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The Study of Lyotropic Mesomorphism of a System of Sodium Pentadecyl Sulfonate-Polyethylene Glycol – Water under the Influence of Temperature

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Abstract. The method of *X*-ray analysis was used to study the structural changes of a multicomponent liquid crystal of sodium pentadecyl sulfonate-polyethylene glycol-water in the lamellar liquid crystal phase under the influence of temperature. Studies were carried out at concentrations in the system from 23 to 98% at different contents of polyethylene glycol. The concentration interval of the lamellar "smooth" phase is established. The characteristic parameters and structural features of this phase and the influence of temperature on them in the range from 293-353*K* are revealed.

Keywords: radiogram, multicomponent liquid crystal, lyotropic liquid crystal, biomembrane models, lamellar phase.

1. Introduction

The formation and stability of lyotropic liquid crystals (LLC) is due to the balance of hydrophilic-hydrophobic interactions in a system of molecules [1, 2]. Just this determines the ability to control the structure and properties of LLC through the influence of non-mesogenic additives that can effectively change the interaction forces between the matrix molecules and the included components, therefore, there should be significant differences in the nature of the effects of various non-mesogenic substances on the structure of LLC . From this point of view, it is of interest to study multicomponent models of biomembranes based on lyotropic liquid crystals.

Under certain conditions, biomembrane lipid suspensions can form aggregates of various structures, that is lipids have the property of polymorphism. Polymorphic transformations were also found in biological membranes [3–11]. Structural thermal rearrangements in eukaryotic membranes containing relatively many cholesterol or membrane proteins found by various physicochemical methods indicate that they are the result of structural rearrangements affecting the lipid and protein components of membranes [12] The question arises whether structural rearrangements are caused observed in the region of $283-303K$, crystallization of membrane lipids or polymorphic transformations of a gel-liquid crystal.

Each of the biomembrane models was studied in order to understand and explain some of the facts observed in the study of membranes. But not one of them is able to explain satisfactorily all the data accumulated by science. Thus, the question of the nature of the occurring thermal and lyotropic rearrangements remains open.

In this work, we studied the effect of temperature on a model system of biomembranes containing macromolecular non-mesogenic additives and mesomorphic transformations depending on their characteristic parameters.

Since LLC is determined by the equilibrium of hydrophilic hydrophobic interactions of molecules, it can be assumed that the introduction of a new component into the system effects the structure of LLC through the impacked on the balance of hydrophilic and lipophilic interactions. In this case, LLC can act as a matrix for the orientation of molecules that do not have the ability to independently form a liquid crystal phase. To this aim, the influence of temperature on the system of sodium pentadecyl sulfonate (SPS) -polyethylene glycol (PEG) -water capable of effectively changing the interaction forces between the molecules of the matrix and the macromolecule at different temperatures was studied.

The choice of PEG as a macromolecular additive is due to its widespread use in light industry, in the food industry, in the cosmetics industry, and is used to restore and preserve wet wood, in archaeological finds, and to model underwater eruptions. Based on PEG, lubricants, cutting fluids, and solvents are produced. PEG is also used for the manufacture of biomembranes, water-soluble films, and drugs. With the help of PEG, the Italian neurosurgeon Sergio Canavero expects to connect the nerve cells responsible for transmitting vital impulses from the brain to organs and limbs. PEG is also capable of repairing a damaged membrane, facilitating the fusion of two damaged cells into one large nerve cell.

Thus, a set of methods, including a key component - PEG was used in practice. However, more work remains to be done to make its application reliable and to ensure confidence in the correct selection of many variables that are important for a successful outcome.

2. Experimental Approaches

To study LLC, it is necessary to consider the phases of not individual molecules, but of structural elements, which are supramolecular formations. The nature of the symmetry of the structural element is determined by the symmetry of the arrangement of the molecules that form it - the bilayer, cylinder, sphere. Polymorphic transformations relate to objects consisting of many structural elements [13, 14].

Our task is to create experimental conditions for studying the structural elements of both molecular and supramolecular formations, for which requires a preliminary solution of a number of technical and methodological problems.

