Armenian Journal of Physics, 2020, vol. 13, issue 3, pp. 301-309

X-ray Study of the Lyotropic Mesomorphism of Sodium Dioctyl Sulfosuccinate-Water System

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Received 24 June 2020

Abstract. In the work, the structural changes of the lamellar liquid-crystal phase of the sodium dioctyl sulfosuccinate (Aerozol-OT(AOT))-water system were studied by the method of X-ray analysis. The concentration of AOT in the system was from 23 to 98%. It was established that in this concentration range, the lamellar "smooth" phase is realized. The characteristic parameters and structural features of this phase are revealed.

Keywords: x-ray analysis, lyotropic liquid crystal, mesomorphism, models of biomembranes, lamellar phase.

1. Introduction

Numerous studies show that lyotropic liquid crystals are typical representatives of biological phospholipid membranes, and the use of the latter as models of biomembrane organization has been proven. Our task is to consider membranes as liquid crystal systems and to clarify mesomorphism in these systems.

To solve the main task of this work in terms of analyzing the structural rearrangements that underlie the shifts from the amorphous-crystalline properties of model membranes, the method of X – ray diffraction at small angles was used.

2. Experiment

X – ray structural studies to explore the dynamic behavior of molecules in liquid crystal systems require predetermined solutions of a number of technical and methodological problems. Sampling was carried out on the SURS-60 and URS-2 X – ray installations with cameras of the type KRON, RKSO intended for shooting on flat film, which were modified to study small angles at distances of samples from films in the range $0.05-0.1m$. The converted camera provides an opportunity to get reflexes in the range of angles from 1^0 to 45^0. Schematic images of the camera are shown in Fig.1

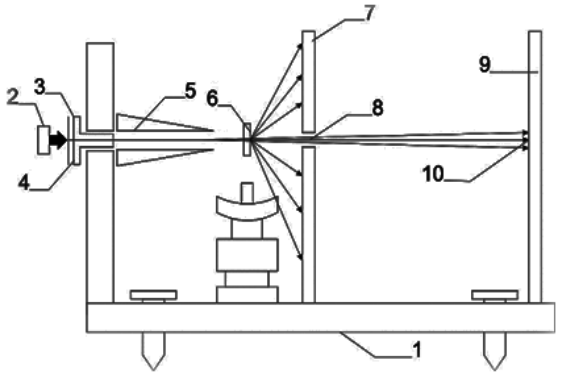

Fig. 1. Schematic images of the camera

$X-$rays coming out of the focus of the $X-$ray tube 2 pass through the nickel filter 3, diffraction 4 and collimator 5 and fall onto sample 6. The diameter of the aperture opening is $1\times10^{-4}m$, the length of the collimator $8\times10^{-2}m$, the diameter of its opening at $1\times10^{-4}m$. Such collimation provides fairly good accuracy.

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

Tubes of the types BSV-24, BSV-11 with an anticatode from Cu, producing radiation in the region of relatively long waves were used. The $K\alpha$ lines of copper were distinguished using nickel filters with a thickness of $0.015mm$. Anode voltage is $40kV$, anode current is $20mA$. The exposure time was chosen 4 hours. It was used films type RTG-B Company of Primax Berlin Germany. Quartz thin-walled capillaries (made in Germany) with a wall thickness of $0.01mm$ and a diameter of $0.4-1mm$ were used to prepare the sample. Absorption of rays and the appearance of the background on radiographs when using these capillaries is almost absent.

The $X-$ray diffraction method that we redesigned will allow us to obtain information on the size, shape, and compactness of the colloidal formations.

3. Samples

The structures of mesophases obtained on the basis of Aerosol-OT (AOT) and water are studied in this paper.

Production description - production name –Dioctylsulfosuccinatesodiumsalt, formula - $C_{20}H_{37}NaO_7S$, molecular weight of formula - $444.56\,g/mole$, color - white, appearance-hard,

analysis (according to USP) - purity $97.0-103.0\%$, water (according to Karl Fischer) - 2%, manufactured by,, Sigma-Aldrich,, USA, website - www.sigmaaldrich.com.

