Lyotropic Nematogenic System Potassium Laurate–1-Decanol–Water: Method of Synthesis and Study of Phase Diagrams

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Abstract—The results of the study of the potassium laurate–1-decanol–water lyotropic composition are presented. The procedure of preparation of micellar solutions provides the good reproducibility of the phase diagrams. The configurations of the domains of the liquid crystal order are constructed on the concentration plane at the constant temperature as well as the temperature sections (T, C_{1-decanol}) (at the constant ratio of potassium laurate to water) and (T, C_{water}) (at the constant ratio of potassium laurate to 1-decanol). The liquid-crystal phases observed are described. © 2000 MAIK “Nauka/Interperiodica”.

INTRODUCTION

As is well known [1, 2], mesogenic systems, i.e., compounds that can form liquid crystal phases, are divided into two classes—thermotropic and lyotropic. The division reflects the fundamental distinctions, which can be traced even at the level of the elementary structural units. For thermotropics, such a unit is a molecule, whereas for lyotropics, it is an associate of molecules called a micelle. The complexity of the structural units makes a lyotropic a complex compound as a whole. Because of the relatively low energy of the shape-forming bonds, micelles are very sensitive to the composition and the external conditions (they change their shape and size).

To identify the systems of such type, de Gennes [3] even has purposely introduced the term soft matter. In turn, the Mesoscopic transformations occurring in soft matter, influence the symmetry of the implemented order [4], the macroscopic parameters of the material [5], etc.

The chemical aspect of the synthesis of a thermotropic liquid crystal reduces to the requirement to synthesize the material with a sufficiently high purity grade, whereas for the synthesis of lyotropic (micellar) systems, the composition of the mixture used is also a key factor, because the domain of liquid crystal order on the ternary phase diagram is rather small, whereas its position is sensitive to the effect of impurities. At present, a number of nematogenic lyotropic compositions are known [6]. They posses rather interesting properties, namely, the existence of several nematic-phase modifications [7], the occurrence of the second-order isotropic → nematic transitions [8, 9], very low light scattering in the visible range, and the ability to keep dispersed particles in the composition [9, 10].

The present paper is devoted to the study of the nematogenic system potassium laurate (KL)–1-decanol–water. The choice of the composition was dictated by the fact that it is the most well known [6] phase and, at the same time, is far from being exhaustively studied. Moreover, the known experimental results [7, 11, 12] are inconsistent.

The article consists of sections three. First, the necessary requirements to chemical purity and the aggregate state of each component are formulated. The second section describes the method of the composition preparation and the studies of liquid-crystal states proper. We found the method for mixing the components that provides the synthesis of lyotropic solutions with well reproducible physicochemical properties. And finally, the phase diagrams constructed are discussed in Section 3.

1. PREPARATION OF LYOTROPIC KL–1-DECANOL–WATER SOLUTIONS

1.1. Potassium laurate. The main component of the composition, potassium laurate (KL), was synthesized from the following commercial products: (1) lauric acid, LA (Fluka) with M_r = 200.32 g/mol and the nom-

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inal content of the main product not less than 99% and potassium hydroxide (KOH) (Prolabo) with $M_r = 56.11$ g/mol and the nominal content of the main product not less than 86%. The total content of other alkali metals did not exceed 1%.

The lauric acid solution in a 50% water–alcohol medium was neutralized with the aqueous KOH solution (~9 M) until the attainment of pH of 10.8–10.9. The dried product was a white crystalline substance.

The purity of potassium laurate was checked by recording IR spectra on a UR-20 spectrometer. The comparison of the LA and KL, absorption spectra (Fig. 1) shows that the main difference is caused by the absence of a hydrogen atom in a KL molecule. The carboxyl group of LA gives an intense peak due to non-symmetric valence vibrations in the range 1650–1725 cm$^{-1}$ [13]. The absorption spectrum of potassium laurate shows the shift of this maximum observed due to the appearance of a heavy potassium atom. Another essential difference in the spectra consists in disappearance of the bands due to deformation vibrations of the hydroxyl group in the ranges 850–960 and 1240–1300 cm$^{-1}$ and the valence vibration band in the range 2500–3400 cm$^{-1}$ [13–15]. Thus, the absence of hydroxyl bands in the spectrum can serve an indicator of the purity of potassium laurate from the lauric acid.

1.2. Components. The components for preparing the ternary system the components were water, 1-decanol, and an aqueous solution of potassium laurate. Water was purified by single distillation and had the pH ~ 6. The commercial chemical 1-decanol (Fluka) with $M_r = 158.3$ g/mol with the nominal content of the main product not less than 99%. The potassium laurate aqueous solution was prepared preliminary by dissolving crystalline KL in water at the temperature 80–100°C until the attainment of the concentration of ≥35 wt % and then was cooled down to 22°C. It should be emphasized that, unlike the previous studies [7, 8, 11, 12], we excluded the solid KL from the set of components used, because it is difficult to control in situ its complete dissolution.

1.3. Method of mixing. The components were always mixed at room temperature. To prepare a sample of the composition corresponding to the given point on the ternary phase diagram, the calculated component amounts (KL, 1-decanol, and water) were placed into the mixing vessel. Upon pouring each portion of water, the vessel was sealed and weighed with an accuracy of 10 μg on an electronic scale (Mettler). This pro-
provided a more accurate determination of the mixture composition than the use of the volume dosage of liquid components. The weighing procedure continued within 5–10 s. The mixing vessels were 9 ml-test tubes of the volume with tight silicone covers. The preparation in the tube occupied a volume not exceeding 3–4 ml.

