The effect of molecular self-diffusion on NMR linewidth and relaxation in micellar lyotropic phases

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1. Introduction.

Molecular structure and dynamics of lyotropic liquid crystals are not yet completely understood. NMR is one of the methods which can be successfully used for this purpose. NMR studies of several lyotropic mesophases [1-13] have been published by now. The field has been recently reviewed by Charvolin et al. [14].

Because of the complicated structures formed by aggregates of amphiphilic molecules embedded in a solvent the linewidth and spin-relaxation problem in lyotropic liquid crystals is considerably more complex in comparison with thermotropic mesophases. In addition to the aggregates of « infinite » length (lamellar, hexagonal phase), lyotropic mesophases with finite aggregates have been found [15]. Depending on the temperature and composition, finite aggregates — micelles — can be either spherical forming an isotropic phase, or they take the shape of discs or cylinders forming nematic lyotropic phases with properties similar to those of thermotropic nematics. Recently several investigations have been devoted to the lamellar — discotic nematic phase transition [16-18] and to the transition of the discotic...
nematic phase via the biaxial nematic phase into the cylindrical \([6, 19, 20]\). The homogeneous orientational ordering of nematic lyotropic phases can be achieved either by the magnetic field in the case of positive diamagnetic anisotropy (cylinders), or together with the spinning around the axis perpendicular to the magnetic field in the case of the negative diamagnetic anisotropy (discs). Lyotropic nematic phases are thus suitable for NMR linewidth and relaxation studies. When treating the problem of molecular dynamics, one should take into account both the motions of molecules within the aggregate and the motion of aggregates themselves, i.e.:

- conformational changes of alkyl chains of amphiphilic molecules around a mean stretching axis (in analogy with thermotropic liquid crystals called also long molecular axis),
- orientational fluctuations (possibly collective) of those axes about the local normal to the interface,
- translational diffusion of molecules within the aggregate,
- deformations of micelles,
- rotation of spherical micelles, rotation of discs and cylinders around their symmetry axes, and orientational fluctuations of aggregate axes,
- translational diffusion of micelles,
- collective fluctuations of aggregate axes, i.e. director fluctuations,
- decaying and fusing of micelles.

Characteristic correlation times of micellar motions are expected to be longer than those corresponding to intramicellar motions. We assume that different motions are not coupled.

Molecular translational diffusion in systems with uniform molecular orientation (thermotropic nematics \([21]\), smectics \([22]\), lamellar lyotropic phase) modulates only the intermolecular coupling. On the other hand, in systems with spatially nonuniform molecular alignment (cholesteric and smectic \(C^*\) phases \([23, 24]\), several lyotropic systems) translational diffusion is accompanied by the reorientation of molecular long axes. This causes a strong slow modulation of the intramolecular coupling and slightly affects the intermolecular coupling as well. In this paper we study in detail the influence of molecular diffusion along a curved interface of the aggregate, i.e. of molecular «rotation induced by translational diffusion» (hence abbreviated as TR process), on the NMR linewidth and relaxation rate. The minor changes of the shape of micelles and their finite life time (long on the NMR time scale) do not modulate the intramolecular coupling significantly. The theory of the TR process is worked out for the proton pair dipolar coupling in rigid spherical, cylindrical and discotic micelles. It can be easily extended to the aggregates of any other shape which can also slowly (on the NMR time scale) change. The theory can be applied with minor modifications to other types of intramolecular coupling (deuterium quadrupole coupling etc.) as well. In lyotropic nematics the modulation of the intermolecular coupling by the TR process shows all characteristics of finite two-dimensional systems \([25]\). As it is less dramatically affected by the shape and the size of micelles it is not treated in this paper. The particular effects of translational diffusion along curved surfaces on the DMR line shape have been earlier described by Charvolin \([16, 26]\) for the lamellar and hexagonal phase, and by Chidichimo \textit{et al.} \([12]\) for the ribbon phase.

Parts of this paper have been presented at the Conferences in Bovec, 1984 \([27]\) and in York, 1984 \([28]\).