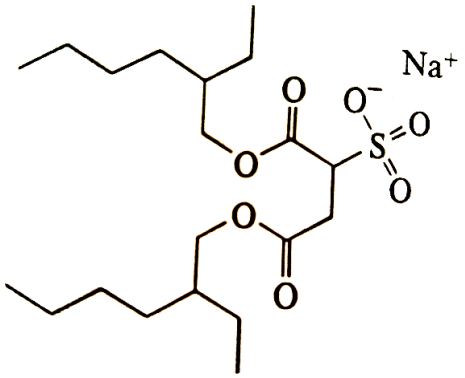

Fig.2. The structural formula of the AOT molecule.

Quartz capillaries were used to prepare the samples.

$X-$ray diffraction samples were prepared according to the following method: heat treatment was carried out - the specimen was kept at a temperature of $353K$ before taking radiograms for half an hour, after which an isotropic melt of the corresponding concentration was introduced into the capillary, sealed on both sides and cooled to room temperature. The finished sample was examined immediately after processing, as well as at certain intervals. Studies were conducted in the temperature range of $293-300^0 K$.

The orientation of the samples in the absence of water was carried out using mechanical stretching. Radiograms of the stretched "anhydrous" specimens, 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

On $X-$radiograms, the reflexes were obtained, having the form of homogeneous circles, indicating the presence in the sample of randomly arranged relative to each other domains, within which the AOT molecules are arranged in order, forming liquid crystal mesophases. Samples were taken with concentrations from 23% to 93% and "dry" solutions, which were obtained with open-length aging. In the latter samples, only reflexes of hydrated water remained. "Dry" samples were taken without a capillary.

Interplanar distances and relative intensities at various concentrations of AOT-water solutions are given in Table 1 [6].

Table 1. Interplanar distances and relative intensities of the AOT-water system

N	AOT concentrations in %	C_w / C	Interplanar distances d_w (Å)	Relative intensities
1	26	2.9	58	4
2	31	2.2	50	5
3	38	1.6	51.4 ; 22	9
4	42	1.4	38.2 ; 23	9
5	48	1.1	38.5 ; 22	6 ; 5
6	50	1	35 ; 21	7 ; 5
7	59	0.7	30 ; 28 ; 15.6	6 ; 4; 2
8	60	0.66	24.7	8
9	64	0.56	24.6 ; 21	5 ; 7
10	70	0.43	25 ; 22	6 ; 8
11	75	0.33	22	8
12	84	0.19	21.5 ; 4.6 ; 3.6	9 ; 5 ; 3
13	91	0.09	22 ; 4.6 ; 3.9 ; 3.6	9 ; 5 ; 3 ; 4
14	94,7	0.05	21 ; 4.6 ; 3.9 ; 3.6	10 ; 5 ; 2 ; 5

In the presence of a forced mechanical orientation - (by pulling the sample into the capillary), there is a mutual orientation of the domains. The X – radiogram of samples of the oriented domains is shown in Fig. 3.

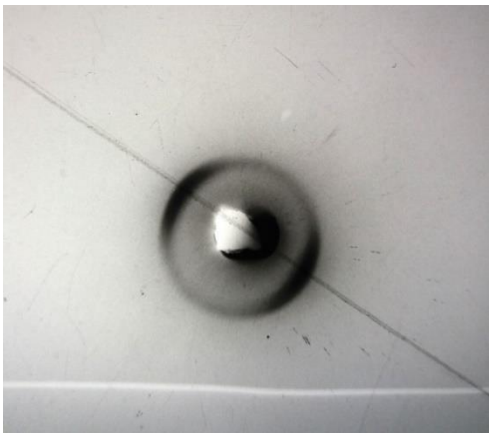

Fig. 3. X-radiogram of the orientated sample with 75% AOT concentration

With prolonged exposure of the samples, without changing the concentration, the circles on the X – radiogram become grainy (Fig. 4).