The following requirements are imposed on the experiment: $X-$ray collimation, slit width, small-diameter holes, focusing, exposure, sample size and preparation, $X-$ray radiation wavelength, data recording methods, effects arising from small-angle $X-$ray scattering, diffuse scattering, results obtained and their discussion. Samples were taken on URS-60 and URS-2 $X-$ray

installations with KRON and RKSO cameras intended for shooting on a flat film and modified for studying simultaneous scattering at large and small angles of reflexes in the range of angles from 3^0 to 85^0 at sample-film distances $0.05-0.3\,m$. A schematic image of the camera is shown in Fig. 1.

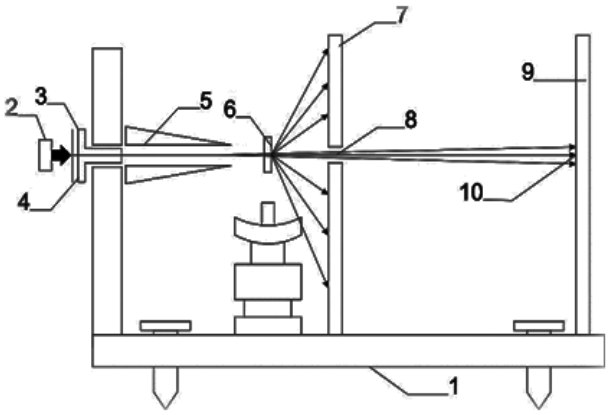


Fig. 1 Schematic picture of the camera

$X-$rays coming out of the focus of the $X-$ray tube 2 pass through a nickel filter 3, the diaphragm 4 and the collimator 5 and fall onto the sample 6. The diameter of the aperture is $1\times10^{-4}m$, the length of the collimator is $8\times10^{-4}m$, the diameter of its hole at the exit is $0.8\times10^{-4}m$. The improvement in the beam collimation consisted in the optimal reduction of the width of the slit placed in the beam path. The main advantage of small-hole collimation is the absence of distortion in the $X-$ray diffraction patterns when studying oriented samples. The main disadvantage is associated with a rather long exposure time necessary for obtaining undistorted paintings. Such collimation provides a fairly good accuracy.

Diffracted at large angles, the rays are recorded on an x-ray film placed in the cassette 7. The latter has a hole in the middle 8 through which the transmitted rays are fixed on the film placed on the cassette 9. The primary beam is absorbed by the absorber 10. The modified camera makes it possible to register reflections within the angles 1^0-45^0 (the small-angle part is 1^0-5^0).

We used tubes of the BSV-24, BSV-25, and BSV-11 types with a Cu cathode that emits radiation in the region of relatively long waves. Copper $K\alpha$ lines were extracted using nickel filters $1.5\times10^{-5}m$ thick. The voltage at the anode is $40kV$, the anode current is $20mA$. The exposure time was selected 4 hours. Films of the RTG-B type from Primax Berlin Germany were used. To prepare the sample, quartz thin-walled capillaries (manufactured by Germany) with a wall thickness of $1\times10^{-5}m$ and a diameter of $0.4\times10^{-3}m$ to $1\times10^{-3}m$ were used. Absorption of rays and the appearance of the background on radiographs when using these capillaries are practically absent.

The reconstructed method of x-ray diffraction allows us to obtain information about the size, shape, compactness of the location of colloidal formations.

3. Samples

The structures of simplified three-component models of liquid crystal systems, obtained on the basis of highly concentrated aqueous solutions of the surfactant SPS - $(C_{15}H_{31}SO_3Na)$ and PEG, are studied.

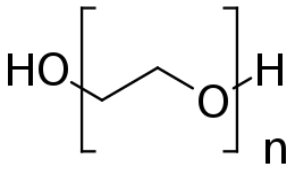
The mid-range SPS product of Veb Leuna contains the following impurities:

The main substance ……n / m	98%
Sodium chloride ……n / a	1.4%
Sodium sulfate ……n / a	0.1%
Neutral oils ……n / a	0.1%
Water ……n / a	0.2%
Sodium hydroxide ……n / a	0.1%
Iron ……n / a	0.5%

At room temperature, the studied sample has the appearance of a dull white paste containing 6% hydrated water. The spatial structure of the SPS molecule can be represented as shown in Fig. 2

Fig. 2. Schematic structure of the SPS molecule and its arrangement in the lamella

PEG with a molecular weight of $2000\,g/mol$ was used as a high molecular weight additive. PEG with a mass of up to $2000\,g/mol$ - highly-shaped flakes or cream-colored powder. The structural formula has the following form:



$HO-(CH_2-CH_2-O)_n-H$, rational formula - $C_{2n}H_{4n+2}O_{n+1}$, density $1.1-1.2\,g/sm^3$.

