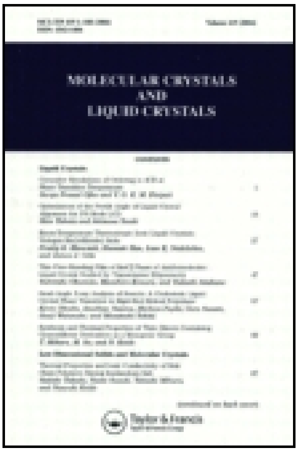

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ELECTROPHYSICAL PROPERTIES OF A LAMELLAR LYOTROPIC LIQUID CRYSTALLINE MESOPHASE

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Abstract The present paper shows the results of a study of the temperature behaviour of electroconductivity and the electroconductivity anisotropy of lamellar mesophase formed by amphiphil+water and amphiphil+water+alcohol lyotropic systems.

Keywords: lamellar mesophase, polymorphism, electroconductivity, shift flow, effective diameter, contraionic diffuse cloud

INTRODUCTION

Recently the physical properties of lyotropic liquid crystalline systems have attracted much attention[1-4], particularly for optical properties and structural investigations. However electrophysical and dielectrics properties have hot been studied well enough. Furthermore lyotropic liquid crystals as systems in which structural units are formed by polar or nonpolar molecules are of great interest, and their study yields valuable information on the structure of micellar aggregates and intermolecular interactions, on the mechanisms of electroconductivity and dielectric polarization in the above systems, and allows to solve the essential problems of the connection between the electrophysical parameters and micro- and macroscopic characteristics in lyotropic liquid-crystalline systems.

The present paper shows the results of studying the temperature behaviour of electroconductivity anisotropy of lamellar mesophase formed by sodium pentadecylsulphonat (SPDS)+water and SPDS+water+octanol lyotropic systems. The average statistical sizes of micellar aggregates of the mesophase D have been obtained when studying the electroconductivity anisotropy characterizing the orientational shift flow, and revealing the dynamics of orientation processes.

MATERIALS AND INVESTIGATION METHODS

As in electrophysical investigations peculiar requirements are imposed upon the frequency of the compounds studied, the SPDS amphiphil compound used was throughly cleaned by multiple recrystallization and its purity of 99.5% was controlled chromatographically. The water used as a solvent was twice distilled with simultaneous deionization.

Preliminarily, the characteristic textures and the dynamics of their transformations were investigated and the phase states of SPDS+water+octanol ternary system were determined according to$^{5-7}$ by polarization microscopy methods. The phase diagram of this system is shown in Fig.1.

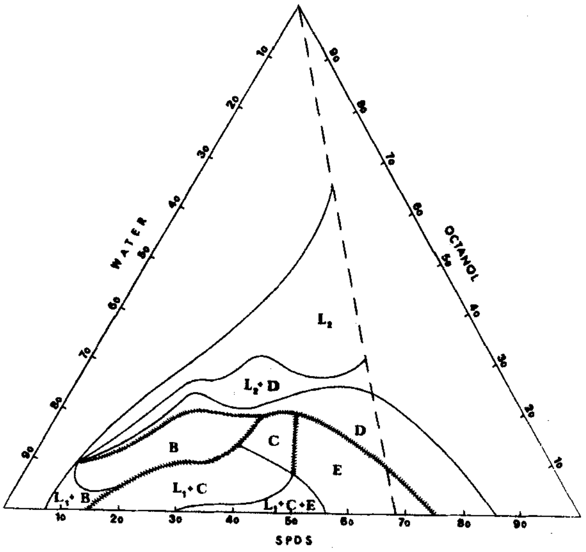

Fig.1. Phase diagram of SPDS+water+octanol lyotropic liquid-crystalline system (22°)

The system exhibits polymorphism and reveals the hexagonal E, tetragonal C, lamellar D and deformed lamellar B mesophases. The mesophase D under study was observed in rather wide temperature and concentration ranges. The above mesophase with low alcohol concentrations was revealed by pseudoisotropic texture (Fig.2a) which can further transform into the shallow-fan ones, while at relatively high alcohol concentrations the mesophase D was revealed by highly birefringent lobe textures (Fig.2b) which are typical of the layer lamellar mesophase D.

