Lyotropic La-Containing Lamellar Liquid Crystals: Phase Behaviour, Thermal and Structural Properties

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This supporting information file contains the structural parameters of the lamellar mesophases in the $C_{12}EO_4/La^{3+}/H_2O$ system obtained by X-ray powder diffraction, the optimized structure of $C_{12}EO_4/La(NO_3)_3$ · GH_2O complex and details of the transverse relaxation experiment.

| NՉ | System | φ | d <i>,</i> Å | d ₁ , Å | d _w , Å | V _m , Å ³ | A, Å ² | d _∟ , Å |
|----|---|-------|--------------|--------------------|--------------------|---------------------------------|-------------------|--------------------|
| 1 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 35%/65% | 0.363 | 39.24 | 14.25 | 24.99 | 639 | 89.71 | 3.98 |
| 2 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 45%/55% | 0.464 | 39.18 | 18.18 | 20.99 | | 70.28 | 5.08 |
| 3 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 55%/45% | 0.564 | 38.69 | 21.82 | 16.87 | | 58.56 | 6.09 |
| 4 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 65%/35% | 0.663 | 39.14 | 25.94 | 13.19 | | 49.26 | 7.24 |
| 5 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 75%/25% | 0.761 | 38.91 | 29.65 | 9.34 | | 43.09 | 8.27 |
| 6 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 85%/15% | 0.857 | 38.32 | 32.84 | 5.48 | | 38.91 | 9.17 |
| 7 | C ₁₂ EO ₄ / La ³⁺ /H ₂ O 95%/5% | 0.953 | 39.22 | 37,36 | 1.86 | | 34.21 | 10.43 |
| 8 | C ₁₂ EO ₄ / La ³⁺ 100% | 1 | 39.38 | 39.38 | 0 | | 32.45 | 10.99 |

 Table S1 Structural parameters of the lamellar mesophases in the C12EO4/ La3+/H2O system



Fig. S1 Three-dimensional structure of the $C_{12}EO_4/La(NO_3)_3 \cdot 6H_2O$ complex. Geometric characteristics of complex: X=8.6 Å, Y=9.0 Å, Z=22.8 Å

Nuclear magnetic resonance method allows to measure the diffusion coefficient without the intervention to the sample, without using any additional labeled substances. By the action of at least two pulses of magnetic field gradient information on the movement of atoms in space is saved in the amplitude of the NMR signal. In particular, in the case of free isotropic diffusion NMR signal dependence on the diffusion coefficient and the experimental parameters is given by the expression:

$$I = I_0 \cdot \exp\left[-D \cdot k\right],$$

where I_0 – NMR signal intensity in case of absence of magnetic field gradient, D – diffusion coefficient, k – experimental coefficient that depends from experiment setup. For the diffusion coefficient measurement the experiment was performed several times for different values of the magnetic gradient values (different k values). The dependence of NMR signal intensity I from k was approximated by following expression $I = I_0 \cdot \exp[-D \cdot k]$. After this one gets the value of diffusion coefficient D. Exponential behavior of I = I[k] dependence was shown by diffusion of water molecules in the sample (Fig. S2).



Fig. S2 Experimental dependence of NMR signal from squared magnetic field gradient amplitude for water molecules; all data points approximation

In most experiments, which are presented in the article, I = I[k] dependence was not exponential. This can take place in case, for example, when there are several different types of motion diffusion motion with different diffusion coefficients. Since the liquid crystal - anisotropic medium, the diffusion in different directions within the sample occurs with different diffusion coefficient (diffusion coefficient have to be substituted by diffusion tensor). In this case, the dependence I = I[k] is not monoexponential:

$$I = \sum_{i=1}^{N} I_i \cdot \exp\left[-D_i \cdot k\right]$$

In such cases one usually uses initial approximation using one exponent on initial part of the I = I[k]dependence (section of small values k):

$$I = \sum_{i=1}^{N} I_{i} \cdot \exp\left[-D_{i} \cdot k\right] = \sum_{i=1}^{N} I_{i} \cdot (1 - D_{i} \cdot k + ...) = \sum_{i=1}^{N} (I_{i} \cdot 1 - I_{i} \cdot D_{i} \cdot k + ...),$$

$$I = \sum_{i=1}^{N} (I_{i}) - \sum_{i=1}^{N} (I_{i} \cdot k) \cdot D_{i} + \sum_{i=1}^{N} (...) = \sum_{i=1}^{N} (I_{i}) \cdot \left(\frac{1}{\sum_{i=1}^{N} (I_{i})} - \frac{\sum_{i=1}^{N} (I_{i} \cdot k)}{\sum_{i=1}^{N} (I_{i})} \cdot D_{i} + \frac{\sum_{i=1}^{N} (...)}{\sum_{i=1}^{N} (I_{i})}\right),$$

$$I = \sum_{i=1}^{N} (I_{i}) \cdot \left(\frac{1}{\sum_{i=1}^{N} (I_{i})} - \sum_{i=1}^{N} \left(\frac{I_{i}}{\sum_{i=1}^{N} (I_{i})} \cdot D_{i}\right) \cdot k + \frac{\sum_{i=1}^{N} (...)}{\sum_{i=1}^{N} (I_{i})}\right) = \sum_{i=1}^{N} (I_{i}) \cdot \exp\left[-\sum_{i=1}^{N} \left(\frac{I_{i}}{\sum_{i=1}^{N} (I_{i})} \cdot D_{i}\right) \cdot k\right],$$

$$I = I_{0} \cdot \exp\left[-D' \cdot k\right],$$

$$D' = \sum_{i=1}^{N} \left(\frac{I_{i}}{N} \cdot D_{i}\right) - \text{averaged diffusion coefficient.}$$

In our work we used such method of approximation on initial part of the dependence (Fig. S3).

where

 $\overline{I_{i=1}} \sum_{i=1}^{i=1} (I_i)$



(magnetic field gradient amplitude)²

Fig. S3 The experimental dependence of the signal amplitude from the squared amplitude of magnetic field gradient for surfactant molecules diffusion experiments; approximation for the initial segment

T₂ measurements

Almost any NMR experiment begins from the creation of non-equilibrium magnetization of the sample: the magnetic moments are "turning" from the direction of "external magnetic field" to the perpendicular direction. The nuclear magnetic moments precess around the direction of the external magnetic field. Nuclear magnetic moments of neighboring nuclei create at adjacent nuclei additional magnetic field For this reason, the angular frequency (rate) of rotation of the magnetic moments changes, since $\omega = \gamma \cdot H$. The magnetic moments begin to rotate at different speeds. And eventually they get different angles of rotation - there is a loss of phase coherence. This process is known as spin-spin or transverse relaxation. This process characterized by relaxation time: T₂-relaxation. It is known that in most cases NMR signal dependence in T₂-measurement experiments obeys the exponential decay:

$$I = I_0 \cdot \exp\left(-\frac{t}{T_2}\right),$$

where I_0 – initial amplitude of NMR signal, T_2 – transverse relaxation time. The value of the relaxation time T_2 is strongly influenced by the nature of motion of the nucleus. In the case of an active molecular motion of the molecular fragment containing nucleus, the magnetic fields of neighboring cores are averaged by this motion, which leads to a slower process dephasing and therefore - larger values of T_2 . The measurements of the transverse relaxation time were carried out using the method of Carr-Purcell-Meiboom-Gill. The intensity of the NMR signal for different values of time of the experimental t was

approximated by exponential dependence $I = I_0 \cdot \exp\left(-\frac{t}{T_2}\right)$. The result of the approximation was T_2

value.