



Invited lecture/Scientific contribution

Dielectric Study of Induced Phase Transitions in Lyotropic Liquid Crystals

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Abstract

Lyotropic liquid crystals are multicomponent systems of fundamental importance. They can also construct model structures for biological systems. The richness of their phases allows for the theoretical prediction of behaviour and the planning of model experiments enabling an approximation of the description of a living cell.

In this work, we present experimental results for lyotropic liquid-crystalline lamellar phases, which may be used as a physical model of phospholipid bilayer. Dielectric measurements were performed under temperature and high-pressure conditions. Complex dynamics, dielectric response, static properties as well as electric conductivity were considered and analysed on the basis of the critical phenomena theory. Other dielectric/electrostatic properties were also calculated and compared to evidence for biological systems.

Keywords: Lyotropic liquid crystals, Dielectric constant, Phase transition, Critical phenomena, Electric properties



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1. Introduction

Lyotropic liquid crystals are mixtures of amphiphilic molecules and solvents. The properties of this mesophase change with temperature, pressure and the relative concentration of the individual components of the solution. An important property of lyotropic liquid crystals is the self-assembly of amphiphilic molecules into supramolecular structures, which are the basic components of the mesophase (de Gennes and Prost, 1993; Figueiredo and Salinas, 2005). The physicochemical properties of these liquid crystals are closely related to many fields of science, especially biological and engineering sciences used in technical and technological research (Sasi et al., 2016) of cosmetics, detergents, crude oil, biomass and finally food (Mezzenga et al., 2005; Sagalowicz et al., 2016).

Lyotropic systems can also be considered as supramolecular colloids. This is especially true for the first family of lyotropic liquid crystals. Individual micelles are particles dispersed in a polar solvent. The methods of colloid physics can be used in the analysis of these systems.

Amphiphilic molecules, which form organisationally higher structures, can arrange themselves in them in two ways. It depends on the concentration of the individual components of the mixture. If there is a higher concentration of water or another polar solvent in the system, the amphiphilic molecules align themselves with hydrophobic chains towards the centre of the structure formed. If, on the other hand, the situation is reversed, i.e. the concentration of the amphiphilic molecules is greater than the concentration of water, then they arrange themselves so that their hydrophobic parts protrude from the resulting structure.

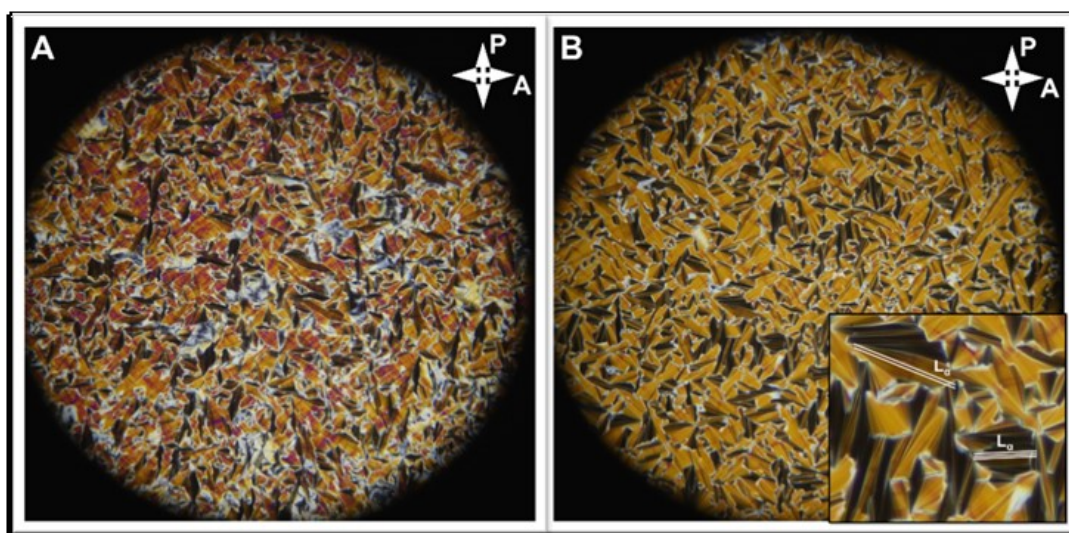


Figure 2. Frequency dependencies of the real parts of complex electric permittivity (A) and conductivity (B) for different pressures at $T = 310$ K. The static part of electric permittivity ϵ_s and conductivity σ_{DC} are marked.