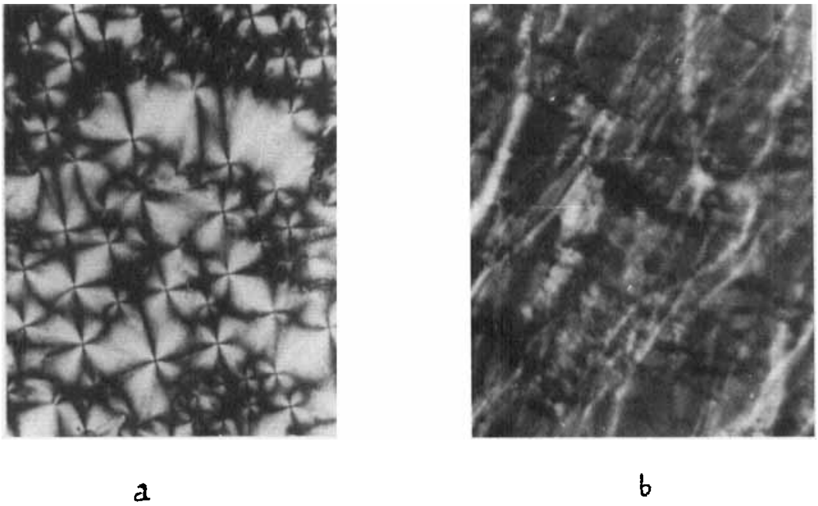

Fig.2. Lamellar mesophase typical textures of SPDS+water+octanol lyotropic liquid-crystalline system

In the SPDS+water binary system previously investigated in[8] the mesophases E and D are only observed , i.e. as usual the adding of alcohol into amphiphil+water lyotropic system leads to the formation of the new mesophase types which are not revealed in the binary system.

The study of the temperature dependences of electroconductivity was carried out with a bridge E8-2 the frequency of 10^3 Hz and with the accuracy of 0.1%.

The studies of the character and the sign of electroconductivity anisotropy of lyotropic systems were performed by the methods developed for viscoelastic polydispersive media[9-11] and used for determining the shape and sizes of micellar aggregates of lyotropic mesophases[12-15]. The experimental set-up represents a Couette system of two coaxial cylinders: the outer cylinder is a stator and the internal one is a rotor. A rotor pre-assigning a shift flow velocity can rotate relative to the stator with a regulated velocity. A velocity gradient of the flow in this case was determined as[16]

$$q = \frac{2\pi r}{d}\nu$$

where r is the outer cylinder radius, d is the band gap between the rotor and the stator where the lyotropic system was inserted.

The method used consists in orientation of micellar aggregates of lyotropic systems with translation mobility anisotropy and with certain electrical charge in a shift flow parallel to each other. Therefore, the anisotropy of micellar aggregate translation mobility in the flow is also responsible for the electroconductivity. In case of rod-like micelles in the direction of flow (the Y-direction) the electroconductivity increases, and the directions perpendicular to the flow (the X-direction) the conductivity was found to decrease. In case of plate micelles the electroconductivity in Y- and Z-directions increases while in the X-direction the conductivity drops.

When measuring, a full orientation of a lyotropic liquid-crystalline system in the flow was observed. After stopping of the rotor, the micellar aggregates due to thermal motion are disoriented. This was shown by the curves of time dependence of electroconductivity. Such a process has an exponential character. The relaxation velocity in this case depends on the vicosity of lyotropic system and micellar aggregate sizes. When calculating a relaxation constant, τ_r , the curve, i.e. the time during of which the electroconductivity decreases by e times, the rotation diffusion coefficient D_r was determined[8]:

$$D_r = \frac{1}{6\tau_r}$$

with the known rotation diffusion coefficient D_r and the lyotropic liquid-crystalline system viscosity, η , one can define the micellar aggregate sizes. Thus, the diameter of the plate micellar aggregates was determined as follows[10]:

$$\ell = \sqrt[3]{\frac{4KT}{\pi \eta D_r}}$$

RESULTS AND DISCUSSION

The dependence of electroconductivity anisotropy of the mesophase D (SPDS+water and SPDS+water+octanol systems) on the rotation frequency (the velocity gradient of the shift flow) in X- and Z-directions relative to the shift flow is presented in Fig.3. The sign and the character of the above mentioned dependence confirm the existence of the compositions studied in the corresponding concentration range in lamellar mesophase D.

