



Shape of Micelles and Temperature and Concentration Behavior of Optical Refractive Properties: Single Amphiphilic and Mixed Bicomponent Amphiphilic Lyotropic Systems

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Received: 22 September 2017 / Accepted: 2 April 2018 / Published online: 9 April 2018
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Abstract

Lyotropic systems are bicomponent and/or multicomponent mixtures display physically isotropic and physically anisotropic properties and exhibit various types of isotropic lyotropic phases and anisotropic lyotropic mesophases. Structure units in lyotropic phases and mesophases are the nano-size three-dimensional nanoparticle supramolecular aggregates as the isometric and anisometric micelles. In this work, comparative investigations of the optical refractive properties of lyotropic micellar systems as mixtures of single amphiphile and mixed bicomponent amphiphiles in polar solvent have been carried out. Lauryltrimethyl ammonium bromide (LTAB) + water, cetyltrimethyl ammonium bromide (CTAB) + water, and (LTAB + CTAB mixture) + water lyotropic systems have been studied. Shapes of micelles in single component amphiphilic and bicomponent amphiphilic lyotropic systems have been estimated. Temperature and concentration dependences of the optical refractive index have been determined. Effect of the LTAB/CTAB concentration ratio on the refractive properties of mixtures under investigations has been found. Effect of length of the hydrophobic chain of amphiphile molecules with the same hydrophilic part on the refractive index of lyotropic systems is analysed.

Keywords Lyotropic systems · Micellar phase · Hexagonal mesophase · Isometric micelle · Anisometric micelle · Optical refractive properties

1 Introduction

Lyotropic micellar systems are bicomponent or multicomponent mixtures of amphiphile materials, which have a hydrophilic head and a hydrophobic tail, in polar and/or non-polar solvents. These systems can contain co-surfactant, optical active matrix, nonorganic salts, etc. Lyotropic systems display physically isotropic and physically anisotropic properties and exhibit various types of isotropic lyotropic phases and anisotropic lyotropic mesophases. Structure units in lyotropic phases and mesophases are the three-dimensional nanoparticle supramolecular aggregates as the isometric and anisometric micelles (Ekwall 1975; Petrov 1999; Figueiredo Neto and Salinas 2005; Alfutimie

et al. 2014; Sonin 1987). In dependence of temperature, concentration, type, and number of components, these formations as multimolecular aggregates have the spherical, plate (disc-like), or cylindrical (rod-like) shapes.

The isometric and anisometric micelles are characterized by definite spatial structure, character of packing and point-like symmetry, and form physically isotropic phases and physically anisotropic mesophases (Lingmann and Wennerström 1980; Burducea 2004; Nesrullajev 2007; Perez-Rodriguez et al. 1998; Guo et al. 2010). Physically, isotropic and physically anisotropic nature of lyotropic micellar systems makes these systems important objects for both fundamental investigations and applications in various fields of technique, technology, and industry.

Important peculiarity of lyotropic liquid crystalline systems is availability of the thermotropic and lyotropic phase transitions between isotropic phases and anisotropic mesophases and also between various lyotropic mesophases. By such transitions, transformation of the space structure of physically isotropic phases and physically

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anisotropic mesophases and also change of the order parameters of mesophases carry out. Thermotropic phase transitions in such systems were theoretically investigated in (Mukherjee and Bhattacharya 2007; Mukherjee 2013a, b; Mukherjee and Rahman 2013; Mukherjee and Lagerwall Giesselman 2005). In these works, using the mean-field model showed that in lyotropic liquid crystals, also as in thermotropic liquid crystals, phase transitions of the first order and second order take place. Lyotropic phase transitions and phase states of lyotropic isotropic phases and anisotropic mesophases were experimentally investigated by various scientists (e.g., Ekwall 1975; Figueiredo Neto and Salinas 2005; Nesrullajev 2007, 2014; Mukherjee 2002; Hoffmann et al. 1987; Santin Fulho et al. 2000; Amaral et al. 2015; Jolley et al. 2001; Mirandi and Schulz 2002; Hoffmann et al. 1994; Figueiredo Neto 2014).

Lyotropic phases and mesophases, which are based on anionic, cationic, and zwitterionic surfactants, exhibit various optical properties, i.e. the refractive properties, birefringence, optical polarizability, etc. (Govindaiah 2016; Vedenov 1984; Kazanci and Nesrullajev 2003; Nastishin et al. 2005). These properties and optical parameters exhibit high sensitivity to various external effects. Because of large application possibility of lyotropic systems, optical properties and optical parameters of such systems are of great importance these days. Besides, investigations of lyotropic systems with amphiphile mixtures are of considerable interest for large technical and technological applications, because amphiphile mixtures enhance interesting performance. Such systems can exhibit new physical and physico-chemical properties. Therefore, investigations of physical and physico-chemical properties of lyotropic liquid crystalline systems as mixtures of different amphiphilic materials attract the intent attention of scientists (Govindaiah 2016; Vedenov 1984; Kazanci and Nesrullajev 2003; Nastishin et al. 2005; Götz and Heckmann 1958; Heckmann and Götz 1958; Rehage 1982; Nesrullajev 1988, 1992, 2010).

In connection with above-mentioned reasons, shape of micelles in three groups of mixtures of binary amphiphile mixtures (LTAB + CTAB) with polar solvent and mixtures of single amphiphile (LTAB and CTAB) with polar solvent have been carried out. Method of the electrical conductivity on orientational shear flow has been used. Maximum values of the electrical conductivity anisotropy vs. concentration of amphiphile have been determined. Mesomorphic and morphologic properties and comparative investigations of the optical refractive properties of lyotropic systems under investigations have been carried out. Temperature $\{n = n(T)\}$ and concentration $\{n = n(c)\}$ dependences of the refractive index have been determined for such mixtures. Effect of the LTAB/CTAB

concentration ratio on the refractive properties of mixtures under investigations has been found.

2 Experimental

2.1 Materials and Samples

In this work, LTAB + water, CTAB + water, and (LTAB + CTAB mixture) + water lyotropic systems have been objects of our studies. Ionic amphiphiles CTAB with molecular formula as $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$ and LTAB with molecular formula as $\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{Br})(\text{CH}_3)_3$ were purchased from Sigma (cat. No.SigmaUltra H9151 of CTAB and cat. No.SigmaUltra D5047 of LTAB). CTAB and LTAB were characterized by the critical micellar concentration CMC value as 0.90×10^{-4} and $1.10 \times 10^{-4} \text{ mol L}^{-1}$ for CTAB and LTAB, accordingly. Molecular structure of LTAB and LTAB is presented in Scheme 1. Water was triple distilled and deionized by Direct-Q8 Water Purification Systems.

