a less defined status than those in thermotropic phases and can be classified from a practical point of view in three partially interrelated types: (i) “dopants”, that is, molecules inducing particular structures and properties to lyotropic phases;^{5–7} (ii) “probes”, that is, molecules that induce slight or no change on the LLC nature but that can be used by specific techniques to detect molecular-level properties of the whole

host matrix;⁶ and (iii) “guests”, that is, molecules that induce a slight change on the LLC nature but experience an effect from their surrounding environment which can be of great interest.⁷ At a microscopic level, in classical surfactant-based LLCs, these host molecules can be considered as (a) included entirely in the aggregates; (b) excluded entirely from the aggregates; (c) in exchange between the previous extreme situations; and (d) mainly in the solvent solution but spending appreciable time on the interface solvent/aggregate. Unfortunately, the monitoring of this microscopic-level behavior of “guest”, “dopant”, or “probe” molecules in lyophases is still marginal in the scientific literature compared with its great potential interest. It is evident that most of the experimental techniques commonly used to study LC phases, such as X-ray diffraction, calorimetry, and microscopy,^{2,8} are more focused on the general mesomorphic behavior of the phases and are useful in characterizing the order–disorder transition, the nature and the stability ranges of different phases, or the shape of their supramolecular aggregates.⁹ Different molecular-level spectroscopic techniques are instead more advised for the survey of single molecules solved in the mesophases, both as a structural components (“mesogen”) and as a simple hosted molecule. Among them, together with fluorescence and ESR/EPR studies,^{7b} nuclear magnetic resonance (NMR) spectroscopy is one of the most important ones,¹⁰ enabling one to investigate the partitioning of LLC components and the dynamic behavior and conformation properties of both “guest” and “host” molecular systems.¹¹ Most of the NMR studies centered on the dynamic properties of LLC systems focus on aqueous lyophases of small molecular weight components.¹² These works concern mostly the mesogens¹³ and rarely “guest” molecules

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solved in the lyotropic phases.¹⁴ Among the different NMR techniques specifically applied to study the dynamic properties of LLC mesogens, ¹H and ²H NMR relaxation methods are the most widely reported, although pulse field gradient spin–echo diffusion experiments and line shape analysis simulation are also used.^{15–29} Several kinds of motion can be characterized by means of these NMR approaches with the help of suitable theoretical models.^{30,31} In the surfactant-based lyotropic phases, due to the complexity of the molecular system, which has usually two or three different components and is generally not homogeneous, the following motions can be found: (i) collective motions, such as order director fluctuations,¹⁰ which can be “three dimensional” ones, or order director fluctuations (ODFs), typical of nematic phase, and “two dimensional” ones, or layer undulations (LUs), typical of smectic and lamellar phases;^{20–25} (ii) reorientational molecular motions¹⁶ of the different molecular components, which can be further divided in overall molecular reorientations and internal motions (particularly important in the amphiphilic molecules, such as, for example, the segmental motion of alkyl chains);^{17,18} (iii) translational diffusion motions, which may be sensibly different inside the micelles, if any, at the interface water/amphiphilic system and in the water bulk.¹⁵ All this considered, the separation among the different dynamic contributions is not straightforward, since in most of the cases a partial overlapping among dynamic motions at a certain frequency occurs especially with very flexible molecular moieties such as surfactant side chains. It should never be forgotten that the base units of a lyophase are usually aggregates instead of molecules, that can show a complex dynamics situation even at their inside. However, some general considerations can be drawn based on several works reported in the literature. ¹H NMR dispersions of spin–lattice relaxation times in various lyotropic phases revealed to be useful in identifying in the internal reorientations and lateral diffusion motions the main dynamic processes of the lyotropic surfactants active in the high frequency regime ($\omega > 10^6$ Hz). On the contrary, according to ¹H NMR relaxation,^{17,23} the low frequency regime ($\omega < 10^5$ Hz) is dominated by collective motions, in particular in the lamellar phases.¹⁸ However, it should be noticed that some exceptions to this classification of motions according to their typical

frequency regime have been reported during the previous years in the scientific literature. The contribution of collective motions in nematic lyophases has been mainly investigated by Halle et al.²⁰ by modeling ²H NMR spin–spin relaxation times (T_2). Significant improvements come also from the development of more sophisticated models for the analysis of T_2 by Khote et al.²³ It is worth noticing that collective motions have been found to influence not only transverse but also longitudinal relaxation (in particular T_{1Q}), thus indicating that their contribution may be not negligible at higher frequencies.^{28,29} ²H, ¹H, and ²³Na NMR relaxation as well as ²H line-shape analysis^{15,25,26} have also been applied to the characterization of translational diffusion through the different regions of isotropic, not-oriented, and oriented LLC systems. Moreover, ²H NMR longitudinal relaxation studies^{13,16} were recently applied to perdeuterated LLC molecules, and the analysis by means of the existing small step rotational diffusion theories³⁰ gave a satisfactory description of the overall molecular and conformational reorientations.

In this Article, we will focus on the dynamic investigation of a deuterium enriched L-phenylalanine-*d*₈ solved in the uniaxial nematic (N^+_D) and lamellar (L_D) phases of the amphiphile cesium pentadecafluorooctanoate/water (CsPFO/H₂O) system^{32–34} by means of ²H NMR spin–lattice relaxation spectroscopy. The analysis of spectral motional densities obtained by relaxation analysis in terms of reorientation diffusion properties of the “guest” will be discussed taking into account the conformational and ordering properties of this molecular system, previously determined.³⁵ The peculiarity of this LLC³⁴ and the scientific interest in the amino acid derivative/liquid crystal interactions have justified the efforts of our group in deeply investigating both orientational³⁵ and dynamic features of the L-phenylalanine-*d*₈ in this particular lyotropic environment. It should be stressed here that the L-phenylalanine molecules stay outside the micellar units in both lyophases and that they are supposed to interact with the micellar surface mainly due to electrostatic forces. Moreover, the orientational study as well as the recorded spectra³⁵ clearly indicate that the “guest” molecules are well oriented, thus feeling the anisotropic environment typical of the lyotropic phases. For this reason, we can assume that the L-phenylalanine-*d*₈ molecules are located mainly outside the micellar aggregates, spending appreciable time on the interface water/micellar aggregate (case (d) in the previous classification).

To our best knowledge, this is the first ²H NMR spin–lattice relaxation study of an amino acid molecule dissolved in a LLC system. The main purpose of the present study is to characterize the dynamic processes affecting the “guest” molecule in the CsPFO/H₂O lyophases in the MHz frequency regime, thus validating the previous results concerning both the conformational and ordering properties.³⁵ Moreover, the obtained results will be discussed in the frame of the molecular dynamics of liquid crystals.^{13,36}

2. Theory

The ²H NMR Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin–lattice relaxation times are directly related, through the