2. Theory.

Magnetic dipolar interaction of protons in amphiphilic aggregates is dominated by two proton contributions. As the translationally induced rotation of the molecule is a relatively slow motion, it affects only the part of the dipolar interaction, which results after averaging over all faster motions (conformational changes, orientational fluctuations of alkyl chains etc.). Therefore we introduce in the following a reduced dipolar interaction corresponding to an effective proton pair with the interproton vector pointing along the average direction \(\mathbf{M}\) of the long molecular axis. The spatial part of such effective dipolar interaction is

\[
F^{(k)} = \frac{s}{r^3} \begin{cases} 
1 - 3 \cos^2 \theta & k = 0 \\
\sin \theta \cos \theta e^{i \rho} & k = 1 \\
\sin^2 \theta e^{2i \rho} & k = 2,
\end{cases}
\]

Fig. 1. — Schematic presentation of the orientation of the interproton vector \(\mathbf{r}\) in the laboratory frame (defined by the direction of the magnetic field \(\mathbf{B}\)) and in the molecular frame where \(\beta(t)\) denotes the angle between \(\mathbf{r}\) and the average direction \(\mathbf{M}\) of the stretching (long) molecular axis. The orientation of \(\mathbf{M}\) in the laboratory frame is given by \(\theta\) and \(\varphi\).
where $\theta$ and $\varphi$ are the polar and azimuthal angles describing the orientation of $\mathbf{M}$ in the magnetic field fixed frame (Fig. 1), $r$ is the actual distance between two protons, and $s$ stands for the reduction factor which includes averaging over conformational changes and orientational fluctuations of the alkyl chain.

$$s = \frac{1}{2} (3 \cos^2 \theta(t) - 1).$$  \hspace{1cm} (2)

Here $\beta(t)$ denotes the angle between the average molecular axis direction and the instant direction of the interproton vector $r$. The above expression can be easily obtained using the well known transformation properties of spherical harmonics of it is assumed that the fast rotation of the interproton vector $r$ around molecular stretching axis is uniform and independent of the fluctuations of the angle $\beta(t)$. The intramicellar reduction factor $s$ is expected to be the same for all types of aggregates under study.

The average direction $\mathbf{M}$ of the long molecular axis is everywhere orthogonal to the micellar interface. Translational diffusion of the molecule along the curved surface is therefore accompanied by molecular reorientation (Fig. 2). For the typical radius of the curvature which is between 10 Å and 18 Å an appreciable rotation ($\sim \pi/2$ radians) takes place if the molecule is displaced for at least several molecular diameters. The resulting modulation of the intramolecular interproton interaction is thus about an order of magnitude slower than the modulation of the intermolecular one. It should be stressed that for the description of the TR process a continuous diffusion model, which neglects the details of the translational diffusion process, represents a much better approximation than in the study of intermolecular interactions [21, 22]. The proton magnetic resonance linewidth and relaxation due to the TR process will be in the following evaluated in detail separately for different kinds of rigid micelles.

2.1 SPHERICAL MICELLES. — At relatively low concentrations of amphiphilic molecules solved in water, spherical micelles are formed and the resulting phase is isotropic. In the isotropic micellar phase of sodium decyl sulfate (SdS)-decanol-water mixtures the diameter $d$ of micelles is about 35 Å [29], while intermicellar distances $b$ range about 50 Å. Molecular rotation induced by translational diffusion in such systems can be described by the well known equation:

$$\frac{\partial}{\partial t} f = D_\alpha \nabla^2 f,$$  \hspace{1cm} (3)

where $f(\Omega, t)$ is the probability of finding a molecule oriented in the direction $\Omega$ at time $t$, and $\nabla^2$ is the Laplacian operator in spherical coordinates. The rotational diffusion constant $D_\alpha$ is related to the translational diffusion constant $D_s$ on a spherical surface [30]:

$$D_\alpha = 4 D_s / d^2.$$  \hspace{1cm} (4)

The solution of equation (3) which at $t = 0$ corresponds to a delta-function centered at $\Omega_0$ has the following form

$$P(\Omega, \Omega_0, t) = \sum_{l,m} Y_l^m(\Omega_0) Y_l^m(\Omega) e^{-i(l+1)D_\alpha t}.\hspace{1cm} (5)$$

It enables us to find [30] autocorrelation functions $G^{(k)}(t)$ of the spatial part of the dipolar interaction, given by equations (1), for the TR process in a spherical micelle:

$$G^{(k)}(t) = \frac{2}{15} s^2 r^{-6} \left\{ \begin{array}{ll} 6 \ & k = 0 \\ 1 \ & k = 1 \\ 4 \ & k = 2 \end{array} \right\} e^{-6D_\alpha t}.\hspace{1cm} (6)$$

The time dependence of autocorrelation functions for different $k$ is described by a single correlation time

$$\tau_s = (6 D_\alpha)^{-1} = d^2/(24 D_s).\hspace{1cm} (7)$$

It falls into the region $5 \times 10^{-8}$ s to $5 \times 10^{-9}$ s if we assume $D_s \approx D_{lamellar} \approx 10^{-7}$ to $10^{-6}$ cm$^2$/s.