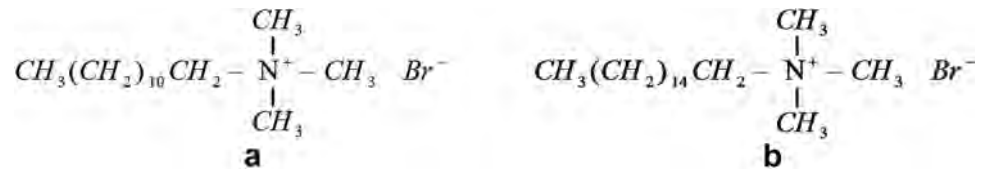
Process of preparation of amphiphile + water lyotropic systems followed known procedures. Amphiphile and water were weight by Shimadzu precision balance with an accuracy of $\pm 10^{-4} \text{ g}$. Hermetically closed glass ampoules with the mixtures were kept in thermostat at $305 \pm 0.1 \text{ K}$ for homogenization. For preparation of (amphiphile 1 + amphiphile 2) + water lyotropic systems, first of all, mixture of amphiphiles was weight by precision balance. Then water was added in corresponding concentration into amphiphiles mixture. For homogenization, hermetically closed glass ampoules with such mixtures were also kept in thermostat at $305 \pm 0.1 \text{ K}$. The mixtures were periodically mixed by a shaker. Homogeneity of obtained lyotropic systems was controlled by examination of these systems, using the crossed polarizers. Compositions of mixtures under investigations are presented in Table 1.

For investigation of the mesomorphic and thermo-morphologic properties, samples as the sandwich cells were used. These sandwich cells were constructed by optical glass surfaces and special adhesive spacer with fixed thickness. The thickness of liquid crystalline layer in the sandwich cells was determined as $120 \pm 1.0 \mu\text{m}$. At once after filling the sandwich cell by liquid crystalline system, samples were hermetically closed.

2.2 Methods

Investigations of the mesomorphic and thermo-morphologic properties of lyotropic systems under investigations have been carried out by the thermo-optical setup. The experimental setup consisted of the trinocular polarizing conoscopic/orthoscopic microscope, Berek compensator,



Scheme 1 Molecular structure of LTAB (a) and CTAB (b)**Table 1** Compositions of lyotropic systems under investigations

Samples	(50 wt%LTAB + 50 wt%CTAB), wt%	LTAB, wt%	CTAB, wt%	Water, wt%
Compositions of lyotropic systems				
S1	30.00	—	—	70.00
S2	32.50	—	—	67.50
S3	35.00	—	—	65.00
S4	37.50	—	—	62.50
S5	40.00	—	—	60.00
S6	—	30.00	—	70.00
S7	—	32.50	—	67.50
S8	—	35.00	—	65.00
S9	—	37.50	—	62.50
S10	—	40.00	—	60.00
S11	—	—	30.00	70.00
S12	—	—	32.50	67.50
S13	—	—	35.00	65.00
S14	—	—	37.50	62.50
S15	—	—	40.00	60.00

quartz wedge, optical filters, λ -plates, and object-micrometer from Olympus Optical Co., Ltd., and also special heater thermostat with Leybold digital temperature control system, Keithley multimeters, and power supply. Registration of microphotographs has been carried out by digital microphotographic system from Olympus Optical Co. and Cannon 6D digital system. For investigations of the optical refractive properties, the polythermic refractometry setup with Abbe's High-Temperature Precision Refractometer, Digital Thermometer from Atago Co. Ltd, and recirculation immersion thermostat Ultraterm 200 Selecta has been used. Accuracy of measurement of the refractive indices measurements was as 0.1%. Temperature of liquid crystals under investigation was controlled by the digital temperature controller with accuracy as ± 0.1 K.

Estimation of the shape of micelles in lyotropic systems under investigation has been carried out by the method of the anisotropy of electrical conductivity in the orientational shear flow. This classic method was described in detail in (Götz and Heckmann 1958; Heckmann and Götz 1958; Rehage 1982). This method was modified in (Nesrullajev 1988, 1992, 2010) and allowed to measure the electrical conductivity values simultaneously in three mutually perpendicular directions (i.e., in X-, Y-, and Z-directions). In accordance with above-mentioned method, sum of the anisotropy of electrical conductivity in the X-, Y-, and Z-

directions for both the plate (disc-like) and cylindrical (rod-like) micelles must be equal to zero and $\sum_{i=X,Y,Z} \frac{\sigma_i(v) - \sigma_0}{\sigma_0} = 0$ equation must be fulfilled (Nesrullajev 1988, 1992, 2010; Schwarz 1956; Frolov 1982). Connection between the anisotropy of electrical conductivity in the X-, Y-, and Z-directions for the anisometric micelles, accordingly, is as

$$\left| \frac{\sigma_X(v) - \sigma_0}{\sigma_0} \right| = \left| \frac{\sigma_Z(v) - \sigma_0}{\sigma_0} \right| = 0.5 \left| \frac{\sigma_Y(v) - \sigma_0}{\sigma_0} \right| \quad (1)$$

for the rod-like micelles and

$$\left| \frac{\sigma_Y(v) - \sigma_0}{\sigma_0} \right| = \left| \frac{\sigma_Z(v) - \sigma_0}{\sigma_0} \right| = 0.5 \left| \frac{\sigma_X(v) - \sigma_0}{\sigma_0} \right| \quad (2)$$

for the disc-like micelles. Connection between the electrical conductivity anisotropies in above-mentioned direction for the spherical micelles is as

$$\frac{\sigma_X(v) - \sigma_0}{\sigma_0} = \frac{\sigma_Y(v) - \sigma_0}{\sigma_0} = \frac{\sigma_Z(v) - \sigma_0}{\sigma_0} = 0. \quad (3)$$

Here, $\sigma_X(v)$, $\sigma_Y(v)$, and $\sigma_Z(v)$ values are the electrical conductivity for fully oriented lyotropic system in the X-, Y-, and Z-directions, accordingly; σ_0 is the electrical conductivity value for completely disordered lyotropic system; and v is the rotational viscosity. As seen from Eqs. (1) and (2), estimation of shape of the anisometric micelles is

sufficient to determine the electrical conductivity anisotropy in two directions, e.g., in direction of the shear flow (X -direction) and in direction perpendicularly to the shear flow (Y -direction).