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Redfield theory,³⁷ to the spectral densities of motions, $J_i(\omega)$, at the Larmor frequency and at twice this frequency as follows:

$$\frac{1}{T_{1Z}} = J_1(\omega_0) + 4J_2(2\omega_0) \quad (1)$$

$$\frac{1}{T_{1Q}} = 3J_1(\omega_0) \quad (2)$$

where ω_0 is the Larmor frequency. Generally, several motional processes contribute to the spectral densities, which can be defined as the Fourier transforms of the autocorrelation functions describing the time modulation of the Hamiltonian of the system.¹³ By using suitable theoretical models, it is possible to extract all the information on these motions, which can be divided according to the previous classification.²¹ Among these models, the simplest ones used for describing the overall molecular motions in uniaxial phases for uniaxial molecules are the *diffusion in a cone*,³⁸ the model proposed by Nordio and Busolin,³⁹ and the theoretical approach developed by Freed and co-workers (called *anisotropic viscosity* model).⁴⁰ All of them consider these motions as small step diffusion rotations in a Maier–Saupe mean field potential. Further extension of the *anisotropic viscosity* model is that proposed by Vold and Vold⁴¹ (called *third rate anisotropic viscosity* model), while the theories developed by Tarroni and Zannoni⁴² and Berggren et al.⁴³ take into account either molecular or phase biaxiality. Internal motions, which are usually considered decoupled from the overall molecular ones, can be described in an isotropic potential by means of either small step diffusion⁴⁴ or strong collision models.⁴⁵ However, recent analyses on thermotropics³⁶ have shown that these two models are almost equivalent in the case of achiral molecules, while the small step diffusion fails in describing the internal motion of chiral smectogens. In uniaxial phases, such as the nematic one, collective motions mainly consist of order director fluctuations (ODFs), which were modeled by Pincus⁴⁶ and Blinc et al.,⁴⁷ or layer undulations (LUs), modeled by Blinc et al.⁴⁸ Their contribution to the relaxation processes, and in particular to the spectral density $J_1(\omega_0)$, can be estimated only in the case of multifrequency studies, as that reported in this paper. Different theoretical approaches for the description of collective motions are used in the case of ²H spin–spin relaxation studies^{13,23} and ¹H NMR relaxometry.^{17,18}

The theoretical models cited above have been widely used to investigate the reorientation dynamics of both thermotropic and lyotropic LC systems.^{13,16,36} Moreover, the first ²H NMR longitudinal relaxation studies based on the application of these theoretical models^{38–40} were applied to “guest” molecules solved in thermotropic liquid crystals.^{30,31,49} The application of these models to “guest” molecules diluted in LLC systems, despite their heterogeneity and complexity, seems to be justified in the present

case, since, based on previous ordering studies,³⁵ the L-phenylalanine-*d*₈ feels an average anisotropic environment mainly due to electrostatic interactions with the micellar surface, without entering inside these aggregates. Moreover, translational diffusion or exchange dynamics between the guest molecules interacting with the micellar surface and guest molecules dissolved in the bulk water are expected to have a marginal effect^{10,13} on the ²H longitudinal relaxation process object of this analysis due to its sensitivity and characteristic time. Another important feature, which will be also discussed in the next section, is related to the monoexponential behavior of the magnetization decays measured for each deuteron site. This finding supports and justifies our quantitative treatment of relaxation data. In particular, the analysis of the relaxation times has been here carried out using the Nordio model for the overall molecular motions assuming a uniaxial symmetry for the investigated molecule (also confirmed by the ordering investigation).³⁵ The strong collision model was chosen to describe internal motions (namely, reorientations of the phenyl ring and the CH₂ directly linked to the aromatic moiety). On the basis of the Nordio model, the correlation times $\tau_{m_L m_M}^{(j)}$ related to the overall molecular motions can be expressed in terms of the rotational diffusion coefficients through the following relationship:³⁹

$$\frac{1}{\tau_{m_L m_M}^{(j)}} = \frac{6D_{\perp}}{b_{m_L m_M}^{(j)}} + m_M^2(D_{\parallel} - D_{\perp}) \quad (3)$$

where D_{\parallel} and D_{\perp} are the principal components of the diffusion tensor, diagonalized in a molecular frame, describing the molecular spinning and tumbling motions, respectively. The superscript (j) refers to the fact that the autocorrelation functions solving the rotational diffusion equations take the form of decreasing multi-exponential expressions. To take into account the internal motions, the “superimposed rotations” model⁴⁵ is considered. Within this approach, where the independence of internal with respect to overall motions is assumed, the theoretical expression for the spectral densities J is given by⁴¹

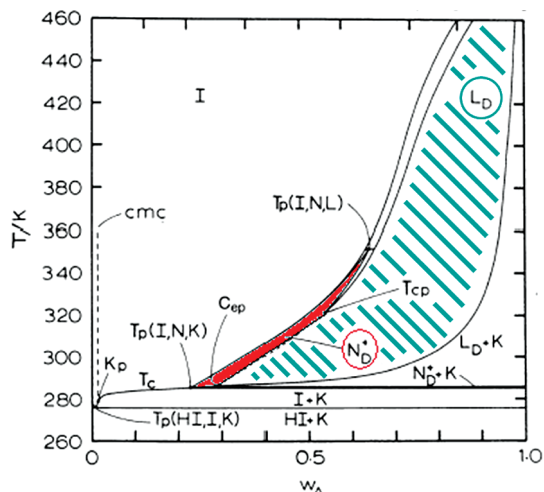
$$J_{m_L}(m_L \omega_0) = \frac{3\pi^2(\nu_q)^2}{2} \sum_{m_M=-2}^2 \sum_{m_R=-2}^2 c_{m_L m_M} \left[d_{m_R 0}^2(\beta_{i, Q_i}) \right]^2 \left[d_{m_M m_R}^2(\beta_{M, i}) \right]^2 \sum_j a_{m_L m_M}^{(j)} \frac{\left(\tau_{m_L m_M}^{(j)} \right)^{-1} + \xi(m_R) D_i}{(m_L \omega_0)^2 + \left[\left(\tau_{m_L m_M}^{(j)} \right)^{-1} + \xi(m_R) D_i \right]^2} \quad (4)$$

where ν_q is the quadrupolar coupling constant, d_{rs}^2 are the reduced Wigner matrices, β_{i, Q_i} is the angle between the C–D bond and the axis about which the internal rotation takes place, $\beta_{M, i}$ is the angle between this axis and the molecular long axis, D_i is the diffusion coefficient relative to the internal rotation of the fragment considered, and $\xi(m_R)$ is $(1 - \delta_{m_R})$ in the strong collision diffusion model for this motion. The coefficients $a_{m_L m_M}^{(j)}$, $b_{m_L m_M}^{(j)}$, and $c_{m_L m_M}^{(j)}$ appearing in eqs 3 and 4 have been calculated in ref 41 as a function of the principal order parameter S_{ZZ} for a Maier–Saupe potential.

The contribution of collective motions in the high frequency regime is usually very small, and it is limited to a contribution at the first order to the spectral density $J_1(\omega_0)$. As reported in the literature for other liquid crystals,¹⁰ this contribution is considered additive to the spectral densities arising from overall and

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Scheme 1. Phase Diagram (Temperature (T/K) versus Weight Fraction (W_A)) of the Amphiphile/Water System CsPFO/ H_2O , Modified from ref 33^a



^a The range of stability of the nematic N_D^+ and lamellar L_D phases are marked in red and green, respectively.

internal motions, reported in eq 4. The following relationship can be considered:

$$J_1^{DF,i}(\omega_0) = \frac{3\pi^2}{2} (\nu_q)^2 d_{00}^2 (\beta_{i,q})^2 d_{00}^2 (\beta_{M,i})^2 S_{zz}^2 T \frac{a_{DF}}{\omega_0^5} \quad (5)$$

where ξ equal to $1/2$ corresponds to the frequency dependence predicted by Pincus⁴⁶ and Blinc et al.⁴⁷ for the ODFs in the nematic and SmA phases,⁵⁰ while ξ equal to 1 refers to layer undulations (LUs), typical of smectic phases, according to the model proposed by Blinc et al.⁴⁸ In eq 5, a_{DF} is a coefficient specific of the chosen models, which depends on macroscopic parameters such as the average Frank elastic constant and, in the case of ODFs, the viscosity coefficient or, in the case of LUs, the coherence length along the layer normal.