2.1.1 Linewidth. — For a molecule diffusing in a spherical micelle all orientations are equally probable and the corresponding correlation time for the TR process is short in a time scale determined by the intramolecular magnetic dipolar coupling ($\approx 5 \times 10^{-5}$ s). The intramolecular spin-spin interactions are therefore completely averaged out and characteristic line-shape for a liquid is expected.

2.1.2 Relaxation rates. — Relaxation rates in the laboratory ($T_{1}^{-1}$) and in the rotating frame ($T_{1\rho}^{-1}$) are given by the well known expressions [30]:

![Fig. 2. — Schematic presentation of spherical, cylindrical and discotic micelles and of the TR motion of amphiphilic molecules therein.](image)
When calculating the relaxation rates due to the TR process, \( J^{(k)}(\omega) \) are spectral densities of the dipolar auto-correlation functions \( G^{(k)}(t) \) at the frequency \( \omega \). The calculated \( J^{(k)}(\omega) \) exhibit a BPP type frequency behaviour \cite{31} for all values of \( k (k = 0, 1, 2) \). Using expressions (6) and (8) we obtain the TR contribution to the relaxation rates in a spherical micelle

\[
(T^{-1})_{\text{sph}} = \frac{1}{80} 9 \gamma^4 \hbar^2 \frac{s^2 d^2}{R^6} \left( \frac{1}{1 + (\omega \tau_s)^2} \right) + \frac{4}{1 + 4(\omega \tau)^2}
\]

(9a)

and

\[
(T^{+1})_{\text{sph}} = \frac{1}{320} 9 \gamma^4 \hbar^2 \frac{s^2 d^2}{R^6} \left( \frac{6}{1 + (2 \tau_s \omega)^2} + \frac{10}{1 + (\omega \tau)^2} + \frac{4}{1 + (2 \omega \tau)^2} \right).
\]

(9b)

A competitive relaxation process due to the rotational diffusion of the micelle as a whole is as well described by equations (9) if \( D_s \) is replaced by \( d^2 D_{\text{MR}} / 4 \). Where \( D_{\text{MR}} \) is the micellar rotational diffusion constant. An estimate of the magnitude of \( D_{\text{MR}} \) can be obtained by using a slightly modified Einstein-Stokes relation:

\[
D_{\text{MR}} = \frac{kT}{\pi d^3 \eta} \left( 1 - \left( \frac{d}{b} \right)^3 \right).
\]

(10)

where \( b \) is an average intermicellar distance and \( \eta \) the viscosity of the surrounding medium. The correction factor \( (1 - (d/b)^3) \) takes into account the fact that the effective rotational friction increases with decreasing intermicellar spacing. We have assumed that each micelle is confined to a spherical volume with the radius \( b/2 \), where it reorients independently. Using the viscosity of pure water (\( \eta \approx 10^{-3} \) kg/ms) one finds that micellar rotation for high water concentrations, \( b \gg d \), is faster than intramicellar molecular rotation. Therefore it masks the effect of the TR process on the relaxation rates. However, this is not the case for low water concentrations where \( b < 2d \). In these systems it is expected that the described TR process is the dominant relaxation mechanism for \( \omega \tau_s \approx 1 \) (i.e. for Larmor frequencies \( v_L \approx 10 \) MHz).

2.2 CYLINDRICAL MICELLES. — This kind of micelles is characteristic for the calamitic type of lyotropic nematic phases. It has been found that in SDS-decanol-water system with concentrations SDS : 40.3 \%, \( \text{H}_2\text{O} : 52.5 \%, \text{decanol} : 7.2 \% \) micelles have the shape of elongated cylinders with diameter \( d \approx 30 \) Å and length / which is at least 150 Å \cite{29}. The lateral distance of nearly parallel cylinders is about 38 Å. As a model for the cylindrical micelle we consider a rigid cylinder closed at both ends by two hemispherical caps (Fig. 2b), which is expected to be a good approxima-

tion except in the vicinity of the phase transition to the biaxial phase \cite{6}.