For the preparation of samples, quartz capillaries with a wall thickness of $1\times10^{-5}m$ and a diameter of $0.4\times10^{-3}m$ to $1\times10^{-3}m$ were used.

Samples for $X-$ray diffraction were prepared by the following method: heat treatment was carried out - until the $X-$ray diffraction patterns were taken, the sample was kept at a $353K$ temperature for half an hour, after which an isotropic melt of the corresponding concentration was introduced into the capillary, hermetically closed on both sides and cooled to room temperature. The finished sample was examined immediately after processing, as well as at certain intervals. The studies were carried out in the temperature range from 293 to $353K$.

The orientation of the samples in the absence of water was carried out using mechanical tension. $X-$ray diffraction patterns of stretched "anhydrous" samples made in the form of cylinders with a diameter of $0.4-1mm$ were taken without a capillary. Orientations of concentrated aqueous solutions were carried out by drawing the solution into the capillary.

4. Results

The studies were carried out at a PEG content of 9% in the SPS-PEG system in the "smooth" phase. The control image of an 86% sample of the SPS-water system revealed the lamellar structure of SPS molecules of a monomolecular layer $27.5\,\text{Å}$ thick. On radiogram revealed a reflex in the form of a uniform circle. When a 67% sample of the SPS-PEG-water system is added to the PEG system in an radiogram with a PEG content of 9%, the reflex becomes clear and slightly grainy. By evaporation of the sample up to 86% at room temperature, the reflex in the radiogram remains clear and oriented, sickle-shaped with an inclination angle of 42^0. When the sample is heated to 308K, the tilt angle increases to 68^0, at a temperature of $313K-80^0$ and at $318K-90^0$. Further heating to $333K$ leads to the disappearance of the sickle-shaped reflex. Pictures of samples at temperatures of 343 and $353K$ give clear and uniform circles on the radiogram.

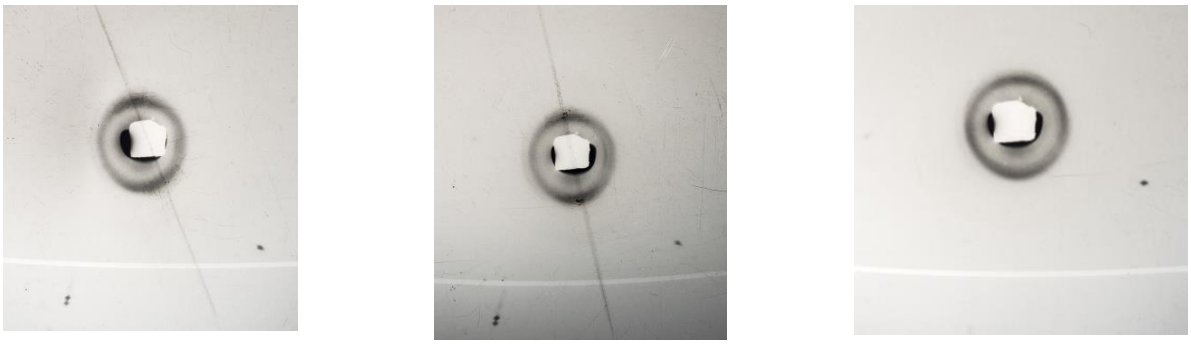


Fig. 3. The radiogram of 86% samples of the SPS-PEG-water system with the content 9% PEG at temperatures of 308, 313, 353K

A sample heated to a temperature of $353K$ was cooled to room temperature. In this case, monocrystallism and reflexes appear at large angles.