The above equations (from eq 1 to eq 5) have been used in the relaxation analysis reported in section 4.

3. Experimental Section

3.1. Materials. The material under investigation is constituted by the perdeuterated amino acid L-phenylalanine- d_8 dissolved in the LLC CsPFO/ H_2O mixture, one of the most used lyotropic aligning media.⁵¹ This particular micellar system, at an amphiphile/water weight ratio of about 0.40, shows two contiguous uniaxial liquid crystalline phases when the temperature is decreased from the isotropic solution: a nematic (N_D^+) phase and a lamellar (L_D) phase, both formed by discotic aggregates of variable size. The CsPFO/ H_2O system is a quite peculiar one,^{32,33} since it is a binary system showing very large temperature and concentration ranges of stability of the nematic phase. Moreover, the nematic phase has a positive magnetic susceptibility; this means that the oblate discotic micelles orient with the normal parallel to the magnetic field, when the system is cooled down from the isotropic phase. This orientation is retained when passing in the lamellar phase, which consists of a planar arrangement of such finite micellar disks. This is also a peculiar feature of the CsPFO/ H_2O mixture. In fact, lamellar phases usually have infinite bilayered structures. The size of these micellar units changes with the

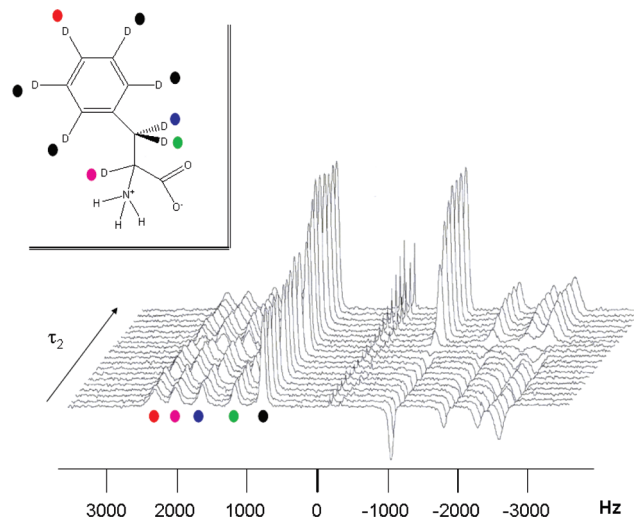


Figure 1. Series of 2H NMR spectra recorded at 28.5 °C (Larmor frequency of 46.0 MHz) by applying the broadband version of the Jeener–Broekaert sequence,⁵⁴ as described in the text. The delay τ_2 increases as indicated by the arrow. The signals of the deuterons of L-phenylalanine- d_8 in the oriented N_D^+ phase are assigned as follows: (red circle) aromatic para (ap), (purple circle) alpha methynic (α), (green circle) methylenic (m1), (blue circle) methylenic (m2), and (black circle) aromatic ortho/meta (om). The thin central peaks are the signal of naturally deuterated water.

temperature and with the concentration in a quite complex way.⁵² In particular, the axial ratio a/b ranges between 0.23 and 0.55 with $a = 2.2$ nm. The aggregation number varies with the temperature in the range 250–300. Scheme 1 reports the phase diagram of the CsPFO/ H_2O system as a function of the amphiphile/water molar fraction.³³ The phase transitions observed in our case are the following: Iso–29.5 °C– N_D^+ –27 °C– L_D . The concentration of the L-phenylalanine- d_8 dissolved in the CsPFO/ H_2O is 0.001 in weight (amino acid/ H_2O). The preparation procedure and the conformational properties of the investigated “guest–host” LLC system studied by means of 1H and 2H NMR are reported in ref 35.

3.2. NMR Measurements. 2H NMR relaxation experiments were performed by using two NMR spectrometers working at different magnetic fields: (i) a 7.05 T Varian VXR-300 spectrometer (deuterium Larmor frequency of 46.0 MHz) and (ii) a 4.70 T Varian Gemini BB-200 spectrometer (deuterium Larmor frequency of 30.7 MHz). In both cases, the LLC system was microscopically aligned within the magnet by slow cooling from the isotropic phase. The analysis of the recorded 2H NMR static spectra in terms of orientational order and conformational properties of the “guest” molecule L-phenylalanine are reported elsewhere.³⁵ As pointed out in the Introduction, the L-phenylalanine molecules stay outside the micellar units in both lyophases and in the present analysis they are supposed to interact with the micellar surface mainly due to electrostatic forces. Previous studies³⁵ clearly indicate that the “guest” molecules are well oriented, thus feeling the anisotropic environment typical of the lyotropic phases. The previous investigation³⁵ indicates that, with respect to the general classification of host molecules in surfactant-based LLCs, our system fits the case (d): the host molecules are mainly in the solvent solution but spend appreciable time on the interface solvent/aggregate.

2H Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) spin–lattice relaxation times of the L-phenylalanine- d_8 diluted in the nematic (N_D^+) and lamellar (L_D) phases of the CsPFO/ H_2O system were measured at several temperatures in the range 24–29 °C by applying the broadband version of the

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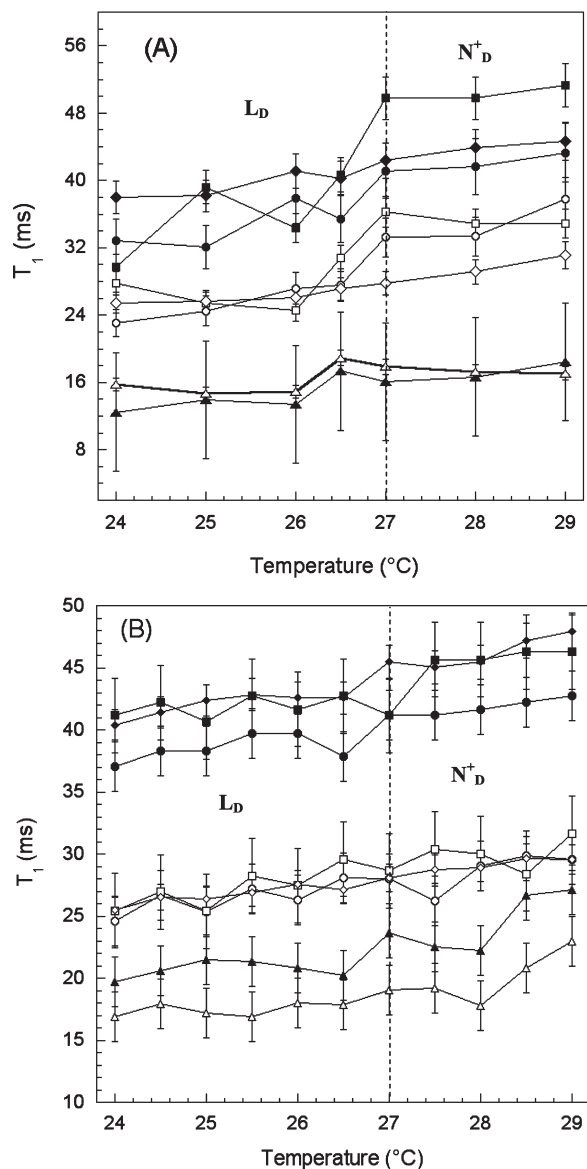


Figure 2. ^2H NMR relaxation times T_{1Q} (full symbols) and T_{1Z} (empty symbols) measured at 30.7 MHz (A) and 46.0 MHz (B). Circles, squares, tilted squares, and triangles refer to methylenic (m1), methylenic (m2), aromatic ortho/meta (om), and aromatic para (ap) deuteron signals, respectively. Experimental errors are also shown.