The rotation induced by molecular translational self-diffusion in the central, cylindrical part of the micelle differs from the one in the hemispherical caps. The TR process in the central part of the cylinder (Fig. 2b) can be described by rotational diffusion equation in two dimensions

\[
\frac{\partial}{\partial t} f = D^0 \frac{\partial^2 f}{\partial \phi^2},
\]

(11)

where \( \phi \) describes the azimuthal angle in the coordinate system with the z-axis parallel to the axis of the cylinder, and \( D^0 \) is the corresponding rotational diffusion constant. Translational diffusion constants in the central part of the micelle satisfy the relations:

\[
\left\langle \frac{d}{2} \cdot \delta \phi \right\rangle = 2 D^c \tau \quad \text{and} \quad \left\langle \delta z^2 \right\rangle = 2 D^c \tau,
\]

(12)

where \( D^c \) corresponds to the diffusion constant in the direction of maximal curvature and \( D^c \) to the direction of zero curvature. The rotational diffusion constant \( D^0 \) is again given by \( 4 D^0 / d^2 \). As in the case of spherical micelles one can use \( D^c \approx D^c \approx D_{\text{lamellar}} \) for rough estimates.

The solution of equation (11), corresponding at time \( t = 0 \) to a delta-function centred at \( \phi_0 \), has the following form:

\[
P(\phi, \phi_0, t) = \frac{1}{2 \pi} \sum_{n = -\infty}^{\infty} e^{-D^0 n^2 \tau} e^{in(\phi - \phi_0)}.
\]

(13)

The autocorrelation function of the dipolar interaction modulated by the TR process in the central, cylindrical part of the micelle, \( G^{(k)}(t) \), can then be written — in the
case of the magnetic field $B$ parallel to the cylinder axis — as:

$$G^{(k)}(t) = s^2 r^{-6} \begin{cases} 
1 & k = 0 \\
0 & k = 1 \\
\exp(-4 D'_n t) & k = 2 .
\end{cases}$$

In hemispherical caps of micelles, on the other hand, we assume that the TR process can be described in the same way as in spherical micelles by equations (3-5) and by the corresponding autocorrelation functions of the dipolar interaction given by equations (6).

2.2.1 NMR linewidth. — In studying NMR spectrum of protons belonging to alkyl chains in cylindrical micelles, one should take into account that:

- Like in spherical micelles, the dipolar broadening of the spectrum due to the nuclei in the hemispherical caps is completely motionally averaged out.
- The contribution to the NMR spectrum due to the nuclei in the cylindrical region of the micelle is affected by intramicellar and micellar dynamics. Besides the averaging due to the conformational changes and orientational fluctuations of alkyl chains which is described by a reduction factor $s$, common to all phases, there is an averaging due to:
  - i) planar molecular rotations about the symmetry axis of the cylinder, which reduce the splitting of the NMR spectrum for a factor $\frac{1}{2}$ [32], and
  - ii) micellar orientational fluctuations which further reduce the splitting for a factor $S_c$, where $S_c$ denotes the micellar nematic order parameter in the cylindrical nematic phase.

When the axes of the cylinders are in the average aligned parallel to the external magnetic field $B$ we can write the line splitting of the NMR spectrum of the nuclei in the cylindrical region of the micelle, $\omega_{cyl}$ in the following simple way:

$$\omega_{cyl} = \frac{3}{2} S_c \gamma^2 \hbar s r^{-3} = \frac{1}{2} S_c \omega_{lamellar} .$$

Here $\omega_{lamellar}$ denotes the maximum line splitting of the oriented lamellar phase which corresponds to the case with the plane normal parallel to $B$ and with amphiphilic molecules aligned in the average along the magnetic field. In the case, however, when the nematic lyotropic sample is oriented away from the direction of the magnetic field, the width of the spectrum is further reduced in the following way:

$$\omega_{cyl} = \frac{3}{4} S_c \gamma^2 \hbar s r^{-3}(3 \cos^2 \Delta - 1)$$

with $\Delta$ denoting the angle between the magnetic field and the symmetry axis of the liquid crystalline phase.