Determining the order parameter in lyotropic liquid crystals was proposed in a model based on Landau-de Gennes' theory (Mukherjee and Bhattacharya, 2007). Experimental data showed that the lamellar phase L_α has the same symmetry as the smectic phase C of thermotropic liquid crystals. This situation is described by the traceless tensor Q_{ij} . Layers in the L_α phase have an order parameter expressed by $\psi(r) = \psi_0 \exp(-i\Psi)$. The complex modulus ψ_0 is defined as the amplitude of a condensed wave with phase Ψ .

The following form of the order parameter for the L_α lamellar phase was therefore proposed:

$$Q_{ij} = \frac{S}{2} (3n_i n_j - \delta_{ij}) \quad (1)$$

where n_i is different from $\nabla_i \Phi_j$, the value of S describes the ordering force of the nematic phase (Mukherjee and Bhattacharya, 2007; Mukherjee, 2013). However, this model needs to be further developed so that it can be applied to other more complex phases of lyotropic liquid crystals.

A much more convenient method of determining the order parameter is to use the modified Haller function. According to Meyer-Saupe's theory, it is based on the temperature of a continuous phase transition 1-2 K below the observed discontinuous transition. Experimental results and simulation data to date have shown that the use of this approach is consistent with theoretical predictions. The order parameter for the nematic and smectic A phases, and thus for the lamellar one, can be presented as follows:

$$\langle P_2 \rangle = \langle P_2 \rangle_{iso} + \left(1 - \frac{T_{meso}^*}{T} \right)^\beta \quad (2)$$

where $\langle P_2 \rangle$ is the second-order Legendre polynomial of rearranged permanent dipole moments $\vec{\mu}$, $\langle P_2 \rangle_{iso}$ is the order parameter of the isotropic liquid, T_{meso}^* denotes the hypothetical ideal phase transition located 1-2 K below isotropic-mesophase one and β is a critical exponent. According to the theory of universality, the critical exponent β is assumed to be in the range of 0.25-0.5 (Buscaglia, 2006).

2. Methods

Dielectric complex permittivity $\epsilon(\omega)^* = \epsilon(\omega)' + i\epsilon(\omega)''$ was measured using impedance Alpha-A analyser (Novocontrol, Montabaur, Germany) in a wide range of frequencies (1 Hz-10⁹ Hz) and temperatures (273-373 K). The sample was placed into a round, parallel steel capacitor with a diameter $2r = 20$ mm and a gap $d = 0.15$ mm. A Teflon[®] ring was used as a spacer. Temperature was stabilised using liquid nitrogen (N₂) in the QuatroCryo system (Novocontrol, Montabaur, Germany) with stability better than $\delta T = 0.02$ K.

The high-pressure measurements were performed in a chamber (Unipress Equipment, Warsaw, Poland). Samples were placed into a rectangle capacitor mounted in a Teflon[®] capsule. Temperature was stabilised by Julabo cooler/heater system (Julabo GmbH, Seelbach, Germany) with stability ca. $\delta T = 0.05$ K. Plexol[®] was used as a pressure medium. Dielectric spectra were measured using Alpha-A analyser (Novocontrol, Montabaur, Germany) ($f \in \langle 1 \text{ Hz}, 10^9 \text{ Hz} \rangle$). Lyotropic liquid crystalline (LLC) phase L_α , based on water and Dimodan[®], was prepared according to a protocol proposed by Mezzenga et al, (2005). Pictures of liquid-crystalline textures were taken using the PZO Studar[®] polarising microscope (PZO, Warsaw, Poland) with a self-built LC chamber and temperature stabilisation $\delta T = 0.5$ K.