Jeener–Broekaert pulse sequence,⁵³ modified by Wimperis:⁵⁴ $90_0-2\tau_1-67.5_{270}-2\tau_1-45_{90}-\tau_1-45_{90}-\tau_2-45_0-\text{ACQ}$. Temperature was controlled with a precision of 0.1 °C and a thermal equilibration of about 30 min before acquiring at each investigated temperature. Figure 1 shows a series of ^2H NMR spectra recorded by varying the delay τ_2 at $T = 26$ °C (deuterium Larmor frequency of 46 MHz). The assignment of the deuteron signals used for the analysis is also reported in Figure 1.

The parameters of the sequence have been optimized⁵⁵ as reported in the following: the value of the delay τ_1 was fixed to 15 μs , the variable delay τ_2 ranged from 0.1 to 630 ms, and a relaxation delay of 0.5 s and a number of scans of 12 000 were used at 46 MHz. The 90 degree pulse was 17.5 μs . At 30.7 MHz, the value of the delay τ_1 was fixed to 12.5 μs , the variable delay τ_2 ranged from 0.1 to 420 ms, and a relaxation delay of 0.52 and 15 000 scans were used. The 90 degree pulse was 9.3 μs .

An IDL routine was developed to obtain the relaxation times T_{1Z} and T_{1Q} for each deuteron site from the fitting of the integrals of the deuteron signals as a function of the variable delay τ_2 . (Interactive Data Language (IDL) is a software product of American ITT Visual Information Solutions, mainly used in astrophysics and meteorology, <http://www.itvis.com/idl/whatsnew.asp>.)

In particular, for each deuteron, T_{1Z} and T_{1Q} were obtained by fitting the sum and the difference of the integrals of each component of the quadrupolar doublet as function of the variable delay τ_2 . The equations used for the fittings,⁵⁶ which differ from those theoretically predicted⁵⁷ for taking into account possible experimental imperfections, are the following:

$$M_+(\tau_2) = A[1 - B \exp(-\tau_2/T_{1Z})] \quad (6)$$

$$M_-(\tau_2) = C + D \exp(-\tau_2/T_{1Q}) \quad (7)$$

It is important to put in evidence that in all cases the trends of both $M_+(\tau_2)$ and $M_-(\tau_2)$ are monoexponential ones. The monoexponential feature of the magnetization decay excludes the presence of different components to the longitudinal relaxation rates, R_{1Z} and R_{1Q} , such as, for instance, different contributions coming from “guest” molecules in the bulk and “guest” molecules at the micellar interface. This finding supports the treatment of the relaxation data reported in section 4.

The relaxation times recorded at 46.0 and 30.7 MHz for the deuteron signals referred as aromatic (ARO) and methylenic (CD_2) groups (see Figure 1) are reported in Figure 2. Experimental spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ were calculated from the measured relaxation times by applying eqs 1 and 2.

4. Results and Discussion

In order to undertake a quantitative analysis of the spin–lattice relaxation times, the knowledge of the orientational ordering features of the studied system, namely, the elements of the Saupe ordering matrix, which is the second rank matrix of the microscopic order parameters, is required. At this purpose, the system of isotopically enriched L-phenylalanine in the uniaxial nematic (N^+D) and lamellar (L_D) phases of CsPFO/ H_2O was previously studied by Borsacchi et al.³⁵ Moreover, the analysis of the ^2H NMR spectral features of this system allowed the determination of a “mean” or “effective” conformation of the L-phenylalanine, which was used for the present study. According to this previous investigation,³⁵ the amino acid molecules feel the micellar environment and preferentially orient with the charged amino group close to the anionic surface of the micelles (see Scheme 2). This finding is also supported on one side by the nature of the CsPFO system which is a fluorinated environment (in fact, the fluorinated inside medium excludes any penetration by a protonated molecule),⁵⁸ and on the other side by its similarity to the ring orientation of the benzyl alcohol dissolved in other LLC phases.^{7c} In this mean conformation, the para axis of the phenyl ring is tilted 145.1° with respect to the “z” molecular axis (Scheme 2).

The orientational ordering matrix, S , previously determined,³⁵ indicates that, despite the complexity and heterogeneity of the system, which typically distinguishes lyotropic from thermotropic cases,¹² the L-phenylalanine- d_8 molecules feel

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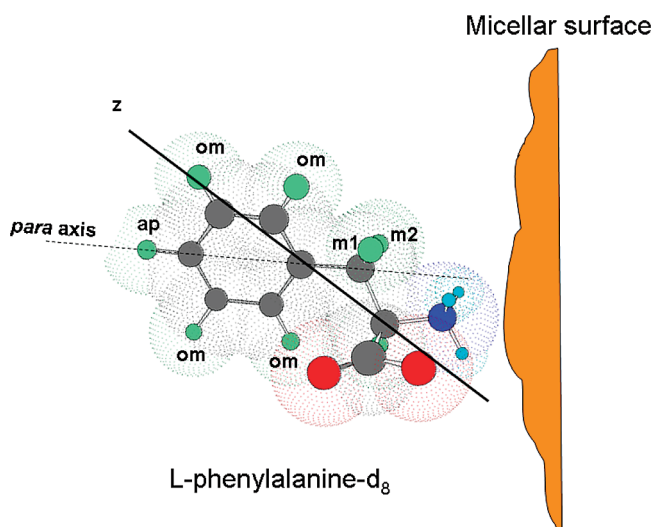
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Scheme 2. Representative Picture of the L-Phenylalanine- d_8 in Its Mean Conformation Diluted in the Uniaxial Nematic (N^+_D) Phase of the CsPFO/H $_2$ O System^a



^a Labels relative to the deuterons are shown. The principal molecular axis, z ,³⁵ and the para axis of the deuterated phenyl ring are also displayed.

an average anisotropic homogeneous environment. In particular, the principal order parameter, S_{zz} , ranges from 0.056 to 0.098 by decreasing the temperature in the range 24–29 °C. These values are comparable with those found in the case of solutes diluted in thermotropic liquid crystals.¹³ Moreover, almost vanishing order biaxiality, $S_{xx}-S_{yy}$ (< 0.01), justifies the assumption of molecular uniaxiality for the L-phenylalanine- d_8 used for the relaxation analysis.

Based on the ordering results, the ^2H NMR relaxation times T_{1Q} and T_{1Z} (see Figure 2) of the L-phenylalanine- d_8 dissolved in CsPFO/H $_2$ O were analyzed in terms of dynamic parameters taking into account the benzylic part of the deuterated solute. Since the benzylic moiety is the most rigid part of the L-phenylalanine- d_8 , it should mimic the behavior of the whole molecule in the LLC environment. Two groups of deuteron signals were considered: (i) the aromatic group (ARO), consisting of the para signal (ap) and the partially overlapped couple of signals (om) corresponding to the ortho/meta positions and (ii) the methylenic group (CD $_2$), consisting of two signals (m1 and m2). The number of different relaxation times measured at each temperature for each Larmor frequency is equal to 8 (4 T_{1Q} and 4 T_{1Z}). In fact, the ortho/meta positions contribute to the same relaxation times. Moreover, the relaxation data were collected at 11 and 7 different values of temperature for the lower (30.7 MHz) and higher (46.0 MHz) Larmor frequencies, respectively. All this considered, the data set was constituted by 144 experimental points. As it can be seen from Figure 2, the relaxation times slightly decrease by decreasing the temperature, indicating a fast regime ($\omega_0\tau_c < 1$) for the motions mainly contributing to the relaxation, in agreement with what usually found for low-molecular-weight thermotropic liquid crystals.^{13,36} In Figure 2, the transition between the nematic and lamellar phases is put in evidence: as it can be seen, the trends of relaxation times do not show any significant discontinuity at the transition except for few data points for the m2 deuterium at the lower frequency. In our treatment of the relaxation data, we have performed several fitting procedures, considering either two separated data sets (one at $T \geq 27$ °C– N^+_D – and one at $T < 27$ °C– L_D) or a whole data set without distinction between the two phases. This last procedure, however, seems to be the

most reasonable for several reasons: (i) the two mesophases are uniaxial ones and are characterized by the same motional processes affecting T_{1Q} and T_{1Z} in the MHz region; (ii) as reported in section 3, there is no difference in the theoretical models to be used to analyze these relaxation data; and (iii) the structural features of the nematic and lamellar phases formed by this particular LLC system are such that a continuous trend is expected at the phase transition.