The strengths of the two contributions to the NMR spectrum depend on the average number of molecules in the corresponding regions. The relative strength of the "spherical" contribution equals therefore approximately to the ratio between the hemispherical surfaces and the total surface of the micelle:

$$\varepsilon_c \approx \frac{d}{l} .$$

Both contributions are expected to be separately observed if the exchange of molecules between spherical and cylindrical regions is slow compared to the spin-spin relaxation time $T_2$. This situation possibly occurs in micelles consisting of different amphiphilic molecules where one kind prefers the position in the central part of the cylinder and the other in its ends. In this case the proton spectrum should consist of two contributions: one liquid-like of the spherical region (proportional to $\varepsilon_c$) and another with the width $\frac{1}{2} S_c \omega_{lamellar}$ corresponding to the cylindrical region (proportional to $1 - \varepsilon_c$).

If there is, on the other hand, a fast, unrestricted exchange of molecules between spherical and cylindrical regions and if cylinders are not longer than $(2 D'_n T_2)^{1/2} \approx 10^2 \text{Å}$, there is a single contribution to the proton NMR spectrum which is averaged over the spherical and cylindrical regions. Its linewidth is smaller than in the lamellar phase oriented along $B$ and given by:

$$\delta \omega \approx (1 - \varepsilon_c) \frac{1}{2} S_c \omega_{lamellar} .$$

The precise study of the lineshape in cylindrical lyotropic nematics can thus help us to distinguish between the above two situations. An estimate of the micellar length or micellar order parameter $S_c$ can be obtained only if the micelles are not too long ($l \lesssim 10 d \sim 300 \text{Å}$).

2.2.2 Relaxation rates. — The proton relaxation process is also influenced by the position of the molecules in the cylinder. If there were no exchange between the central part and the caps of the micelle, two types of TR induced relaxation rates could in principle be detected:

- relaxation rates for the molecules in the hemispherical caps of the micelle are the same as in the spherical micelle and therefore given by equations (9).
  - As mentioned before, $(T_1^{-1})_{sph}$ and $(T_2^{-1})_{sph}$ have no angular dependence;
- relaxation rates in the cylindrical part can be evaluated using autocorrelation functions given by equation (14). Taking into account the transformation properties of spherical harmonics [33], the dependence of both laboratory and rotating frame relaxation rates on the angle $\Delta$ between magnetic field $B$ and liquid crystalline symmetry axis can be written:
Both rates show a BPP type frequency behaviour and a pronounced angular dependence as shown in figure 3.

\[
(T_{1}^{-1})_{\text{cyl}} = \frac{9}{512} \frac{\gamma^2 \hbar^2 s^2 d^2}{r^6 D_c'} \left[ \frac{2 \sin^2 \Delta - \sin^4 \Delta}{1 + (\omega \tau_\text{c})^2} + \frac{8 - 8 \sin^2 \Delta + \sin^4 \Delta}{1 + (2 \omega \tau_\text{c})^2} \right],
\]

\[
(T_{1p}^{-1})_{\text{cyl}} = \frac{9}{512} \frac{\gamma^2 \hbar^2 s^2 d^2}{r^6 D_c'} \left[ \frac{9 \sin^4 \Delta}{4} \frac{1 + (2 \omega \tau_\text{c})^2}{1 + (\omega \tau_\text{c})^2} + \frac{5}{2} \left( \frac{2 \sin^2 \Delta - \sin^4 \Delta}{1 + (\omega \tau_\text{c})^2} + \frac{1}{4} \frac{8 - 8 \sin^2 \Delta + \sin^4 \Delta}{1 + (2 \omega \tau_\text{c})^2} \right) \right]
\]

(18a) (18b)

with \( \tau_\text{c} = d^2/(16 D_c') \).

In the case of fast (on the \( T_1 \) time scale) exchange of molecules between the two regions there is a single magnetization decay rate given by

\[
T_1^{-1} = (1 - \varepsilon_c)(T_1^{-1})_{\text{cyl}} + \varepsilon_c(T_1^{-1})_{\text{sph}}
\]

(19)

where anisotropic contribution is given by equation (18a) and isotropic by equation (9a).