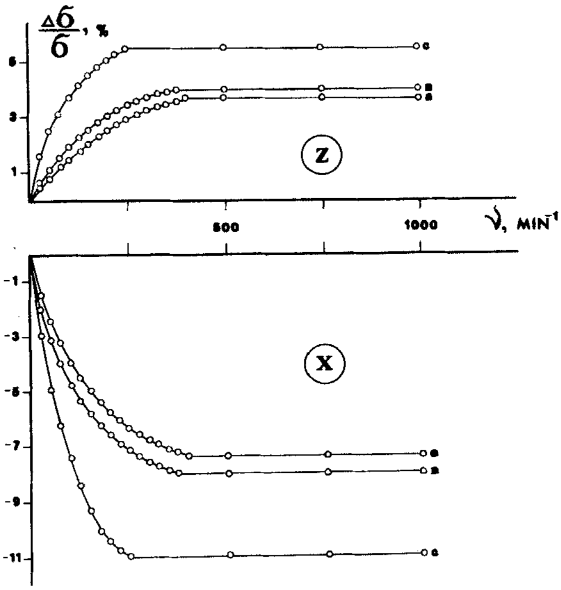

Fig. 3 Electroconductivity anisotropy dependence of the mesophase D on the rotation frequency in X and Z direction

As seen from Fig.3, the behavior of the lyotropic systems containing the alcohol, saturates at rather lower shift flow velocities. Using the obtained values of the coefficient D_r and the rotation viscosity η , the lamellar sizes were evaluated:

a) 79%SPDS+21%water - 2530 Å,
b) 77.07%SPDS+20.49%water+2.44%octanol - 2720 Å,
c) 82%SPDS+18%water - 3170 Å.

Here we should note that taking into account the lamella sizes one should consider their effective diameter or the apparent sizes, i.e. a mean statistical length which can change in rather wide ranges for each particular lamella.

One can see from the given values of the lamellar effective diameters in the binary systems (composition a,c) that their sizes increase with increasing amphiphil concentration in agreement with theoretical conclusions[17-19] on micellar transformations in such systems.

As follows from the above lamellar diameter values in lyotropic systems at a constant amphiphil/water proportion (composition a, b), the addition of alcohol into the amphiphil+water systems leads to a certain increase in effective diameter of the lamellae. The above effect can be attributed to the fact that the alcohol molecules distributed uniformly between amphiphil molecules in micellar aggregates lead to a swelling of lamellae and respectively lead to increase in their sizes.

Figure 4 presents the temperature dependences of a mesophase D for different compositions of the SPDS+water+alcohol and SPDS+water systems:

a) 77.07%SPDS+20.49%water+2.44%octanol,
b) 78.77%SPDS+20.94%water+0.29%octanol,
c) 79%SPDS+21%water,
d) 82%SPDS+18%water.

As seen in Fig.4 the behaviour of $\sigma = \sigma$ (t) dependences in the range of the mesophase D of systems studied is actually similar, i.e. the value increases proportionally to the temperature growth. This is natural if the nature of electroconductivity in such systems is taken into account. In particular, the fact that the ions (which are the charge carriers and forming a contraionic diffuse cloud around micellar aggregates and responsible for a typical distribution of the potential around it) dispersed in water medium increase their mobility with increasing temperature.