3. Results

This part of the paper presents the results of temperature and pressure tests of phase transitions in the lamellar phase. **Figure 2** shows typical dielectric spectra over a wide frequency range. The data presented for the compression show the dependence of the real parts of the electric permittivity ϵ' (f) (**A**) and the conductivity σ' (f) (**B**). Due to the strong variability of the presented functions, the analysis of dielectric data of liquid crystals and biological systems should include static regions corresponding to the maximum polarisation of the sample. For the real permittivity part, it is the so-called dielectric constant ϵ_s , for the conductivity part it is DC-conductivity σ_{DC} (Rzoska et al., 2016; Starzonek et al., 2015). In the further course of the work, their temperature and pressure dependencies are analysed.

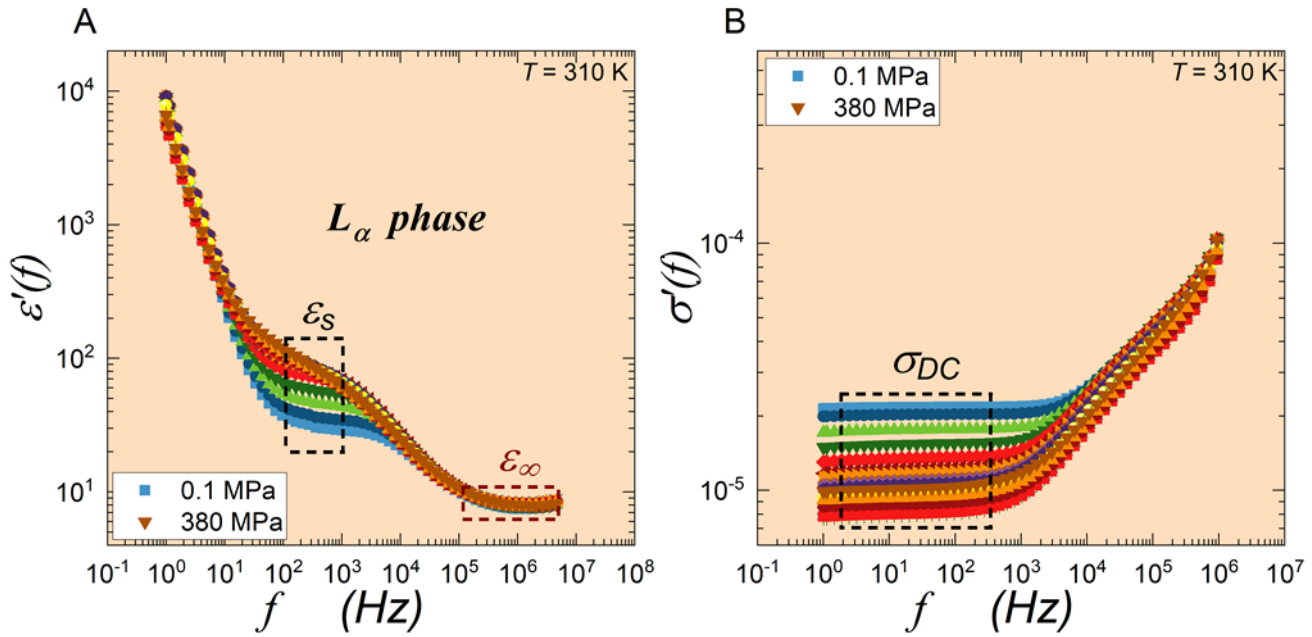


Figure 2. Frequency dependencies of the real parts of complex electric permittivity (A) and conductivity (B) for different pressures at $T=310$ K. The static part of electric permittivity ε_s and conductivity σ_{DC} are marked.