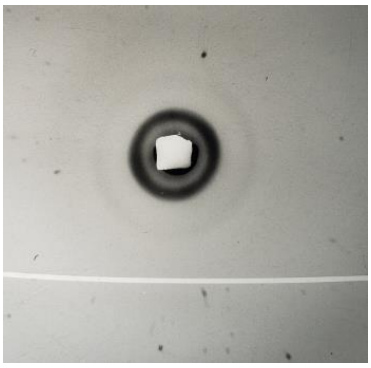


Fig.4. The radiogram of an 86% sample of the SPS-PEG-water system, when PEG 9%, heated to 353K and cooled to room temperature

The texture is also preserved after two days of taken radiogram. When reheating the same sample to $353K$, on the radiogram only traces of monocrystallinity remain, but a clearly defined circle preserved.

With an increase in the concentration of PEG to 36% in the SPS-PEG-water system at room temperature, a characteristic circle with an interplanar distance of $24.7\,\mathring{A}$ appears on the $X-$ray in a 54% sample. With increasing temperature, the interplanar spacing decreases. The results are shown in Table 1

Table 1. Temperature dependence of the 54% SPS-PEG-water system

Temperature in K	*Interplanar distance in Å*
295	27.5
308	27
313	24.7
318	24
333	23.8
343	23.5
353	22.5

On the radiograms of a 70% sample at a PEG content of 36% at room temperature show a crescent circle. The latter is formed when the concentrated solution is drawn into the capillary. With a further increase in concentration, the intensity of reflexes characteristic of the lamellar structure increases and thin weak reflexes appear at large angles. When the sample is completely dry, when it contains only hydrated water, a number of distinct reflexes are revealed at large angles. Interplanar distances and relative intensities of the "dry" sample are shown in Table 2.

a **b**

Fig.5. The radiograms of samples of the SPS-PEG-water system, with a PEG content of 36% a) a concentration of 86%, b) a "dry" sample with a content of hydrated water.

Table 2. Interplanar distances and relative intensities of a highly concentrated sample of the SPS PEG-water system at a PEG content of 36%.

N	*Interplanar distance in Å*	*Relative intensity*
1	27.4	10
2	6.6	1
3	6.2	2
4	5.3	3
5	4.8	9
6	4.3	5
7	3.96	8
8	3.5	4

Studies were also conducted to determine the effect of temperature on highly concentrated SPS-PEG-water systems with a PEG content of 36%. Samples were taken at temperatures of $308, 313, 318, 333, 343, 353K$. Under the influence of temperature, the intensity of reflections at large angles gradually decreased, and at a temperature of $343K$, they completely disappeared. But

at the same time, the reflex with an interplanar distance of $27.4\,\mathring{A}$ was split into two thin, clearly defined reflexes with interplanar distances of $27.4\,\mathring{A}$ and $27.4\,\mathring{A}$. The latter was also revealed at a temperature of $353K$.

5. Discussion

To decipher the obtained X – ray diffraction patterns, we schematically represent the possible intra-domain structures of the lyotropic liquid crystal "smooth" phase (Fig. 6).

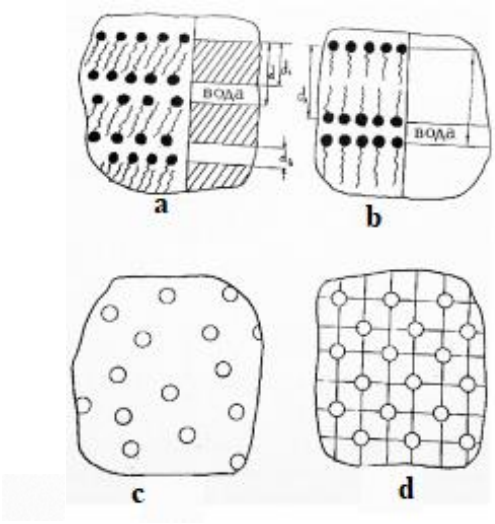


Fig.6. Arrangement of molecules in the "smooth" phase: a-lamellae of monomolecular thickness; b-lamella of bimolecular thickness; c- chaotic arrangement of the heads of the molecules; d-rectangular centered packing of heads.

We found that in the "smooth" phase, in the absence a little water content, an intradomain lamellar structure is realized, there is an alternation of SPS parallel layers of monopolymer and bimolecular thicknesses and water layers. In lamellae, surfactant active molecules can orient themselves at an angle to the lamella-water interface or perpendicular to it. Remaining oriented, the molecules in the lamellae can be located randomly relative to each other or in a certain order. The trans structure of the hydrocarbon skeleton of the SPS molecule is shown in Fig. 2.