In the next part of the section, we will focus on a detailed analysis of the results obtained with the second procedure, namely, without distinction between the N^+_D and L_D phases. However, in the last part, the results obtained by considering two separate data sets will be presented and compared with the previous ones, in order to support our evidence of absence of any discontinuities at the N^+_D – L_D transition.

The analysis of the whole relaxation data set was performed by fitting the experimental spectral densities with the theoretical expressions reported in eqs 4 and 5, by using a Global Target fitting procedure.^{59,60} Three kinds of motion were considered: (a) overall reorientation molecular motions, that is, spinning ($//$) and tumbling (\perp); (b) internal reorientation of the deuterated moieties (R), and (c) collective motions (ODFs or LUs). In the case of overall molecular and internal motions, the temperature dependence of the diffusion constants, $D(T)$, is considered of Arrhenius type, that is

$$D(T) = D^\infty \exp(-\Delta E_a/RT) \quad (8)$$

This means that for each type of diffusion motion two parameters are determined (D^∞ and ΔE_a) from the fitting. As previously mentioned, the Nordio model³⁹ was used to describe the overall molecular motions, while the internal ones were modeled by either the strong collision⁴⁵ or the small step diffusion.⁴⁴ In the present case, the two models demonstrated to be equivalent; for simplicity, the results reported here are all obtained by applying the strong collision model. The availability of relaxation data at more than one Larmor frequency allowed us to evaluate the contribution of the collective motions. ODFs were modeled in terms of the Pincus⁴⁶ and Blinc et al.⁴⁷ theory, and LUs with the Blinc et al. theory.⁴⁸ In both cases, the contribution to $J_1(\omega_0)$ is quantified by the fitting parameter a_{DF} (see eq 5) and, as expected, it is less than 10%, with the maximum value found for $J_1^{\text{ODF}}(\omega_0) \sim 1.5 \text{ s}^{-1}$ and $J_1^{\text{LU}}(\omega_0) \sim 1.1 \text{ s}^{-1}$. In the high frequency regime, as observed for other systems,^{13,61–64} there is no difference between the ODFs and LUs. Moreover, the values of the diffusion coefficients are not influenced by the chosen model for the collective motions. For this reason, in the following part, we are reporting the results obtained by modeling the ODFs. In our dynamic investigation of the L-phenylalanine- d_8 dissolved in CsPFO/H $_2$ O, we focused the attention on the internal motions, since the ^2H longitudinal relaxation times in the MHz frequency regime are very sensitive to internal motions.^{13,61–64} In Figures 3–6, the calculated spectral densities, obtained by means of four Global Target fitting procedures (described in detail below) differing for the assumptions concerning the internal motions, are compared with the

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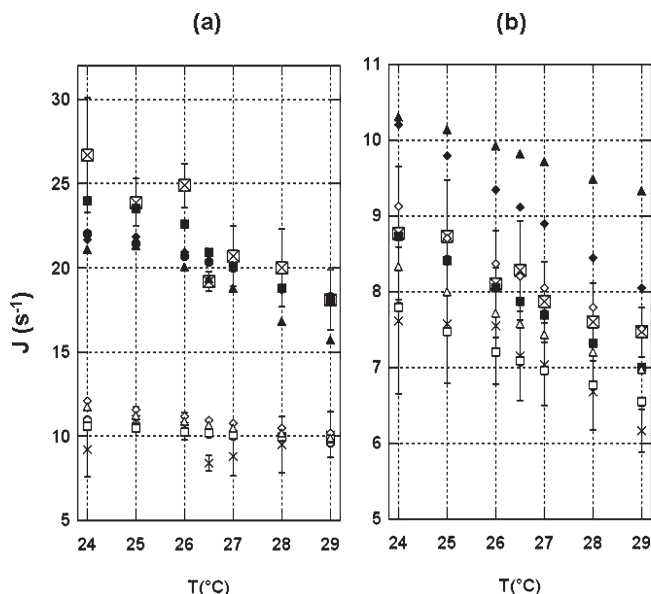


Figure 3. Experimental $J_1(\omega_0)$ (boxed cross) and $J_2(2\omega_0)$ (cross), and calculated $J_1(\omega_0)$ (full symbols) and $J_2(2\omega_0)$ (empty symbols) versus temperature ($^{\circ}C$) for the aromatic deuterons at 30.7 MHz. Circles, squares, tilted squares, and triangles refer to fitting A, B, C, and D, respectively. (a) para signal (ap); (b) ortho/meta signals (om).

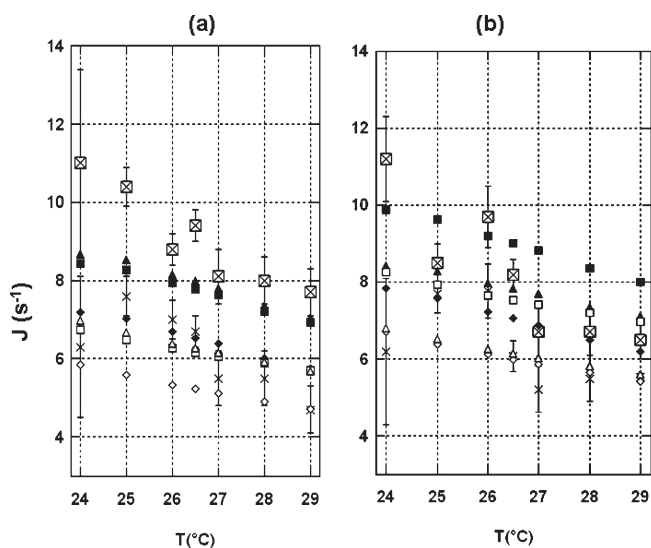


Figure 4. Experimental $J_1(\omega_0)$ (boxed cross) and $J_2(2\omega_0)$ (cross), and calculated $J_1(\omega_0)$ (full symbols) and $J_2(2\omega_0)$ (empty symbols) versus temperature ($^{\circ}C$) for the methylenic deuterons at 30.7 MHz. Squares, tilted squares, and triangles refer to fitting B, C, and D, respectively. (a) Methylenic (m1) signal; (b) methylenic (m2) signal.

experimental ones. The differences among the four fitting procedures are the following:

- The sole aromatic (ap and om) relaxation data are analyzed. Molecular spinning, molecular tumbling, and aromatic ring reorientation are modeled.
- The whole data set is analyzed, by assuming that both ring and CD_2 moieties are free to rotate independently. In addition to the overall motions, two internal reorientations ($D_{R(ARO)}$ and $D_{R(CD_2)}$) are modeled.
- The whole data set is analyzed, by assuming that the aromatic and CD_2 moieties rotate as a rigid block.