Figure 3 shows the dependence of the dielectric constant at the frequency $f = 100$ Hz over a wide temperature range. This representation enables the detection of phase transitions and the determination of their critical-like character. At the temperature $T = 322$ K (at atmospheric pressure), a sudden change in the dielectric constant is observed, which proves the existence of a discontinuous transition between the phases L_α and L_Π . Near the phase transition temperature, a characteristic change in behaviour is observed, which is related to the antiparallel arrangement of the dipole moments. This phenomenon is associated with pretransitional fluctuations and occurs in many liquid crystal systems with a rod-like structure of the molecule. Based on the theory of critical phenomena, an exponential critical function with the critical exponent can be determined (Rzoska et al. 2016; Rzoska et al.,2020):

$$\varepsilon_s(T) = \varepsilon^* + A|T - T^*| + B|T - T^*|^\varphi \quad (3)$$

where (T^*, ε^*) describes a point of hypothetical ideal continuous phase transition, A, B are amplitudes and $\varphi = 1 - \alpha$ is the exponent related to heat capacity critical exponent. For the pressure path one may transform Equation (3) and obtain (Rzoska et al., 2016):

$$\varepsilon_s(P) = \varepsilon^* + A'|p^* - p| + B'|p^* - p|^\varphi \quad (4)$$

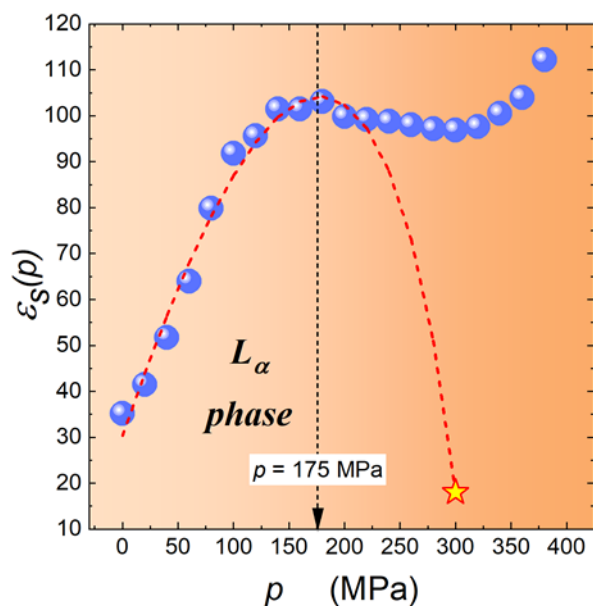


Figure 3. Temperature dependence of dielectric constant $\epsilon_s(T)$ at ambient pressure. Phase transition between two lamellar phases occurs at $T = 322$ K with strong pretransitional effects. Dashed lines present the fitting by the **Equation (3)**, which provides critical-like behaviour with the critical exponent $\alpha=0.5$. Stars denotes points for ideal continues phase transition.

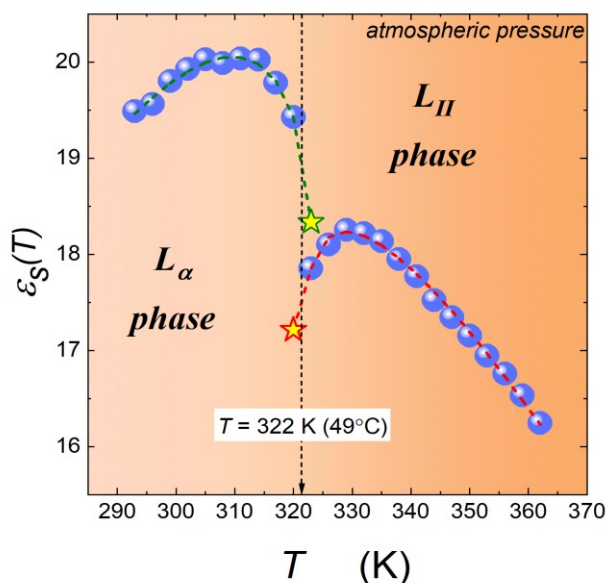


Figure 4. Pressure evolution of dielectric constant $\epsilon_s(p)$ at $T = 310$ K. Dashed line shows the fitting by the **Equation (4)**, which provides critical-like behaviour with the critical exponent $\alpha = 0.5$. The star denotes a point representing ideal continuous phase transition.