The TR process is expected to dominate \( T_1^{-1} \) in cylindrical nematics in the frequency region \( \nu_1 \approx 10 \text{ MHz} \). The rotational diffusion of the whole micelle could be a competitive relaxation mechanism. The corresponding micellar rotational diffusion constant \( D_{MR} \) can be estimated in a similar way as for spherical micelles. However, taken into account previously mentioned intermicellar distances, one finds \( D_{MR} \ll D_D \). The micellar Brownian rotation in cylindrical lyotropic nematics can be thus neglected as an important relaxation mechanism, but it should be taken into account as the micellar orientational order reducing mechanism, what means that the observed angular dependence of the relaxation rates is reduced. On the contrary to \( T_1 \), the TR induced \( T_{1p} \) is probably masked by other slow motion relaxation processes for instance by order director fluctuations.

From the value of the TR induced \( T_1 \) the coefficient \( D_c' \) for a curved surface can be estimated. The anisotropy of both TR induced relaxation rates, \( T_1^{-1} \) and \( T_{1p}^{-1} \), is strongly affected by the micellar anisotropy, i.e. the ratio \( \nu_1/d \) as long as it is not too large \( (\nu_1/d < 10) \). In such case, using a TR induced angular dependence of \( T_1 \), an estimate for the length of the micellar cylinders \( l \) can be obtained.

2.3 DISCOTIC MICELLES. — In several nematic lyotropic phases discovered up to now micelles have the shape of discs. In SDS-decanol-water mixtures, for example, discotic micelles having a diameter \( a \approx 60 \text{ Å} \) and the thickness \( d \) about 20 Å are formed in a definite concentration range [29]. Normals to discs are nearly parallel and in this particular mixture aligned perpendicular to the magnetic field. More extraordinary lyotropic discotic phases with nematic director parallel to the magnetic field have been found as well [9]. The average distance between micellar centres is \( \sim 37 \text{ Å} \) along their symmetry axes and \( \sim 72 \text{ Å} \) in the perpendicular direction for the mixture mentioned above [29].

We describe the discotic micelle by a rigid disc with a central lamellar part surrounded by a curved edge which is the outer surface of a toroid (Fig. 2c). Such a description is expected to be satisfactory except in the nearest vicinity of the phase transitions to the lamellar [16] or biaxial nematic phase [6].

The TR process in discotic micelles is confined to the curved edge of the micelle (Fig. 2c). The molecules therein undergo two types of rotation :

— a rotation induced by radial motion in « \( \varphi' \) direction » (see Fig. 2c), similar to the TR process in cylinders,

— a rotation induced by tangential motion (in the plane parallel to the principal symmetry plane of the disc), which is at least three times slower than the radial one.
In the first approximation both motions can be assumed to be independent and we can write

\[ \frac{\partial f}{\partial t} \approx D'_0 \frac{\partial^2 f}{\partial \varphi^2} + D''_0 \frac{\partial^2 f}{\partial \psi^2} \]  

(20)

where \(D'_0\) is again given by \(4 D'_{1/2} d^2\) and \(D''_0 = 4 D''_{1/2} a^2\).

Here we assume that the radius \(a/2\) is so large that \(D''_0\) used in cylindrical case for the direction of zero curvature can be used. The solution which at \(t = 0\) yields the function \(\delta(\varphi' - \varphi'_0) \delta(\psi - \psi_0)\) can be for an arbitrary time written as

\[ P(\varphi' - \varphi'_0, \psi, t) = \]

\[ = P(\varphi' - \varphi'_0, t) P(\psi - \psi_0, t) \]  

(21)

where \(P(\varphi' - \varphi'_0, t)\) is given by equation (13) and \(P(\psi - \psi_0, t)\) by the same expression where \(\varphi\) is substituted by \(\psi\) and \(D'_0\) by \(D''_0\).