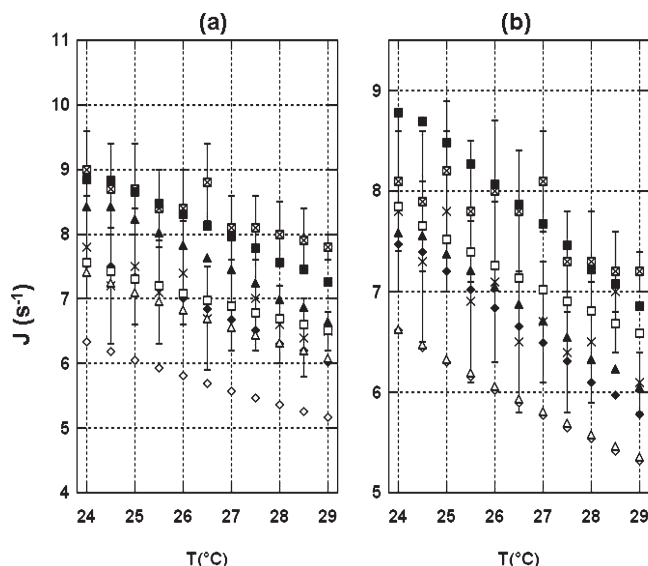


Figure 5. Experimental $J_1(\omega_0)$ (boxed cross) and $J_2(2\omega_0)$ (cross), and calculated $J_1(\omega_0)$ (full symbols) and $J_2(2\omega_0)$ (empty symbols) versus temperature ($^{\circ}C$) for the aromatic deuterons at 46 MHz. Circles, squares, tilted squares, and triangles refer to fitting A, B, C, and D, respectively. (a) para signal (ap); (b) ortho/meta signals (om).

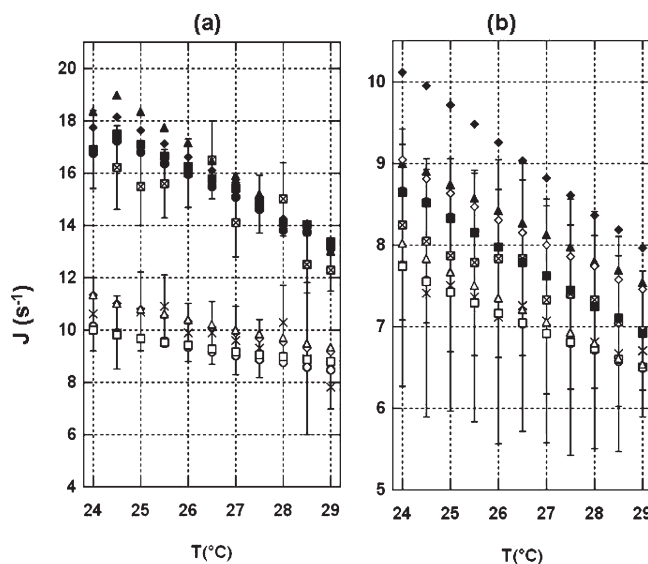


Figure 6. Experimental $J_1(\omega_0)$ (boxed cross) and $J_2(2\omega_0)$ (cross), and calculated $J_1(\omega_0)$ (full symbols) and $J_2(2\omega_0)$ (empty symbols) versus temperature ($^{\circ}C$) for the methylenic deuterons at 46 MHz. Squares, tilted squares, and triangles refer to fitting B, C, and D, respectively. (a) Methylene m1 signal; (b) methylene m2 signal.

In addition to the overall motions, a single internal reorientation ($D_{R(ARO+CD_2)}$) is modeled.

- The whole data set is analyzed, by assuming that the molecule is rigid without internal motions. The sole overall molecular motions are obtained from the fitting.

We have decided to follow and comment on these four procedures in order to better characterize the internal motions affecting the benzylic moiety and to verify the consistency of the orientational ordering study,³⁵ which indicates an “averaged” conformation but, by itself, does not give any indications if this averaged conformation results from an average over different conformations in rapid conversion due to internal motions or if it

Table 1. Best Fitting Results Obtained by Analyzing the Whole Relaxation Data Set: a_{DF} Coefficient for ODFs ($K^{-1} s^{1/2} \text{rad}^{-3/2}$), Activation Energies ΔE_a (kJ/mol), Pre-Exponential Factors $\log(D^\infty)$ (s^{-1}) (See eq 8), and D Average Values (s^{-1}) on the 29–24°C Interval for the Different Parameterizations of Internal Motions; % Symbolizes the Percentage Error^a

case (A)	ΔE_a	%	$\log(D^\infty)$	D average	%
D_\perp	50.19	7	15	1.82×10^6	8
$D_{//}$	40.83	4	16.5	2.45×10^9	4
$D_{R(\text{aro})}$	27.72	5	15.4	4.69×10^9	3
value		%			
a_{DF}	2.21×10^{-7}	5			
case (B)	ΔE_a	%	$\log(D^\infty)$	D average	%
D_\perp	50.98	5	15	1.33×10^6	8
$D_{//}$	29.39	2	15.1	9.55×10^9	5
$D_{R(\text{aro})}$	30.57	3	15	4.73×10^9	5
$D_{R(\text{CD2})}$	32.50	4	15	2.18×10^9	5
value		%			
a_{DF}	2.48×10^{-7}	6			
case (C)	ΔE_a	%	$\log(D^\infty)$	D average	%
D_\perp	47.62	8	14.5	1.62×10^6	13
$D_{//}$	42.24	5	17.2	6.98×10^9	8
$D_{R(\text{aro}+\text{CD2})}$	29.28	5	14.7	3.97×10^9	5
value		%			
a_{DF}	2.48×10^{-7}	5			
case (D)	ΔE_a	%	$\log(D^\infty)$	D average	%
D_\perp	52.14	12	15	1.1×10^6	15
$D_{//}$	35.47	8	16	6.64×10^9	8
value		%			
a_{DF}	3.11×10^{-7}	5			

^a The percentage error “%” reported in Table 1 is evaluated as the largest difference $\Delta p = |p - p_{\min}|$ which corresponds to a difference $\Delta Q = (Q - Q_{\min})$ equal to 1%, where p is the generic parameter and Q is the fitting function $= \sum_i [(J_i^{\text{exp}} - J_i^{\text{calc}})/J_i^{\text{exp}}]^2$.

is a “frozen” conformation preferred by the others due to the peculiar interactions with the LLC environment. The results of these four fittings are summarized in Table 1, and the trends of diffusion coefficients are displayed in Figure 7.

Among the four cases, the last one (D) is the worst, since, despite that the LLC environment is expected to influence the molecular motions affecting the amino acid “guest” solute, the assumption of complete rigidity and, as a consequence, the absence of any internal motions is not physically acceptable in LLC solutions. However, the four fitting procedures are all convergent to the same fitting function minimum as can be seen from the values of the diffusion coefficients displayed in Figure 7 and reported in Table 1.