A similar analysis was carried out in an isothermal pressure experiment ($T = 310$ K) and the results are shown in **Figure 4**. A notable change in the behaviour of the dielectric constant occurs at a pressure of $p = 175$ MPa, which can be considered as a phase transition. Also, the fitting of **Equation (4)** leads to the demonstration of a critical-like behaviour with a strong pretransitional effect with exponent $\alpha = 0.5$.

The analysis of high-pressure data is difficult, so to confirm the existence of a weakly discontinuous phase transition, another physical quantity should be considered. In this case, it was decided to focus on the DC-conductivity, which is related to the mobility of ions in the system. **Figure 5** shows the pressure dependence of the DC-conductivity for the tested



system. At pressures $p = 175$ MPa and $p = 300$ MPa, two anomalies can be observed which can be interpreted as indications of a phase transition. The figure shows the differential analysis of the $\sigma_{DC}(p)$ relation and a clear discontinuity near the indicated points, which confirms the existence of a phase transitions.

Another good quantity to identify the phase transition and the behaviour near the critical point is the order parameter given by **Equations (1) and (2)**. Calculating order parameter $\langle P_2 \rangle$ one may expand **Equation (2)** in the Taylor series what gives (Zanoni, 2022; Starzonek, 2018):

$$\begin{aligned} \langle P_2 \rangle_T &\approx (1 - T^*x)^\beta \text{ for } x = \frac{1}{T} \\ \ln \langle P_2 \rangle_T &= \beta \ln(1 - T^*x) \approx -\beta T^*x = Ax + B \end{aligned} \quad (5)$$

This linearised form allows to easily fit the critical exponent β of obtained data from a slope $\beta = \left| \frac{T^*}{A} \right|$.

For the pressure experiments it is possible to propose an analogue formula for p^* as follows

$$\langle P_2 \rangle_p \approx \left(1 - \frac{p}{p^*}\right)^{\beta'} \rightarrow \ln \langle P_2 \rangle_p = \beta' \ln \left(1 - \frac{p}{p^*}\right) \approx -\frac{\beta'}{p^*}p = Cx + D \quad (6)$$

where p^* denotes continuous phase transition pressure and $\beta' = |p^*C|$.

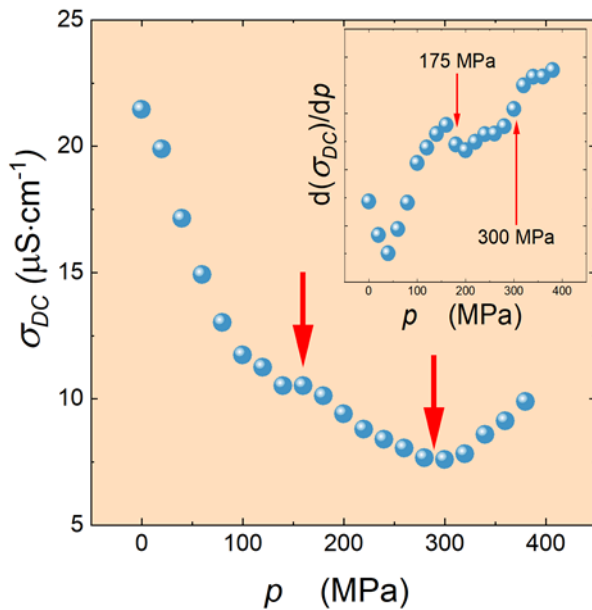


Figure 5. Pressure dependence of DC-conductivity $\sigma_{DC}(p)$ at $T = 310$ K. Arrows present anomaly behaviour and potential phase transitions. The inset shows derivative-based analysis of obtained data with strong discontinuities at marked pressures.