3 Results and Discussion

3.1 Mesomorphic and Morphologic Properties

First of all, the morphologic and mesomorphic properties of lyotropic systems under investigations have been studied. Studies showed that S1–S5 samples exhibit properties of isotropic micellar L_1 phase. S6–S10 samples also exhibit properties of isotropic micellar L_1 phase. This phase in S1–S10 samples is characterized by stable optically isotropic texture. As is known, L_1 phase consists of isometric spherical micelles on water environment (Ekwall 1975; Figueiredo Neto and Salinas 2005; Lingmann and Wenerström 1980; Burducea 2004; Nesrullajev 2007). In Fig. 1, the schematic presentation of spherical micelles in L_1 phase is given.

S11–S15 samples display anisotropic liquid crystalline texture (Fig. 2). As shown in Fig. 2, this texture consists of the prolonged filament-like formations and uniform regions with the planar and tilted alignment. Optical investigations showed that this texture has a low birefringence. Such a type of texture has been observed by different researchers for hexagonal micellar E mesophase in various lyotropic systems (Ekwall 1975; Figueiredo Neto and Salinas 2005; Hyde 2001; September 2014; Özden et al. 2010). Structural units of this mesophase are the rod-like micelles of quasi-infinite lengths (Ekwall 1975; Figueiredo Neto and Salinas 2005; Laughlin 1996; Nesrullajev et al. 2003). Such micelles form the hexagonal structure. E mesophase is a uniaxial optically negative mesophase, and has two-dimensional long-range positional order relatively of the normal to the symmetry axis of the rod-like micelles. In Fig. 3, the schematic presentation of the rod-like micelles in E mesophase is given.

It is interesting that the same compositions of LTAB + water and CTAB + water lyotropic systems display different lyotropic states, i.e., L_1 phase with optically isotropic texture for S6–S10 samples and E mesophase with optically anisotropic texture for S11–S15 samples. It is important to note that LTAB and CTAB are materials of the same homologous series, have the same

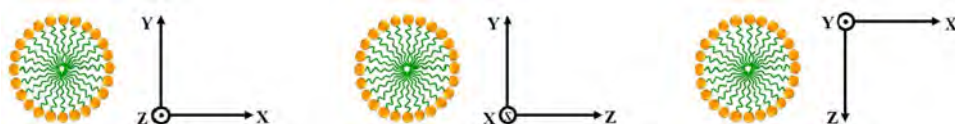
polar part of molecule, but have different lengths of the non-polar tail. Different lengths of the non-polar tail of amphiphile molecule of LTAB and CTAB lead to a difference in the hydrophilicity degree. Such a difference in the above-mentioned length is cause of high CMC value for LTAB as $1.10 \times 10^{-4} \text{ mol L}^{-1}$ and low CMC value for CTAB as $0.90 \times 10^{-4} \text{ mol L}^{-1}$. Such a difference in the length of the non-polar tail of molecules leads also to a shift of the isotropic L_1 phase – anisotropic mesophase and appearance of lyotropic liquid crystalline mesophase for low concentration of CTAB. It is also interesting that LTAB + CTAB + water lyotropic system, with the same compositions of components as in LTAB + water and CTAB + water lyotropic systems, displays optically isotropic texture of L_1 phase (Table 1). That is, in amphiphiles + water lyotropic system, which consists of amphiphile with high hydrophilicity degree and amphiphile with low hydrophilicity degree, amphiphile with higher hydrophilicity degree is more effective in the mixture. Thus, in water mixture with two amphiphiles with different hydrophilicity, amphiphile with higher hydrophilicity degree is more effective.

Investigations showed that in (LTAB + CTAB mixture) + water, LTAB + water and CTAB + water lyotropic systems' different high concentration limits for L_1 phase take place (Table 2). Namely, as shown in Table 2, correlation between amphiphile/water concentration ratios for the high concentration limit of L_1 phase in lyotropic systems under investigations is as the $c_{\text{CTAB}} < c_{\text{LTAB}+\text{CTAB}} < c_{\text{LTAB}}$ inequality. This result indicates that using amphiphile mixtures with the same polar part and different lengths of the non-polar part of amphiphile molecule is possible to regulate the mesomorphic and morphologic properties in lyotropic systems.

3.2 Shape of Micelles

For control and confirmation of the presence of the spherical micelles of L_1 phase and rod-like micelles of E mesophase in the corresponding regions (for S1–S10 samples and S11–S15 samples, accordingly), character of the anisotropy of electrical conductivity has been investigated. Measurements showed that S1–S10 samples in concentration region L_1 phase have not any electrical conductivity anisotropy in the X - and Y -directions. As an example, in Fig. 4 (Plate A), the dependences of the electrical conductivity anisotropy vs. rotational frequency

Fig. 1 Schematic representation of the spherical micelles in L_1 phase



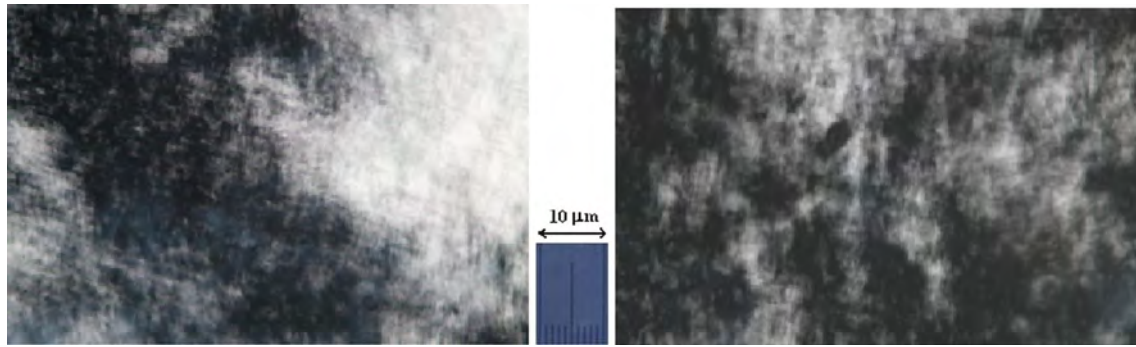


Fig. 2 Typical texture of S11–S15 samples. Magnification $\times 100$; crossed polarizers

Fig. 3 Schematic representation of the rod-like micelles in E mesophase

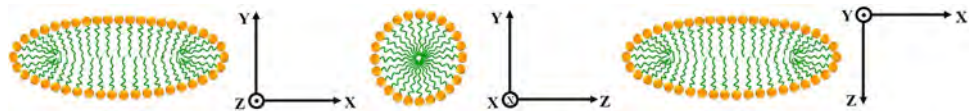


Table 2 High concentration limits for L_1 phase of lyotropic systems under investigations