Now we choose the magnetic field \(B\) parallel to the disc symmetry axis (Fig. 2c). This orientation does not correspond to the equilibrium in the case of negative anisotropy of diamagnetic susceptibility, but it enables us to write the spatial part of the dipolar interaction in a simple way:

\[ F_d^{(h)} = \frac{S}{2 r^3} \times \left\{ \begin{array}{ll}
3 \cos 2 \varphi' + 1 & k = 0 \\
\sin 2 \varphi' e^{i\#} & k = 1 \\
(1 - \cos 2 \varphi') e^{2i\#} & k = 2,
\end{array} \right. \]  

(22)

and consequently the autocorrelation functions:

\[ G_d^{(h)}(t) = \frac{s^3}{4 r^6} \times \left\{ \begin{array}{ll}
\frac{9}{2} e^{-4 D_0 t} + 1 & k = 0 \\
\frac{1}{2} e^{-D_0 t} e^{-4 D_0 t} & k = 1 \\
e^{-4 D_0 t} \left(1 + \frac{1}{2} e^{-4 D_0 t}\right) & k = 2.
\end{array} \right. \]  

(23)

2. 3. 1 NMR linewidth. — Like in the case of cylindrical micelles there are two contributions to the proton NMR spectrum:

- a lamellar-like contribution emerging from the central part of the micelle where no TR effect is present and where only micellar disorder reduces the splitting; the corresponding line splitting equals \(S_d \delta \omega_{\text{lamellar}}\) given in equation (15a) (assuming that \(B\) is parallel to the nematic director and that the micellar order is described by \(S_d\))

- an edge contribution, which is for \(a \sim 10^2 \text{ Å}\) motionally averaged over both TR motions. The splitting is thus reduced to about a quarter of the splitting corresponding to the central part of the disc:

\[ \approx \frac{1}{4} S_d \delta \omega_{\text{lamellar}}. \]

In contrast to the case of spherical micelles rotational motions caused by translational diffusion on the toroidal surfaces are not completely isotropic. For \(a \gtrsim 500 \text{ Å}\) a static distribution over \(\psi\) is expected, and the corresponding maximal width is the same as in the cylindrical case.

The relative strength of the edge contribution is equal to the ratio between the corresponding surface and the total micellar surface:

\[ \eta_d \approx \frac{\pi d}{a + d(\pi - 1.5)}. \]  

(24)

A separate observation of both contributions would be possible only if the exchange between the two regions were slow on \(T_2\) time scale. If, on the other hand, the exchange between two regions is unrestricted, i.e. fast, and \(a \lesssim 10^3 \text{ Å}\) there is a single contribution to the proton spectrum with the width approximately equal to \(S_d \left(1 - \frac{3}{4} \eta_d\right) \delta \omega_{\text{lamellar}}\).

A precise proton lineshape study can thus show us whether there is an exchange between the regions with different curvatures. If the micellar diameter \(a\) is smaller than a few hundred Å we can estimate one of the two parameters, \(a\) or \(S_d\), as well.

2. 3. 2 Relaxation rates. — Only protons in the toroidal part of the disc can relax directly due to the TR process. Using autocorrelation functions given by equations (23) one finds the following relaxation rates for a general direction of \(B\) if \(A\) denotes the angle between \(B\) and the disc symmetry axis:

\[ (T_1^{-1})_{\text{hor}} = \frac{9}{256} \gamma^4 \hbar^2 s^2 r^6 \left[ \frac{18 \sin^2 A - \sin^4 A}{1 + (\omega \tau_{A})^2} + \frac{(8 - 20 \sin^2 A + 16 \sin^4 A) \tau_1}{1 + (\omega \tau_1)^2} \right. + \]

\[ \left. + (2 \sin^2 A - \sin^4 A) \left( \frac{2 \tau_4}{1 + (\omega \tau_4)^2} + \frac{\tau_2}{1 + (\omega \tau_2)^2} \right) \right] \]

\[ + \left( 18 \sin^4 A \frac{\tau_4}{1 + (2 \omega \tau_{A})^2} + \frac{16 \sin^2 A - \sin^4 A \tau_1}{1 + (2 \omega \tau_1)^2} \right) \]

\[ + \left( 8 - 8 \sin^2 A + \sin^4 A \left( \frac{2 \tau_4}{1 + (2 \omega \tau_{A})^2} + \frac{\tau_2}{1 + (2 \omega \tau_2)^2} \right) \right], \]  

(25a)
The correlation times \( \tau_c, \tau_d, \tau_1, \) and \( \tau_2 \) are given by

\[
\begin{align*}
\tau_c &= (4 D_0^a)^{-1} = d^2/(16 D_c^a), \\
\tau_d &= (4 D_0^a)^{-1} = a^2/(16 D_c^a), \\
\tau_1 &= (D_0^a + 4 D_0^b)^{-1}, \\
\tau_2 &= (4 D_0^a + 4 D_0^b)^{-1}.
\end{align*}
\] (26)

Both relaxation rates, \( (T_1^{-1})_{\text{tor}} \) and \( (T_{1p}^{-1})_{\text{tor}} \), show BPP type frequency behaviour with the angular dependence illustrated in figure 4.