Figure 6 shows the temperature (A) and pressure (B) dependence of the order parameters near the phase transition point. The calculations were carried out based on **Equation (2)** with the assumed critical exponent $\beta = 0.25$. A typical change during the function describing the order parameter near the temperature/pressure of the phase transition makes it possible to determine it. It is worth noting that in the case of the temperature dependence, both the L_α and L_{II} phases have a similar degree of order, while in the case of the pressure data at atmospheric pressure $p = 0.1$ MPa, the order parameter is identical to its temperature equivalent, $\langle P_2 \rangle_p(0.1 \text{ MPa}) \equiv \langle P_2 \rangle_T(310 \text{ K})$.

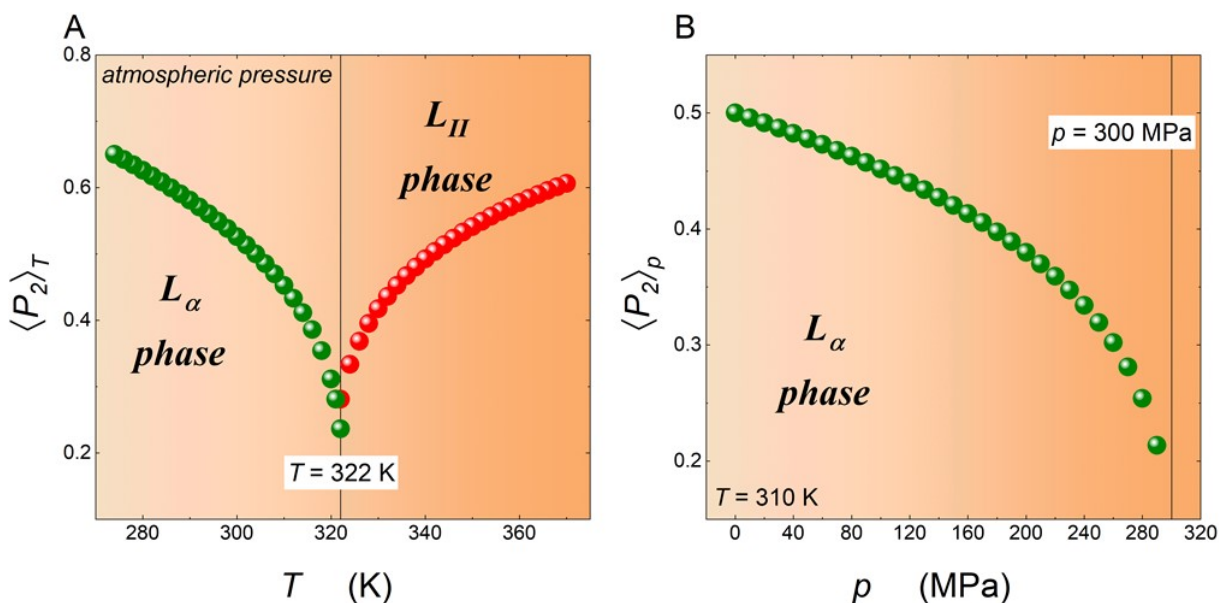


Figure 6. Order parameters for temperature (A) and pressure (B) experiments calculated from **Equation (2)** with a critical exponent $\beta = 0.25$.

4. Discussion

The results presented in this paper are undoubtedly among the first obtained with dielectric spectroscopy methods on this type of system. It is worth mentioning that the analysis of phase transitions of lyotropic liquid crystals plays a significant role in many fields of science, such as biology, food science and materials science. Due to the analysis of the behaviour near the phase transition of a given system, many physical and physicochemical properties can be predicted.

Previous studies of similar systems have focused on computer simulations or theoretical considerations, and few presented model liquid crystal systems with potential utility for the food industry (Sagalowicz et al., 2016). The focus on the lamellar phase is intended to bring the theoretical description closer to the results obtained by experimental methods and to those derived from computer simulations (Mukherjee et al., 2007). It is worth mentioning that the analysis of phase transitions between the L_α phase and the L_{II} phase has not been the basis of research so far. These two phases differ from each other only in details, which makes the transition between them appear to be weakly discontinuous or continuous. Due to the temperature analysis of the dielectric constant, shown in **Figure 3**, the existence of a strong anomaly before the transition between the two lamellar phases has been demonstrated. It can therefore be assumed that this transition is not a subtle structural change, but a strong discontinuous transition with a critical character.