Lyotropic system	High concentration limit for L_1 phase	
	Amphiphile, wt%	Water, wt%
(50 wt%LTAB + 50 wt%CTAB mixture) + H_2O	47.50	52.50
LTAB + H_2O	49.79	50.21
CTAB + H_2O	21.18	78.82

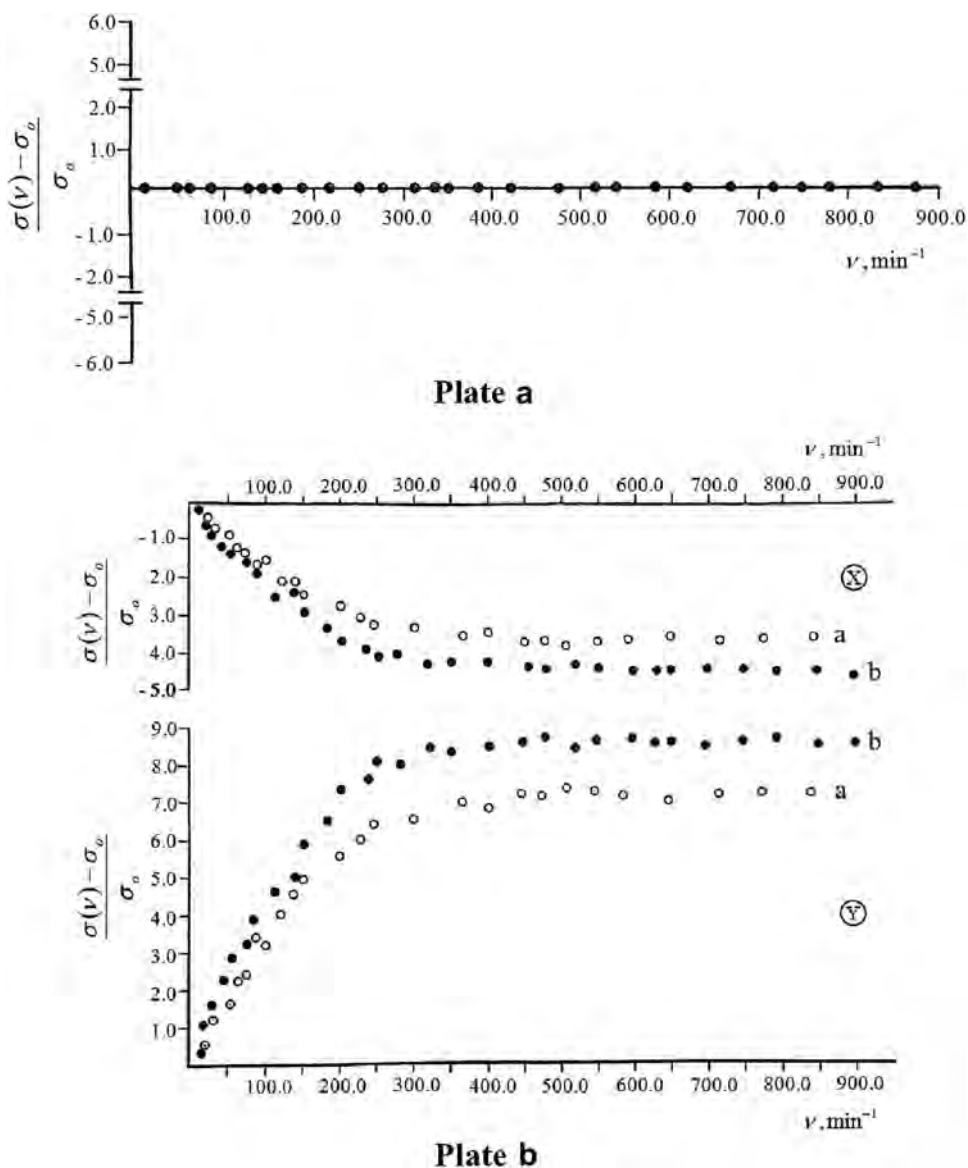
for L_1 phase are presented. Such a character of the electrical conductivity anisotropy vs. rotational frequency indicates on the spherical shape of micelles in lyotropic systems (Götz and Heckmann 1958; Heckmann and Götz 1958; Schwarz 1956; Nesrullajev 2010; Tsvetkov 1986). Measurements showed also that the anisotropy of electrical conductivity vs. rotational frequency for S11–S15 samples in the X -direction is negative and in the Y -direction is positive. As an example, in Fig. 4 (Plate B), the dependences of the electrical conductivity anisotropy vs. rotational frequency for E mesophase (S12 and S14 samples) are presented. As is known, such a behavior of the anisotropy electrical conductivity indicates on the rod-like shape of micelles in lyotropic systems (Götz and Heckmann 1958; Heckmann and Götz 1958; Schwarz 1956; Nesrullajev 2010; Tsvetkov 1986). Thus, results of measurements of the anisotropy of electrical conductivity vs. rotational frequency confirm results of investigation of the mesomorphic and morphologic properties in S1–S15 samples. In connection with these results, we are interested in the maximum values of the electrical conductivity anisotropy $\left| \left[\frac{\sigma(v) - \sigma_0}{\sigma_0} \right]_{\max} \right|$ vs. concentration of amphiphile for E mesophase. Such dependences are presented in Fig. 5. As seen in this figure, an increase of CTAB concentration in CTAB + water lyotropic system leads to an increase of the maximum value of the electrical conductivity anisotropy in

E mesophase. An increase of concentration of CTAB (i.e., ionic amphiphile concentration) in this lyotropic system as 30.00 wt% \rightarrow 32.50 wt% \rightarrow 35.00 wt% \rightarrow 37.50 wt% \rightarrow 40.00 wt% leads to an increase of number of micelles in volume of liquid crystalline system, to a change of packing character of micelles and, accordingly, to a change of interaction between micelles and the counter ions (Figueiredo Neto and Salinas 2005; Sonin 1987; Nesrullajev 2013). Besides, as it is known, by an increase of amphiphile concentration in lyotropic systems (and accordingly by a decrease of water concentration in such systems) leads to an increase of the order degree of polar parts (i.e., the hydrophilic parts) and non-polar tails (i.e., hydrophobic part) of amphiphile molecules in micelles (Petrov 1999; Friberg 1992; Yu and Saupe 1982). All of these effects lead to a change of the electrical conductivity value and, accordingly, to a change of absolute maximum values of the electrical conductivity anisotropy in lyotropic mesophases.