The best fitting results are those obtained with the procedure (A), in which the sole aromatic relaxation times were analyzed, and procedure (B), where the complete data set was analyzed allowing a free independent reorientation of both the ring and CD₂ groups. This is clear, for instance, if we look at the aromatic spectral densities at the two frequencies (Figures 3 and 5): fittings (A) and (B) give substantially the same very good reproduction of the experimental data, with a better result for procedure (B). On the contrary, fittings (C) and (D) fail in reproducing the spectral densities of the ortho/meta deuterons recorded at both frequencies

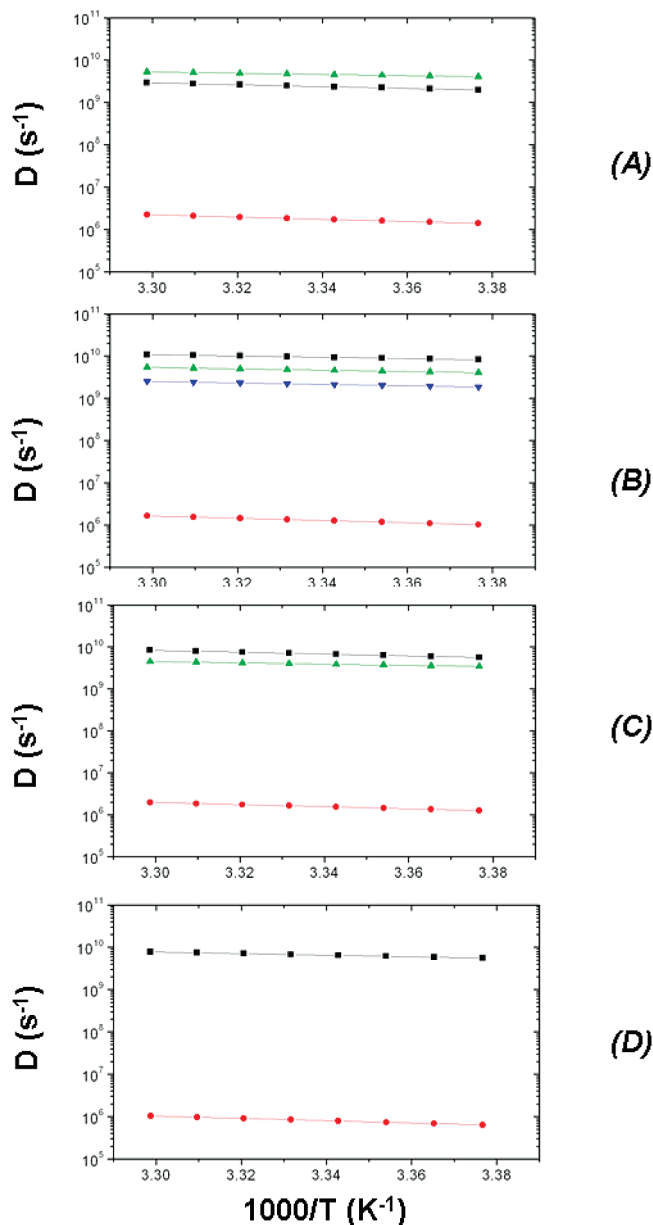


Figure 7. Diffusion coefficients (s^{-1}) on a logarithmic scale versus $1000/T$ (K^{-1}) of the of L-phenylalanine diluted in the uniaxial nematic (N_D^+) and a lamellar (L_D) phases of CsPFO/H₂O, as obtained from the procedures (A), (B), (C), and (D), as described in the text. Overall spinning and tumbling motions are in black and red, respectively. Green and blue values refer to the internal motions.

(Figures 3b and 5b). Moreover, the fitting procedure (B) is the only one giving a satisfactory reproduction of the experimental data for the methylenic deuterons (see Figures 4 and 6).

It is interesting to notice that the values of the diffusion coefficients found in the four cases are very similar among them. In fact, even though the reproduction of the experimental data is not satisfactory in cases (C) and (D), the values of the diffusion coefficients in the minimum of the fitting function are almost equivalent, indicating the existence of a single physically acceptable minimum.

It has been recently shown^{61–63} that when a small set of experimental data is available, the fitting procedure can bring ill-determined results, concerning in particular the diffusion coefficient relative to the overall tumbling motion (D_\perp). This is

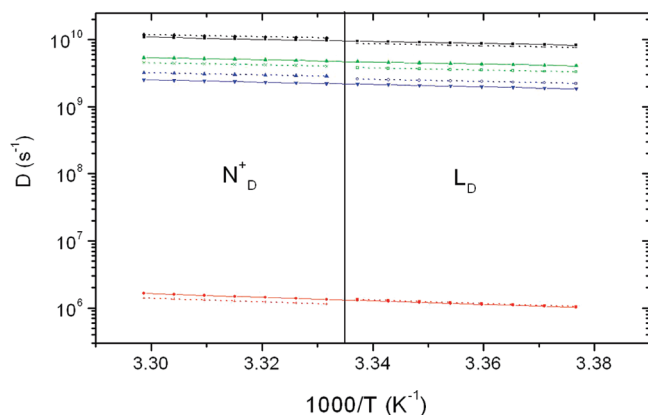


Figure 8. Diffusion coefficients (s^{-1}) on a logarithmic scale versus $1000/T$ (K^{-1}) of the of L-phenylalanine diluted in the uniaxial nematic (N^+_{D}) and a lamellar (L_{D}) phases of CsPFO/ H_2O , as obtained by fitting all relaxation data in a single Global Target procedure corresponding to case (B) of Figure 7 (solid curves) or by fitting separately the relaxation data in the N^+_{D} and L_{D} phases (dotted lines). Overall spinning and tumbling motions are in black and red, respectively. Green and blue values refer to the internal motions of the phenyl and CD_2 moieties, respectively.

not our case, considering that in our analyses we have a large set of relaxation data, that is, a good number of deuterons available and data recorded at two frequencies. This allows us to have a self-consistent analysis and a good quantification of the collective motions affecting our system in the high frequency regime. It should be stressed here that the quality of the global fitting of the relaxation data was highly increased by the introduction of the contribution of collective motions to the spectral density $J_1(\omega_0)$, thus indicating that the occurrence of a lower-frequency dynamic process has to be taken into account in this peculiar lyotropic system. In particular, the a_{DF} parameter (see eq 5), obtained from our analyses in the four fittings for the ODF motions (see Table 1), is essentially independent of the chosen procedure (cases A–D), and it leads to a maximum contribution of the ODFs to the spectral density $J_1(\omega_0)$ of about 8%. A similar result was obtained by replacing the model describing the ODFs with that describing the LUs: in this case, the maximum contribution to $J_1(\omega_0)$ is of about 6%. This value is significant if compared with other studies both in thermotropic^{13,56–58} and lyotropic phases,^{20–26} and it would confirm that longitudinal ^2H NMR relaxation times measured at frequencies in the MHz region may be influenced by order director fluctuations (2D or 3D ones).^{28,29} In the literature, most of the studies centered on the characterization of collective motions in lyotropic systems, such as order director fluctuations in nematic and lamellar phases, explore the low frequency regions (1 MHz to 1 kHz), by means of field cycling ^1H NMR^{17,18,22,23} and ^2H NMR spin–spin relaxation (T_2) investigations.²⁶ According to these studies, collective motions are mainly active at lower frequencies than at higher ones. Our results are not in contrast with this general statement, but this finding certainly adds a piece of information in the understanding of these particular cooperative motions also in the high frequency regime, showing that it is possible to “probe” order director fluctuations by using a small “guest” molecule in LLC systems.