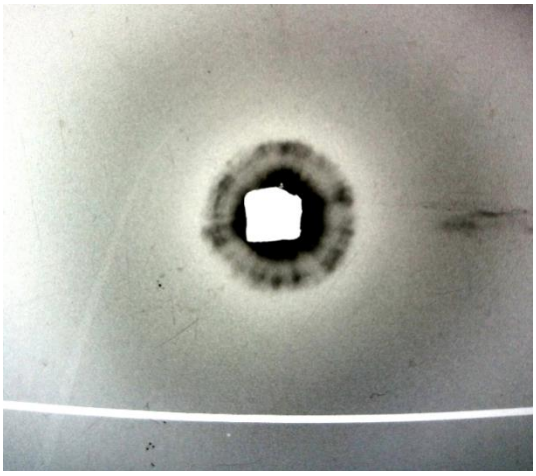

Fig. 4. The X-radiogram of AOT-water sample with 75% concentration of AOT

On X – radiograms of the concentrated samples, thin reflections at large angles are revealed. In the circumference, which characterizes the lamellar phase, intensity blobs appear in the form of - radiograms (Fig. 5).

Fig. 5. The X-radiogram of the concentrated sample of AOT- water**.**

5. Discussion

AOT molecules possess high amphiphilic properties, as a result of which they form micelle solutions and liquid crystal mesophases. Due to the amphiphilicity of AOT molecules, their lyotropic mesomorphism is manifested. The peculiarities of their behavior in the aquatic environment are determined by the balance of hydrophilic and hydrophobic interactions, which ensure, on one side, the maximum contact of polar groups of molecules with water, and on the other - the contact of hydrocarbon sections mainly with each other. At low concentrations, AOT in water forms micellar solutions and, beginning with 23%, lyotropic liquid-crystal "smooth" phases are formed with intradomain lamellar structures, i.e. there is an alternation of parallel layers of AOT mono- (L_2) and bimolecular (L_1) thickness and water layers [2,4]. In lyotropic mesophases, at higher concentrations of AOT, the structure stability and the presence of long-range order are detected. With the help of $X-$ray diffraction, the ordering of the long-range order and the dimensions of the diffracting cell of LCC [5] are determined. On $X-$radiograms revealed reflexes, having the form of homogeneous circles. They indicate the presence in the samples of domains randomly located relative to each other, within which the AOT molecules are arranged in an ordered manner. Besides these lines there are two fuzzy diffuse halos, characteristic of "liquid" paraffins and water.

The presence of halos on $X-$radiograms indicates that there are areas with unoriented molecules in the sample and hydrocarbon tails are in the "liquid" state. Under certain external influences, orientation order may be lost in lamellae. Even in the orientational state, due to the presence of rotational and oscillatory motions around the axis of the molecule, identical carbon atoms located in different molecules can be located in different planes passing through the axis of the AOT molecule at any given moment. Since a large number of molecules are involved in the appearance of a reflex during $X-$ray, the "average" or "statistical" molecule will have a look of cylinder (Fig. 2). The $X-$ray reflexes due to the dynamic state of the AOT molecules in the lamellae are poorer compared to the case when carbon atoms located in different molecules, have a certain spatial arrangement. The latter state is average between the crystalline and gel state, i.e. represents "coagel". AOT "coagel" is found starting from an AOT concentration of 84%. High-angle, thin reflexes that show up at large angles indicate an orderly packing of AOT molecules at the AOT-water interface. Based on the obtained $X-$radiograms, we construct the dependence of the interplanar distance d on the ratio of water concentration (C_w) to AOT concentration (C) (Fig. 6).

As can be seen from the figure, with an increase in the concentration of water, a linear increase in d from C_w/C occurs. At an AOT concentration of less than 23%, only diffuse halo of water is present on $X-$radiograms. As the concentration increases, a second diffuse halo appears, which is characteristic of "liquid" paraffins. With an increase in the concentration of AOT, the reflexes become thin and clear. An analysis of the registration data revealed that a "smooth" lamellar phase appears in the AOT-water sample over time. Extrapolation of direct from C_w/C to zero water

content, according to the data in Fig.6, the lamella thickness is determined: $d_l = 17.5\,\text{Å}$. This value corresponds to the length of a monomolecular lamella. The difference $d - d_l = d_W$ is the minimum thickness of the interlamellar water layer, that is the amount of water bound to the lamella surface.