3.3 Optical Refractive Properties

In this work, the temperature and concentration dependences of the refractive index of three groups of lyotropic systems have been investigated. As the objects of our investigations, water mixtures of two ionic amphiphiles with different lengths of alkyl length, 50 wt%LTAB + 50 wt%CTAB (S1–S5 samples), and also water mixtures

Fig. 4 Electrical conductivity anisotropy vs. rotational frequency in the X - and Y -directions. Plate **a** L_1 phase (for S1–S10 samples). Plate **b** E mesophase for samples S12 (a) and S14 (b)



of LTAB (S6–S10 samples) and CTAB (S11–S15 samples) have been chosen. The amphiphile/water compositions in these groups of lyotropic systems were the same (Table 1). We would like to note that the refractive index is a general optical parameter for isotropic phases and anisotropic mesophases in lyotropic systems. This parameter determines the optical refractive properties and optical density of media and can change with concentration, temperature, pressure, number, and types of components in lyotropic liquid crystalline systems. We would like to emphasize that the optical refracting properties and refractive index are the most important parameters for fundamental investigations and application of lyotropic systems (Mitra et al. 1991; Pan et al. 2004; Kumar 2013).

In Fig. 6, temperature dependences of the refractive index $\{n = n(T)\}$ for (LTAB + CTAB mixture) + water

lyotropic system (S1–S5 samples) are presented. As seen in this figure, a monotonous decrease of the refractive index with an increase of temperature has been observed for these samples. Behavior of the $n = n(T)$ dependences for S1–S5 samples can be characterized by the $y = 1.3944 - 2.66 \times 10^{-4} \times x$ equation. Besides, as seen in this figure, an increase of (LTAB + CTAB)/water concentration ratio leads to an increase of the optical refractive properties of these samples. In Fig. 7, the concentration dependences of the refractive index $\{n = n(c)\}$ for S1–S5 samples for various temperatures are presented. Monotonous linear behavior of the $n = n(T)$ and $n = n(c)$ dependences without any fluctuations indicates the stability of the refractive properties in (LTAB + CTAB mixture) + water lyotropic system.



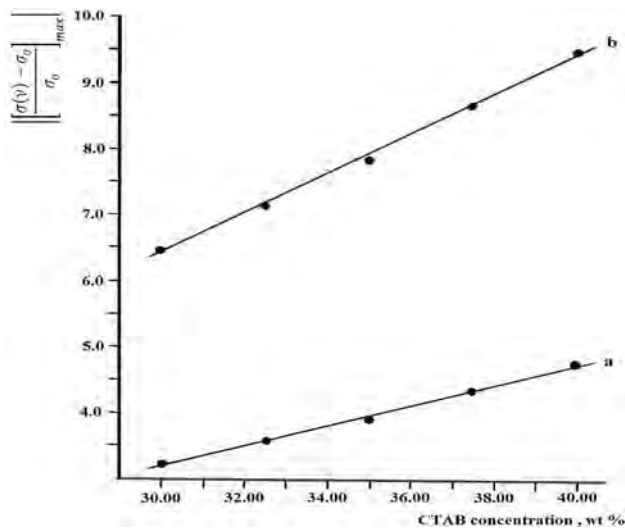


Fig. 5 $\left[\frac{\sigma(v) - \sigma_0}{\sigma_0} \right]_{\max}$ values vs. concentration of amphiphile for S11–S15 samples. a: X-direction; b: Y-direction

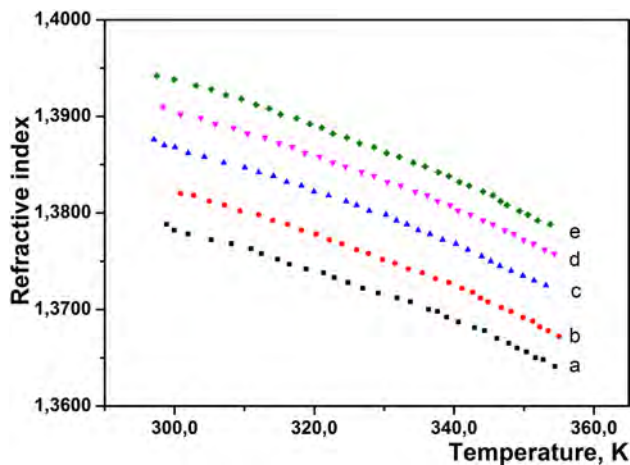


Fig. 6 Temperature dependences of the refractive index for (LTAB + CTAB mixture) + water lyotropic system. a: S1 sample; b: S2 sample; b: S3 sample; c: S4 sample; d: S5 sample

The $n = n(T)$ dependences for LTAB + H₂O (S6–S10 samples) and CTAB + H₂O (S11–S15 samples) lyotropic systems are presented in Figs. 8 and 9. As seen in these figures, for these lyotropic systems, also as for (LTAB + CTAB mixture) + water lyotropic system, monotonous linear decrease of the refractive index with an increase of temperature takes place. Behavior of the $n = n(T)$ dependences for S6–S10 and S11–S15 samples can be characterized by the $n = 1.3947 - 2.80 \times 10^{-4} \times T$ and $n = 1.3949 - 2.93 \times 10^{-4} \times T$ equations, accordingly. Such a behavior of the $n = n(T)$ dependences in (LTAB + CTAB mixture) + water, LTAB + water, and CTAB + water lyotropic systems showed that character of the refractive properties in these systems has the same nature. As it is seen from comparison of Figs. 6, 8 and 9,

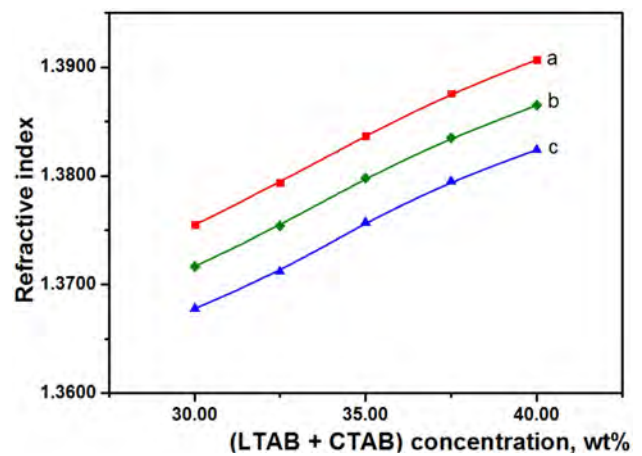


Fig. 7 Concentration dependences of the refractive index for (LTAB + CTAB mixture) + water lyotropic system. a: 313.0 K; b: 328.0 K; c: 343.0 K