The obtained results are consistent with the hypothesis that the “mean” or “average” conformation found by combining NMR and *ab initio* calculations³⁵ is not a “frozen” molecular geometry but an average over different conformers that rapidly convert into each other due to fast internal motions. In case (B), which is the best fitting, the order of magnitude of the diffusion coefficients for

Table 2. Best Fitting Results Obtained by Treating Separately the Relaxation Data for the Two Mesophases: a_{ODF} ($\text{K}^{-1} \text{s}^{1/2} \text{rad}^{-3/2}$)/ a_{LU} ($\text{K}^{-1} \text{rad}^{-3/2}$) Coefficients, Activation Energies ΔE_{a} (kJ/mol), Pre-Exponential Factors $\log(D^\infty)$ (s^{-1}) (See eq 8), and D Average Values (s^{-1}); “%” Symbolizes the Highest Percentage Error on the Relative Parameter

nematic phase (N ⁺ _D)	ΔE _a	%	log(<i>D</i> [∞])	<i>D</i> average	%
<i>D</i> _⊥	51.4	5	15	1.3 × 10 ⁶	13
<i>D</i> _{//}	28.5	5	15	1.1 × 10 ¹⁰	10
<i>D</i> _{R(a_{ro})}	31.3	5	15	4.3 × 10 ⁹	12
<i>D</i> _{R(CD₂)}	31.0	5	15	3.0 × 10 ⁹	13
value		%			
<i>a</i> _{ODF}	2.2 × 10 ^{−7}	5			
lamellar phase (L _D)	ΔE _a	%	log(<i>D</i> [∞])	<i>D</i> average	%
<i>D</i> _⊥	51.5	3	15	1.2 × 10 ⁶	9
<i>D</i> _{//}	28.6	3	15	8.1 × 10 ⁹	8
<i>D</i> _{R(a_{ro})}	30.0	4	15	3.5 × 10 ⁹	10
<i>D</i> _{R(CD₂)}	32.1	5	15	2.4 × 10 ⁹	10
value		%			
<i>a</i> _{LU}	1.1 × 10 ^{−3}	8			

the internal motions (aromatic reorientation around the para axis and CD_2 rotation around the tetrahedron axis) is about 10^9 s^{-1} , in agreement with what was found in common low weight thermotropic liquid crystals.^{61–64} However, it is important to notice the large ratio found between D_{\parallel} and D_{\perp} which is about 10^3 – 10^4 . Usually in thermotropic phases, this ratio is in the range 10 – 10^2 .^{13,36,56–58} In lyotropic systems, this value was determined only in one case,¹⁶ but for a surfactant molecule and never for a “guest”. A possible explanation for the large value found here is related to the fact that the L-phenylalanine has a preferred orientation with the amino group anchored to the micellar surface and a tumbling rotation would imply a positioning of the amino group far from the micellar surface. In this kind of LLC system, the electrostatic interactions are expected to play an important role in the alignment of small ionic molecules and this electrostatic force can justify the large value of the ratio D_{\parallel}/D_{\perp} found in our study.

For completeness in this last part of the paper, we are reporting results obtained by separating the relaxation data in two sets, one for the nematic phase (N^+_{D}) and one for the lamellar phase (L_{D}). The first phase is stable in a relatively small temperature range from 29.5 to 27 °C, and the data set is constituted by 64 data points, including the data recorded at the nominal transition temperature. The lamellar phase is stable below 27 °C, and the available data set is constituted by 80 data points. The two data sets were analyzed by assuming that both ring and CD_2 moieties are free to rotate independently, analogously with case (B) reported in the previous treatment. The collective motions, namely, ODFs for the nematic phase and LUs for the lamellar phase, were modeled according to eq 5. The four diffusion coefficients, D_{\parallel} , D_{\perp} , $D_{\text{R(ARO)}}$, and $D_{\text{R(CD}_2\text{)}}$, determined by the Global Target fittings are reported in Figure 8, and the best fitting parameters are shown in Table 2 together with the a_{DF} coefficients determined for the collective motions in the two mesophases.

The main aspects concerning the separate analysis for the two LLC phases are here summarized: (i) The two fittings are affected by larger errors with respect to the previous analyses due to the smaller data sets. As a consequence, the percentage errors of the best fitting parameters, reported in Table 2, are larger than those in Table 1. (ii) There is not any significant discontinuity in the

trends of the diffusion coefficients at the phase transition $N_D^+ - L_D$, thus justifying the previous treatment of the data as a whole data set. (iii) The contribution of collective motions, ODFs and LUs, is between 5 and 8% in the two mesophases, similarly with the previous results (see Table 1).

5. Conclusions

In this work, we have quantitatively investigated the dynamic behavior of the amino acid L-phenylalanine- d_8 solved in the uniaxial nematic (N_D^+) and lamellar (L_D) phases of the amphiphile cesium pentadecafluorooctanoate/water (CsPFO/ H_2O) system by means of 2H NMR spin–lattice relaxation times, T_{1Q} and T_{1Z} , recorded at two Larmor frequencies.

Relaxation data have been analyzed for the benzylic moiety by modeling three types of motions: overall molecular spinning and tumbling, internal reorientations affecting the aromatic ring and the CD_2 fragment, and collective motions, namely, the ODFs and LUs. A detailed analysis of the relaxation times based on different assumptions concerning internal motions has been performed exploiting a Global Target fitting applied to the whole data set, without distinctions between the nematic and lamellar phases. In fact, separate fittings for the two phases confirmed a continuous behavior for the main motional processes active in the MHz regime.

The main results of this study can be here summarized:

- (i) The fittings of the experimental spectral densities turn out to be quite good, leading to well determined best fitting parameters. The best and satisfactory reproduction of the experimental data, within the experimental error, was found in case (B), where free and independent reorientations of the two fragments (ARO and CD_2) were assumed.
- (ii) The relation $D_{\perp} \ll D_{\parallel}$ always holds between tumbling and spinning molecular diffusion, while internal motion(s) (if determined) is of the same order of magnitude and highly correlated to the spinning one (about $10^9 s^{-1}$).
- (iii) Ring rotation activation energy is generally the lowest one, as expected for internal motions. However, the values of the ring activation energy found in this study are of the same order of magnitude as those usually found in uniaxial thermotropic LCs.
- (iv) The introduction of the collective motions (ODFs or LUs) in the analysis considerably improves the fitting quality (a_{DF} values are the same for all the fitting procedures and their values are physically reasonable), contributing to $J_1(\omega_0)$ for about 5–8%.

The results here summarized validate our approach adopted to quantitatively analyze the 2H NMR longitudinal relaxation times of a solute, namely, L-phenylalanine- d_8 , in a lyotropic environment. This theoretical approach is indeed quite popular in the study of molecular dynamics in the case of “guest” molecules dissolved in thermotropic LCs, while the same models have been applied to “guest” molecules solved in lyotropic LCs only rarely. This study proves that it is possible to apply this approach to get self-consistent information about both internal and overall reorientational motions of a small molecule diluted in a LLC system. Moreover, this work completely agrees with a previous ordering and conformational investigation on the same “guest–host” LLC system. In fact, the dynamic analysis demonstrates that the “effective” conformation of the L-phenylalanine- d_8 results from an averaging over fast internal reorientations (D_R values of about $10^9 s^{-1}$), while the relation $D_{\perp} \ll D_{\parallel}$ indicates that the electrostatic interactions between the charged amino acid and the micellar surface (namely, the CsPFO) allow a molecular fast rotation about the spinning axis but hinder perpendicular fluctuations, as expected for a calamitic probe aligned perpendicular to the micellar surface.

Another important result concerns the evidence of a sensible improvement of the global fitting as collective motions are taken into account. This finding allows us to state that the 2H NMR longitudinal relaxation in the high-frequency region is influenced not only by single molecule motions but also by collective ones, usually more active in the low-frequency region (below 1 MHz). Certainly, due to the complexity of the dynamic processes in a lyotropic system, we cannot exclude that other typically “slow processes” may occur, such as translational diffusion or molecular exchanges among different positions on the micellar surface. However, these processes are expected to be active at lower frequencies, and they should not influence 2H NMR longitudinal relaxation times. Different NMR techniques, such as 1H NMR relaxometry and 2H NMR transverse relaxation measurements, could be of help in giving a complete description of the molecular dynamics of this particular system also at lower frequencies.

All this considered, the present study represents a step forward in the understanding of the dynamic behavior of “guest” molecules in the lyotropic environment, showing that this kind of study can also represent an alternative approach to investigate collective motions in complex systems, such as LLCs, through their “guests”.

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