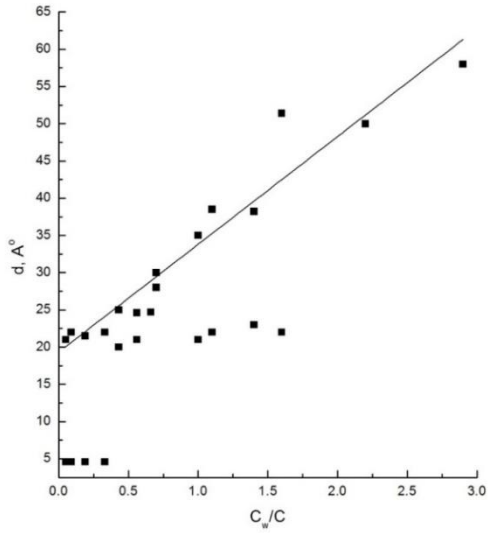

Fig. 6. Dependence between distance d and C_w/C.

This value is $4.5\,\text{Å}$ (Fig.6.). As can be seen from the figure, at high AOT concentrations, the interplanar distances remain unchanged. When $C_W/C \le 3$, it does not depend on the concentration of water. This indicates that "bound" water (hydrated water) remains in the interlamellar space. At the same time, the "coagel" phase is realized in the system, as evidenced on $X-$radiograms by the appearing reflexes at large angles [5].

According to the method developed by Luzati, one can determine the changes in the interplanar distances (d) from concentration of amphiphilic substance [4]. For the lamellar phase, this formula has the form:

$$d = d_l\left(1 + pC_W / p_w C\right), \tag{1}$$

where $d = d_l + d_W$, d_w and d_l respectively the thickness of the water layer and lamella. p, p_W density of lamellae and water, C and C_w concentration of AOT and water. Equation (1) makes it possible to determine the density of a lamella without hydrated water, which is a measure of the structural organization of the hydrophobic core of the lamella. From the slope of the straight line d

from C_w/C for the density of the AOT lamellae, obtained at $C_w/C = 0.3,\ p = 0.938 p_W = 1.0323\, g/sm,$ at $C_w/C = 0.25,\ p = 1.276 p_W = 1.404\, g/sm.$

Since a measure of the compactness of the location of AOT molecules in a lamella, in addition to density, is also the specific surface S, i.e. the size of the area on the surface of the lamella, coming to the polar group of one AOT molecule, then, having determined the values of the density and thickness of the lamella, we obtain values for 75% of the solution $S = 88 \overset{o}{\text{A}}^{2}$, and for 80% of the solution $S = 64.5 \overset{o}{\text{A}}^{2}$.

The presence of homogeneous circles in X – radiograms proves a chaotic location of domains in the sample. But in X – radiograms also present cresent-like circles (Fig. 3). This takes place at presence of forced mechanical stretching and extrusion of the sample in capillary. It may be assumed that an orientation of domains and consequently lamells as well takes place. The angle of inclination of molecules axis can be determined directly from analyzing the intensity distribution relative to equator (for the equator direction it is taken the direction parallel to the plane of lamella multilayer plane) in X – radiogram diffraction image from orientated samples according to intensity bunches (cycles) in Fig. 3, that corresponds to results 38^o [1, 3].

While long keeping the samples in AOT-water system, the orientation of domains takes place. This proves by the grainity of circles in the X – radiograms (Fig.4). For more concentrated solutions the circles become intermittent. In X – radiograms of concentrated samples during further long drying while containing only hydrated water in a "dry" sample it was revealed an ordered hexagon, which enables to assume about the reorientation of lamellas parallel to the walls of the capillary (Fig. 5). In the "coagel" state of a complex two-dimensional hexagonal packing of AOT moleculae, it must correspond to the following Brague distancs ratio: $1:\sqrt{3}/2:1/2...,$ that is weakly seen in X – radiogram - $4.5:3.8:2.25.$

Thus in the Aerosol OT-water system when water concentration more than 23%, "smooth" liquid-crystal mesophasa with lamella single-molecular thickness is realized. The molecules in lamellas are bent at angle 38^0 to the surface of separation lipid-water phase. In the system the liquid-crystal "gel" phase is realized that when lipid concentration is high is turned into the "coagel" phase. In the AOT sample when only hydrate water is present the "coagel" state is realized.

Acknowledgments

The authors are grateful to the Hovhannes Semirjyan for his technical support.

Funding

The paper has been supported from Basic financing of IAPP NAS RA.

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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