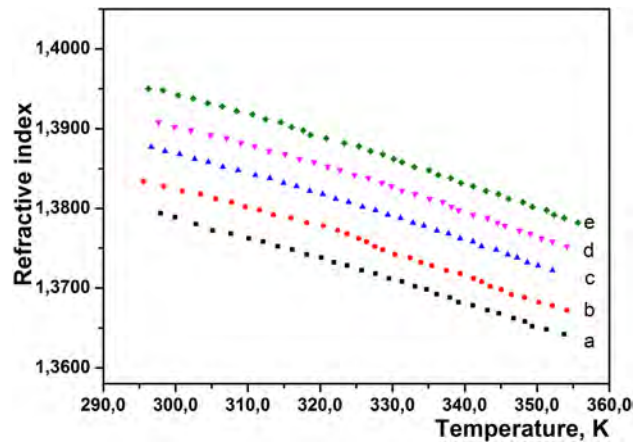


Fig. 8 Temperature dependences of the refractive index for LTAB + water lyotropic system. a: S6 sample; b: S7 sample; b: S8 sample; c: S9 sample; d: S10 sample

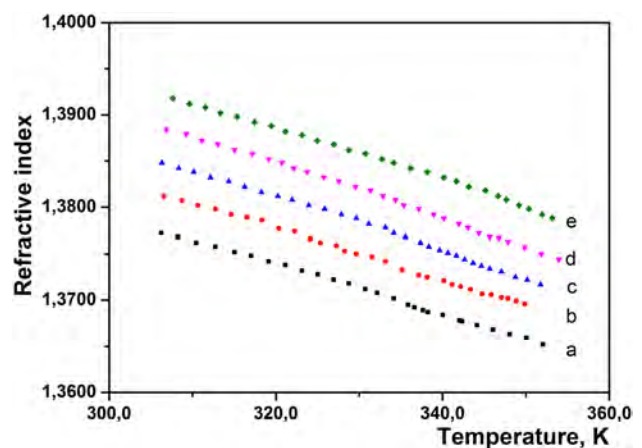


Fig. 9 Temperature dependences of the refractive index for CTAB + water lyotropic system. a: S11 sample; b: S12 sample; b: S13 sample; c: S14 sample; d: S15 sample

correlation between the refractive indices of lyotropic systems under investigations is as the $n_{CTAB} < n_{LTAB+CTAB} < n_{LTAB}$ inequality. This result indicates that using amphiphile mixtures is possible to regulate the refractive properties in lyotropic systems. Besides, as it is seen from comparison of Figs. 6, 8, and 9, intervals of changes of the refractive indices δn in (LTAB + CTAB mixture) + water, LTAB + water, and CTAB + water lyotropic systems are quite different. Namely, for (LTAB + CTAB mixture) + water lyotropic system $\delta n = 0.0153$, for LTAB + water lyotropic system $\delta n = 0.0167$, and for CTAB + water lyotropic system, $\delta n = 0.0130$ take place. These results show that using mixtures of amphiphiles with different lengths of the alkyl tail is possible to control the interval δn of changes of the refractive index in lyotropic systems.

In Figs. 10 and 11, the concentration dependences of the refractive index for LTAB + water and CTAB + water lyotropic systems are presented. As seen in these figures, an increase of amphiphile concentration in these amphiphile + water lyotropic systems leads to an increase of the refractive index. Such a behavior is similar to a behavior, which is presented in Fig. 6 for (LTAB + CTAB mixture) + water lyotropic system. That is, nature of the concentration dependences of the refractive index in lyotropic systems under investigations is the same.

As it is known, an increase of amphiphile concentration in definite lyotropic phase leads to an increase of number of micelles in such a phase of lyotropic system (Ekwall 1975; Lingmann and Wennerström 1980; Perez-Rodriguez et al. 1998; Puvvada and Blakshtein 1992). An increase of number of micelles leads to an increase of the optical density of this system. The optical density of medium is a measure of the refracting power and the refracting properties of such medium. Thus, variation of concentration of amphiphile or concentration ratio in mixture of

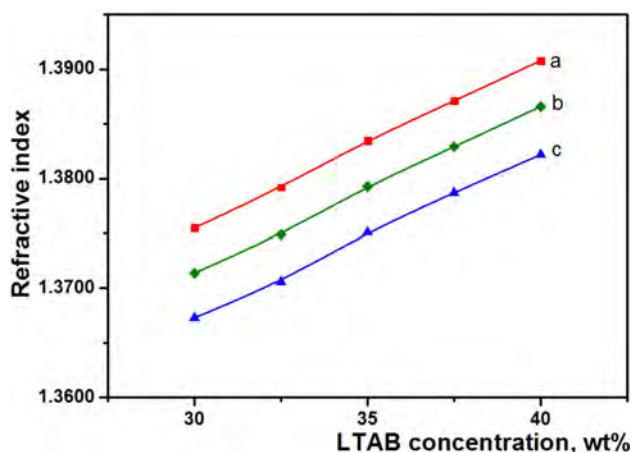


Fig. 10 Concentration dependences of the refractive index for LTAB + water lyotropic system. a: 313.0 K; b: 328.0 K; c: 343.0 K

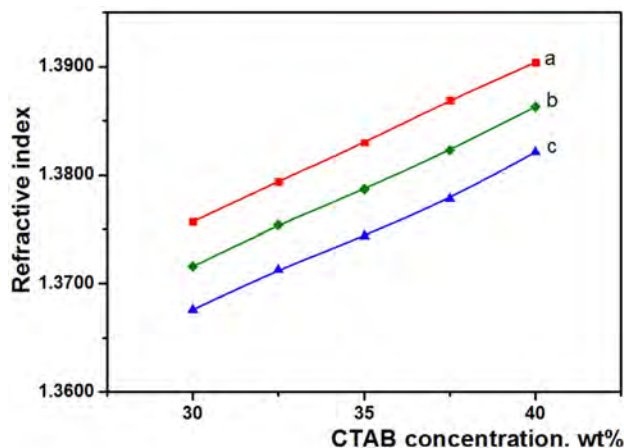


Fig. 11 Concentration dependences of the refractive index for CTAB + water lyotropic system. a: 313.0 K; b: 328.0 K; c: 343.0 K

amphiphiles with different lengths of the non-polar tail gives possibility to regulate the optical density and refracting properties of lyotropic systems.