Similar conclusions can be drawn for high pressure data. In this type of experiment, it is extremely important to maintain isothermal and isobaric conditions at each measurement point. Therefore, there are few experimental results for liquid crystals under high pressure conditions, especially for lyotropic materials. The phase transition observed and shown in **Figure 4** is a weakly discontinuous transition. Therefore, only the use of additional extremely sensitive methods, which include differential analysis, leads to the detection of the phase transition. However, the main problem with a pressure experiment is the identification of the individual phases. This is due to the lack of a phase diagram, i.e. the nature of the materials as a function of pressure. While in the case of the temperature experiment, the identification of the individual phases is not a problem and corresponds to what was previously postulated in the literature, the compression of the system can lead to the complete destruction of the lamellar structure and the formation of, for example, a micellar structure or even inverted structures. Undoubtedly, such experiments require further work and analysis. The tested system consists of an amphiphilic agent and water, which makes the investigation of DC-conductivity reasonable. In the temperature tests, no significant changes in DC-conductivity were observed, clearly indicating a phase



transition near the characteristic temperature (Starzonek et al., 2015; Starzonek, 2018; Rzoska et al., 2016; Rzoska et al., 2020). In pressure tests, however, the DC-conductivity becomes a key parameter for identifying phase transitions. With increasing pressure, the density of the system under investigation increases, and in systems consisting of amphiphilic molecules and water, we are only dealing with a rearrangement of the molecular positions. Thus, observing the released ions, which are from the water, allows us to assess how the molecules arrange themselves in individual lyotropic phases. It would be possible to transfer the phase diagram in the temperature scale to the pressure scale and conclude that above the phase transition pressure the lamellar structure is destroyed. However, it is not possible to say unequivocally whether this is not accompanied by a phase change with the release of bound water.

Due to the analysis of the order parameters in liquid crystalline phases, it is possible to determine what kind of transition we are dealing with as well as to calculate other physical parameters. One of the most used functions for the order parameter is the so-called Haller function, which is based on the Meyer-Saupe theory (Zanonni, 2022; Starzonek, 2018). This function assumes, based on the classical isotropic liquid-nematic phase transition, that the critical point for this type of transition is a discontinuous transition. However, previous studies have shown that in the presence of a strong anomaly before the transition, the critical point, which is the site of a continuous phase transition, is much lower than the temperature of the observed phase transition. Therefore, in this work it was decided to use the modified Haller function based on the Landau-de Gennes theory of phase transitions of liquid crystals, thanks to which the exponent contained in **Equation (2)** can be considered as the critical exponent. Numerous theoretical experiments and computer simulations have shown that the value of this exponent is about 0.25 for both the nematic and smectic phases. If we assume that the lamellar phase can be approximated by the smectic phase, then the critical exponent beta equal to $\beta = 0.25$ can be easily assumed for theoretical considerations of professional transitions (Buscaglia et al., 2006; Zanonni, 2022).

Summing up, the presented results are undoubtedly a valuable contribution to the development of soft matter physics, as well as biology, food science and materials science. Thanks to the approach presented by the theory of critical phenomena, it is possible to fully analyse the phase transitions between the L_α and L_{II} phases. The existence of strong pre-transition effects, characteristic of both the nematic and smectic phases, allows the use of existing theoretical tools to analyse the obtained results. Undoubtedly, the calculated critical exponents $\alpha = 0.5$ and $\beta = 0.25$ allow to assign the tested system to the same universality class in which we can find other liquid crystal structures. Further analysis of the ordering parameter based on computer simulations and in-depth theoretical description will allow to link the symmetry of the system with molecular dynamics. This type of research is a valuable contribution to the creation of a modern model of the biological membrane, considering its interactions with nanoparticles or microorganisms (Raval et al., 2021).

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Conflicts of Interest: The authors declare no conflict of interest.

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