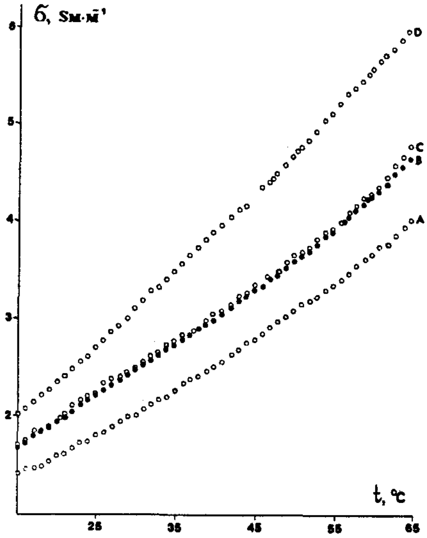

Fig. 4 Temperature dependence of electroconductivity of a mesophase D for SPDS+water+octanol (a,b) and SPDS+water (c,d) systems.

A dissociation power in lyotropic system is also increased in this case. Simultaneously, the lamellar sizes and the lyotropic system viscosity decrease and the electroconductivity increases.

As seen from the comparison of the б (t) dependences for the compositions b), c) (Fig.4), the adding of small quantities of alcohol into the amphiphil+water system is found not to change considerably the values. A certain decrease of electroconductivity value in the a) composition is attributed to the amphiphil concentration decrease in the amphiphil/solvent system.

Thus the study of the alcohol adding effect on mesomorphic and electrophysical properties lyomesophases in general and of lamellar mesophases in particular showed that such addings lead to a considerable change of micro- and macroscopic properties of lyotropic liquid-crystalline systems that in turn results in polymorphism, increase of the types of characteristic lyomesophase textures, decrease in lamellar effective diameters and a certain decrease of electroconductivity values.

REFERENCES

1. N.Boden, R.J.Bushby, L.Ferris, C.Hardy, F.Sixi, Liquid Crystals, 1, 109, (1986)
2. L.Coppola, L.C.Mesa, G.A.Ranieri, M.Terenzi, Colloid and Polymer Science, 267,86, (1988)
3. J.Kalus, H.Hoffmann, Journal of Chem.Phys., 87, 714, (1987)
4. H.Gutman, Z.Luz, E.J.Wachtel, R.Poupko, J.Charvolin, Liquid Crystals,7, 335, (1990)
5. P.Ekwall, Advance in Liquid Crystals, 1, 1, (1975)
6. F.B.Rosevear, Journal Soc. Cosmetic Chemists, 19, 581, (1968)
7. A.Saupe, Journal of Colloid and Interface Science, 58, 549, (1977)
8. A.N.Nesrullajev, F.A.Rustamov, A.S.Sonin, Kristallografia (Sov.), 29, 1133, (1984)
9. K.Heckmann, Z. fur Phys. Chem., Neue Folge, 9, 318, (1956)
10. K.Heckmann, K.G.Götz, Z. fur Elektrochemie, 62, 281, (1958)
11. G.Schwarz, Z. für Physics, 145, 563, (1956)
12. K.Heckmann, K.G.Götz, Disc. Faraday Soc., 25, 71, (1958)
13. A.N.Nesrullajev, Kolloidnyi Zhurnal (Sov.), 51, 1037, (1989)
14. H.Rehage, Rheologische Untersuchungen an viskoelastischen Tensidlosungen, Dissertation, Bayreuth, BRD, 1982
15. G.Platz, Ber. Bunsenges. Phys. Chem., 85, 1155, (1981)
16. K.G.Götz, K.Heckmann, Journal of Colloid Science, 13, 266, (1958)
17. G.J.T.Tiddy, M.F.Walsh, In: Aggregation Processes in Solution, (Amsterdam-Oxford-New Jork), 1983, pp. 151-185
18. B.Lindman, H.Wennerström, In: Micelles, (Springer-Verlag, Berlin-Heidelberg-New York), 1980, pp. 1-85
19. D.J.Mittal, P.Mukerjee, In: Micellization, Solubilization and Microemulsions, edited D.J.Mittal, (Plenum Press, New York), 1977, pp. 1-21