4 Summary

The results obtained in this work can be summarized as follows:

- Single amphiphilic (LTAB + water and CTAB + water) and bicomponent amphiphilic {(LTAB + CTAB mixture) + water} lyotropic systems with the same amphiphile/water concentration ratio exhibit different mesomorphic and morphologic properties.
- An increase of amphiphile concentration in CTAB + water lyotropic system leads to an increase of the maximum value of the electrical conductivity anisotropy in the shear flow for hexagonal *E* mesophase.
- In water-based lyotropic system of two amphiphiles with high hydrophilicity degree (CTAB) and low hydrophilicity degree (LTAB), the general degree of hydrophilicity in (LTAB + CTAB mixture) + water lyotropic system is increased. That is, in water mixture with two amphiphiles and different hydrophilicity degrees, amphiphile with higher hydrophilicity degree is more effective. This peculiarity can provide control of the hydrophilicity degree of amphiphile–water mixtures and is effective for the mesomorphic and morphologic properties of lyotropic systems.
- An increase of amphiphile concentration in amphiphile + water and {(amphiphile1 + amphiphile2 mixture) + water} lyotropic systems leads to an increase of value of the refractive index. The correlation between the refractive indices in

LTAB + water, CTAB + water and (LTAB + CTAB mixture) + water lyotropic systems is as the $n_{\text{HDTMABr}} < n_{\text{DDTMABr+HDTMABr}} < n_{\text{DDTMABr}}$ inequality.

- The correlation between amphiphile/water concentration ratios for the high concentration limit of isotropic micellar L_1 phase in lyotropic systems under investigations is as the $c_{\text{CTAB}} < c_{\text{LTAB+CTAB}} < c_{\text{LTAB}}$ inequality. This result indicates that using amphiphile mixtures in lyotropic systems is possible to regulate the mesomorphic, morphologic, and optical properties in such systems.

Acknowledgements This work has been partially supported by the Research Foundation of Mugla Sitki Kocman University, Grant No. 17/132.

References

- Alfutimie A, Curtis R, Tiddy GJD (2014) In: Goodby J, Collings PJ, Kato T, Tschierske C, Gleeson H, Raynes P (eds) Handbook of liquid crystals. Wiley, London, pp 1–44
- Amaral LQ, Santos OR, Braga WS, Kimura NM, Palangana AJ (2015) Biaxial phase and coexistence of the two uniaxial nematic phases in the system sodium dodecyl sulphate–decanol–D₂O. *Liq Cryst* 42:240–247. <https://doi.org/10.1080/02678292.2014.981604>
- Burducea G (2004) Lyotropic liquid crystals. I. Specific structures. *Rom Rep Phys* 56:66–86
- Ekwall P (1975) Composition, properties and structures of liquid crystalline phases in systems of amphiphilic compounds. In: Brown GH (ed) Advances in liquid crystals, vol 1. Academic, New York, pp 1–142
- Figueiredo Neto AM, Salinas SRA (2005) The physics of lyotropic liquid crystals: phase transitions and structural properties. Oxford University Press, Oxford
- Figueiredo Neto AM (2014) Micellar cholesteric lyotropic liquid crystals. *Liq Cryst Res* 2:47–59. <https://doi.org/10.1080/21680396.2014.938783>
- Friberg S (1992) Organized solutions: surfactants in science and technology. CRC Press, New York
- Frolov YG (1982) Colloid chemistry: surface effects and disperse systems. Chemistry Publ. Moscow, Moscow
- Götz KG, Heckmann K (1958) The shape of soap micelles and other polyions as obtained from anisotropy of electrical conductivity. *J Colloid Sci* 13:266–272. [https://doi.org/10.1016/0095-8522\(58\)90034-5](https://doi.org/10.1016/0095-8522(58)90034-5)
- Govindaiah TN (2016) Optical density and ultrasonic measurements of lyotropic chromonic phase of liquid crystalline materials. *Mol Cryst Liq Cryst* 637:92–98. <https://doi.org/10.1080/15421406.2016.1149023>
- Guo C, Wang J, Cao F, Lee RJ, Zhai G (2010) Lyotropic liquid crystal systems in drug delivery. *Drug Discov Today* 15:1032–1040. <https://doi.org/10.1016/j.drudis.2010.09.006>
- Heckmann K, Götz KG (1958) Die Bestimmung der Form gelöster Polyionen aus dem Leitfähigkeitsanisotropie-Effekt. *Z für Elektrochem* 62:281–288. <https://doi.org/10.1002/bbpc.19580620312>
- Hexagonal phase. http://wapedia.mobi/en/Hexagonal_phase. September 2014
- Hoffmann H, Oetter G, Schwandner B (1987) The aggregation behavior of tetradecyldimethylaminoxide. *Progr Coll Polym Sci* 73:95–106. https://doi.org/10.1007/3-798-50724-4_68
- Hoffmann H, Hofmann S, Illner JC (1994) Phase behaviour and properties of micellar solutions of mixed zwitterionic and ionic surfactants. *Progr Colloid Polym Sci* 97:103–109
- Hyde ST (2001) Identification of lyotropic liquid crystalline mesophase. In: Holmberg K (ed) Handbook of applied surface and colloid chemistry. Wiley, London, pp 299–332
- Jolley KW, Smith MH, Boden N, Henderson JR (2001) Nature of the liquid crystalline phase transitions in the cesium pentadecafluorooctanoate (CsPFO)-water system: the nematic-to-isotropic transition. *Phys Rev E* 63:051705–051707. <https://doi.org/10.1103/PhysRevE.63.051705>
- Kazanci N, Nesrullajev A (2003) Refracting and birefringent properties of lyotropic nematic mesophases. *Mater Res Bull* 38:1003–1012. [https://doi.org/10.1016/S0025-5408\(03\)00077-1](https://doi.org/10.1016/S0025-5408(03)00077-1)
- Kumar A (2013) Determination of orientational order and effective geometry parameter from refractive indices of some nematics. *Liq Cryst* 40:503–510. <https://doi.org/10.1080/02678292.2012.761355>
- Laughlin RG (1996) The aqueous phase behaviour of surfactants. Academic, London
- Lingmann B, Wennerström H (1980) Amphiphile aggregation in aqueous solutions. In: Micelles. Springer, Berlin, pp 41–57
- Mirandi RM, Schulz PC (2002) Vuano B (2002) Triangular phase diagram of the catanionic system dodecyltrimethylammonium bromide–disodium dodecanephosphonate–water. *Coll Surf A* 197:167–172. [https://doi.org/10.1016/S0927-7757\(01\)00876-7](https://doi.org/10.1016/S0927-7757(01)00876-7)
- Mitra M, Gupta S, Paul R, Paul S (1991) Determination of orientational order parameter from optical studies for a homologous series of mesomorphic compounds. *Mol Cryst Liq Cryst* 199:257–266. <https://doi.org/10.1080/00268949108030937>
- Mukherjee PK (2002) Nematic-isotropic phase transition in lyotropic liquid crystals. *Liq Cryst* 29:863–869. <https://doi.org/10.1080/02678290210145120>
- Mukherjee PK (2013a) Isotropic micellar to tilted lamellar phase transition in lyotropic liquid crystals. *J Mol Liq* 187:90–93. <https://doi.org/10.1016/j.molliq.2013.03.05.031>
- Mukherjee PK (2013b) Isotropic micellar to lamellar phase transition in lyotropic liquid crystals. *RSC Adv* 3:12981–12984
- Mukherjee PK, Bhattacharya J (2007) Phenomenological theory of the nematic to lamellar phase transition in lyotropic liquid crystals. *J Chem Phys* 126(1–6):024901. <https://doi.org/10.1063/1.2426343>
- Mukherjee PK, Lagerwall JPF, Giesselmann F (2005) Electrolyte effects on the nematic–isotropic phase transition in lyotropic liquid crystal. *Liq Cryst* 32:1301–1306. <https://doi.org/10.1080/02678290500361963>
- Mukherjee PK, Rahman M (2013) Isotropic to biaxial nematic phase transition in an external magnetic field. *Chem Phys* 423:178–181. <https://doi.org/10.1016/j.chemphys.2013.07.012>
- Nastishin YA, Liu H, Schneider T, Nazarenko V, Vasyuta R, Shiyankovskii SV, Lavrentovich OD (2005) Optical characterization of the nematic lyotropic chromonic liquid crystals: light absorption, birefringence, and scalar order parameter. *Phys Rev E* 72(1–14):041711. <https://doi.org/10.1103/physreve.72.041711>
- Nesrullajev A (1988) Anisotropy of electroconductivity and shapes of micellar aggregates: amphiphile + water lyotropic liquid crystalline system. *Electrochemistry (Sov.)* 24:570–572
- Nesrullajev A (1992) Mesomorphism and electrophysics of lyotropic liquid crystalline systems. DSc Dissertation. Institute of Physics, Academy of Sciences, Baku
- Nesrullajev A (2007) Lyotropic liquid crystals. amphiphilic systems. Mugla University Press, Mugla
- Nesrullajev A (2010a) Sizes and anisometricity of micelles in lyotropic liquid crystalline mesophases: sodium lauryl sulphate/water/decanol lyotropic system. *Tenside Surf Det* 47:179–183