When 9% PEG is added to the system in the "smooth" phase, the reflex appears more distinct, slightly granular, and characteristic of a layered structure with alternating layers of SPS and water. It can be assumed that PEG is located in the water layer and leads to the strengthening of the layers. With an increase in the concentration of the sample — by evaporation, the interplanar spacing decreases, and starting from a concentration of 60% it equals $27.4\,\mathring{A}$ and does not change with

further evaporation. But with a further increase in concentration, the reflex with an interplanar distance of $27.4\,\text{Å}$ becomes sickleshaped. This indicates that the SPS molecules in the layers are inclined to the lamella-water interface. It can be assumed that this is the effect of PEG, which, located in the water layer of "bound" water, compresses the lamella, tilting the molecules. In a 86% sample at room temperature, the SPS molecules are tilted at an angle of 42^0 to the interface.

By heating the sample, the tilt angle increases and already at $318K$ equals 90^0. This can be explained by the fact that an increase in temperature leads to partial loosening of the structure and a decrease in the thickness of "bound" water: since the interplanar distance remains unchanged - equal to $27.4\,\text{Å}$. A further increase in temperature to $353K$ does not change the structural parameters. This states that the PEG shields the lamellar structure of the SPS, ensuring its strength and stability with respect to water and temperature.

After cooling to room temperature in a heated sample, the "smooth" phase is retained in the sample but the crystallinity of the system increases. The SPS molecules, remaining perpendicular to the surfactant SPS – water interface, are compressed, and their heads are oriented on the surface. Clumps of surfactant SPS molecules are detected in the system, forming monocrystals. It can be assumed that the domains in the system are located randomly relative to each other, but in the domains there is a partial crystallization of the system. A mixed phase "gel" - "coagel" is formed. The resulting phase does not change over time. Upon repeated heating of the same sample to $353K$, crystallinity decreases, but the formed phase is preserved.

With a further increase in the concentration of the system at room temperature, the molecules in the layers orient themselves in a "dry" image, where only hydrated water is contained, the heads of the molecules on the surface of the surfactant-water are distributed in an orderly manner, as evidenced by reflexes at large angles in $X-$ray diffraction patterns. The interplanar distances and relative intensities of highly concentrated samples of the SPS-PEG-water system at PEG content of 36% are shown in Table 2.

The effect of temperature on highly concentrated systems leads to a decrease in the crystallization of the system. The intensity of reflexes at large angles gradually decreases and at a temperature of $343K$ they completely disappear. This is because hydrocarbon chains become "liquid". The ordering of the molecular heads on the lipid-water phase interface also disappears. But two types of ordering coexist in the system: lamellae of monomolecular thickness with interplanar spacings of $27.4\,\text{Å}$ and $24.7\,\text{Å}$. This can be explained by the fact that at high concentrations in the system, the possibility of PEG penetrating into the aggregate is limited and an inhomogeneity is formed. In lamellae with an interplanar distance of $24.7\,\text{Å}$, PEG, penetrating the interlamellar water layer, compresses the layers, leading to compaction and in lamellas with an interplanar distance of $27.4\,\text{Å}$, the effect of PEG is not very pronounced.

Thus, the study found that the effect of PEG on the liquid crystal structure of models of biomembranes based on SPS-water leads to the compaction of the system, penetrating into interlamellar water layers, spreads on the surfaces of the heads, compresses the layers by tilting the

hydrocarbon chains at an angle to the lipid-water interface. The influence of temperature reduces the compactness of the system, but the liquid crystal mesophase is retained.

An increase in the PEG content leads to a phase transition from the “gel” to the “collagen”. Under the influence of temperature, the reverse process takes place: the “coagel” turns into a “gel” phase. The liquid crystal “smooth” phase is retained in the system with the coexistence of different types of lamellae. The influence of temperature leaves a residual effect on the system, but the liquid crystal phase is retained.

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Conflicts of interest

The authors declare no conflict of interest.

Author Contributions

Authors Ts.M. Jomardyan, S.M. Grigoryan and M.A.Ghukasyan invented and developed the experiment; authors A.G. Sargsyan and A.A. Shahinyan participated in data processing and carried out theoretical calculations.

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