If there is a fast exchange of molecules between two parts of the micelle all protons have the same relaxation rate, which is given by equations (25a) or (25b) but reduced for a factor \( \alpha_d \). It should be stressed that the effectiveness of the TR mechanism strongly decreases with increasing ratio \( a/d \) (Fig. 5). For large disc diameters, \( a > 500 \, \text{Å} \), a part of the TR process induced by the change of \( \psi \) becomes slow on the \( T_2 \) scale and can no more induce the relaxation. That can be simply taken into account by assuming \( D_0^d = 0 \) in equations (22) and (23), what additionally reduces the relaxation rates.

Comparing the competing Brownian micellar rotation — which can be treated similarly as in previous cases — and the TR process, one can see that the latter is a more efficient relaxation mechanism. The TR process in discotic lyotropic nematics is expected to be the relevant or the dominant relaxation mechanism in MHz region as long as the micelles are not too large.
(a < 10 d). In such a case the studies of T_{1} and T_{1p}
can yield \( D' \), \( D'' \) and \( a \). For larger micelles the influence of the TR process is strongly reduced.

3. Conclusions.

Translational diffusion in systems with inhomogeneous molecular alignment is always accompanied by molecular reorientation. This process strongly affects intramolecular coupling and to a much smaller extent intermolecular coupling. The characteristic correlation time of the intramolecular coupling modulation is by a factor \( A^2 \) longer than the one of the intermolecular part, where \( A \) is the ratio between the average distance, in which the molecular orientation changes appreciably (\( \sim \pi/2 \)), and the molecular diameter. It should be mentioned that in the case of the quadrupolar coupling there is only intramolecular interaction which matters. Our treatment can be easily modified for the description of such a case.

The effect of molecular rotation induced by translational diffusion in lyotropic micellar systems is expected to be the dominant relaxation mechanism in the frequency region where \( v_L \) or \( \omega_1 \) < \( 16 D'/a^2 \) for cylindrical micelles and \( v_L \) or \( \omega_1 \) < \( 16 D'/a^2 \) for discotic micelles. \( T_1 \) and \( T_{1p} \) show a BPP type frequency behaviour and two characteristic correlation times in contrast to translationally modulated intermolecular relaxation process where there is a distribution of correlation times [21, 22] even in the case of restricted diffusion [25]. The relaxation induced by the TR process can be used for the determination of the diffusion constants and of the micellar anisotropy (if it is not larger than about 10). The relaxation induced by the TR process could be masked by a competing relaxation mechanism, Brownian micellar rotation, only in the cases when intermicellar distances become larger than a typical bilayer thickness and when the micelles have small anisotropy.

The NMR line shape strongly depends on the micellar anisotropy and orientational order in systems with relatively small micelles. Unfortunately, both parameters, i.e. micellar anisotropy and orientational order, cannot be determined from the line shape data alone.

The only today existing experimental evidence where the theory of the TR process, developed in this paper, can be applied are the DMR line splittings obtained in relatively limited temperature and concentration regions [4, 6]. Saupe et al. explained the behaviour of the DMR splitting in the vicinity of the biaxial nematic phase using Landau expansion of the free energy based on the molecular (not micellar) order parameter. Using previously mentioned micellar sizes together with our formulae (17) and (24) one can find \( S_c/S_d \sim 2 \delta \omega_{s1}/\delta \omega_{sis} \), where both \( \delta \omega_{s1} \) and \( \delta \omega_{sis} \) for \( B \) parallel to the aggregates’ symmetry axes must be used. From the available DMR data [4, 6] one finds then \( S_c/S_d \sim 2 \), except near the phase transition. In this way estimated higher order in the cylindrical nematic phase than in the discotic seems to be consistent with larger anisotropy of the corresponding micelles.

It should be mentioned that the theory evaluated in this paper can be easily extended to phases with other types of aggregates: lamellar phases with holes or other local fluctuations of the interfacial curvature [16, 34], phases with distorted discs and cylinders [6, 16], ripple phases, ribbon phases, hexagonal and cubic lyotropic phases.

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References

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