- Nesrullajev A (2010b) Shape and sizes of micelles in nematic-calamitic and nematic-discotic mesophases: sodium lauryl sulphate/water/decanol lyotropic system. *Mater Chem Phys* 123:546–550. <https://doi.org/10.1016/j.matchemphys.2010.05.012>
- Nesrullajev A (2013) Structural peculiarities of micelles in lamellar mesophase of lyotropic liquid crystalline systems: shape, sizes and anisotropy. *J Mol Liq* 187:337–342. <https://doi.org/10.1016/j.molliq.2013.08.017>
- Nesrullajev A (2014) Comparative I, investigations of phase states, mesomorphic and morphologic properties in hexadecyltrimethyl ammonium bromide/water and hexadecyltrimethyl ammonium bromide/water/1-decanol lyotropic liquid crystalline systems. *J Mol Liq* 200:425–430. <https://doi.org/10.1016/j.molliq.2014.10.036>
- Nesrullajev A, Kazancı N, Yıldız T (2003) Hexagonal lyotropic liquid crystalline mesophase: change of rod-like micelles sizes with changes in concentrations. *Mater Chem Phys* 80:710–713. [https://doi.org/10.1016/S0254-0584\(03\)00079-8](https://doi.org/10.1016/S0254-0584(03)00079-8)
- Özden P, Nesrullajev A, Oktik S (2010) Phase states and thermomorphologic, thermotropic, and magnetomorphologic properties of lyotropic mesophases: sodium lauryl sulphate-water-1-decanol liquid-crystalline system. *Phys Rev E* 82(1–7):061701. <https://doi.org/10.1103/physreve.82.061701>
- Pan RP, Tsai TR, Chen CY, Wang CH, Pan CL (2004) The refractive indices of nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl in the THz frequency range. *Mol Cryst Liq Cryst* 409:137–144. <https://doi.org/10.1080/15421400490431039>
- Perez-Rodriguez M, Prieto G, Rega C, Varela LM, Sarmiento F, Mosquera V (1998) A comparative study of the determination of the critical micelle concentration by conductivity and dielectric constant measurements. *Langmuir* 14:4422–4426. <https://doi.org/10.1021/la980296a>
- Petrov AG (1999) *The lyotropic state of matter: molecular physics and living matter physics*. Gordon & Breach Science Publishers, London
- Puvvada S, Blakschtein D (1992) Thermodynamic description of micellization, phase behaviour, and phase separation of aqueous solutions of surfactant mixtures. *J Phys Chem* 96:5567–5579. <https://doi.org/10.1021/j100192a070>
- Rehage H (1982) *Rheologische Untersuchungen an viskoelastischen Tensidlösungen*. PhD Dissertation. Bayreuth University, Bayreuth
- Santin Fulho O, Itri R, Amaral LQ (2000) Decanol effect on the structure of the hexagonal phase in a lyotropic liquid crystal. *J Phys Chem B* 104:959–964. <https://doi.org/10.1021/jp993240d>
- Schwarz G (1956) Zur theorie der Leitfähigkeitsanisotropie von Polyelektrolyten in Lösung. *Z für Phys* 145:563–584
- Sonin AS (1987) Lyotropic nematics. *Sov Phys Usp* 30:875–912. <https://doi.org/10.1070/PU1987v030n10ABEH002967>
- Tsvetkov VN (1986) *Hard-chain polymer molecules*. Science Publ, Moscow
- Vedenov AA (1984) *The physics of solutions*. Science Publ, Moscow
- Yu LJ, Saupé A (1982) Deuteron resonance of D₂O of nematic disodium cromoglycate-water system. *Mol Cryst Liq Cryst* 80:129–134. <https://doi.org/10.1080/00268948208071026>