Components were stirred for 60–100 min in the closed mixing vessels by a vibromixer at a frequency of 10–20 Hz. To remove the stable foam, the mixture in the mixing vessel was centrifuged for 1–3 min at the rotational velocity of 1000–2000 rev/min, which restored the solution homogeneity. The small amount of highly dispersed foam at the free surface did not hinder any further work.

The compounds obtained were used to study the behavior of the phases in the ternary system KL–1-decanol–water at 20 ± 1°C. The results obtained are summarized in the phase diagram shown in Fig. 2.

The sections of the concentration phase diagram and its temperature sections (the concentration–temperature diagrams) were obtained as follows. First, the solution of the composition corresponding to the initial point of the diagram was prepared. The mixing vessels were 50 ml glasses. They were filled up to 3/4 of their volumes, closed with screw Teflon tops, and the content was homogenized as described above.

The solution prepared was poured into 8 to 10 9 ml-test tubes, which were preliminarily carefully weighted. This procedure provided the identity of the starting material for all 8–10 points on the sections of the phase diagram to be studied. The filled tubes were weighted and an appropriate portion of the admixture–components was introduced, and the tube was weighted anew in order to determine the amount of admixture and to calculate the composition of the final mixture. Then, the material in tubes was homogenized by stirring and the subsequent centrifuging.

The addition of 1-decanol resulted in the formation of a number of mixtures with the constant water/KL ratio and various content of 1-decanol (Sections 1, 2, and 3 in Fig. 2). The addition of water resulted in the mixtures with the constant KL/1-decanol ration but variable water content (Section 4 in Fig. 2). Similar sets of solutions were also used to study the behavior of various phases as function of temperature.

Consider the lyotropic compositions obtained. The solutions formed in mixing vessels under the above conditions were homogeneous transparent liquids occupying the whole sample volume. Each of the observable phases existed for not less than six months. Upon five months, the samples showed no noticeable changes in the phase diagrams.

The laboratory practice of synthesizing KL and the final product, the lyotropic nematogenic composition, provided the formulation of the conditions necessary for obtaining the lyotropic nematics with reproducible phase diagrams. The content of unreacted lauric acid in the KL should not exceed 1 wt %, the pH of the solutions obtained at the liquid crystal concentrations used (KL ~ 25–33 wt %) should be within 10.4–10.8. The IR spectroscopy control should be used at all stages of the synthesis.

2. PHASE DIAGRAMS OF LYOTROPIC SOLUTIONS IN THE VICINITY OF THE NEMATIC DOMAIN

2.1. Equipment and materials. The lyotropic solution was poured out either into 1 ml-cylindrical glass test tubes closed with a polyethylene cover or into flat 0.1 mm-thick and 2.0 mm-wide capillaries (Vitro Dynamic) placed onto slides carefully sealed up with molten paraffin. Then, these preparations were coated with several layers of the transparent water-repellent varnish.

Each of the solution samples (corresponding to one point on the concentration diagram) consisted of three identical test tubes or 4–6 capillaries necessary for studying the conditionally reversible phase transformations (see Sect. 3.4). The phases were identified visually on a crystallographic polarizing microscope.
POLAM R-11, LOMO) adjusted to observe the menisci in inclined tubes and determine the sign of the optical anisotropy [16]. The fast control the solutions was made in crossed polarizers.

2.2. Methods of phase observations. A number of tubes with preparations corresponding to a given concentration section were placed into a thermostat and were kept there for about 40 min until thermal equilibrium was reached. The preparation stop showing any visual changes, which indicated the attainment of the phase equilibrium. Each tube was taken out of the thermostat for about 1 min for the identification of the phase type in a microscope. A special device allowed the fixation of the test tube at an angle of 10°–25° to the direction of observation. A meniscus edge was located between the crossed polarizers, thus providing the configuration of a wedgelike layer with a free boundary which yields sufficient information for phase identification (the criterion of the phase identification is considered below). The meniscus of the isotropic phase was black. The nematic phase showed the characteristic texture typical of this state (Fig. 3). The meniscus in the state G-1 appears as the suspension of colored droplets against the background of isotropic medium (Fig. 4). The meniscus in the states H and C showed the smectic-like texture (Fig. 5).

The above phases and states could be also reliably identified visually in the polarized light. For the qualitative identification phase identification we used the polarization cell with crossed polaroids.

Special observations were performed to understand the effect of temperature variation on the phase organization of the solutions under study. For about one minute, no phase changes were recorded. This allows us to conclude that short abrupt changes in the thermal mode produce no effect on the phase state of the solution.

Some solutions were studied in the “classic” way as well [1, 2]. A flat capillary was filled with the preparation. Then the sign and the symmetry of the orientational order were determined by the conventional methods [16]. Being rather laborious, this procedure was employed only for a limited number of the samples, whose composition corresponded to the characteristic points of the phase diagram.

2.3. Phases and heterogeneous states of lyotropic solutions. The state of the solution is considered to be equilibrium, if it shows no apparent changes for a long period of time (several months). The phase diagram constructed from the data measured at 20°C is shown in Fig. 2. The lines, representing the domain boundaries

![Fig. 3. Marble texture characterizing the nematic order. It is observed for all the solutions within the domain N on the phase diagram.](image3)

![Fig. 4. Emulsion of flat liquid-crystal droplets in an isotropic medium which characterizes the G-1 state.](image4)

![Fig. 5. Texture corresponding to the H domain (presumably, the hexagonal mesophase); on the phase diagrams, this zone is shown by slanted hatching.](image5)
are drawn using the data analyzed for more than 300 samples. Figure 2 shows only eight of these points (black circles). Straight lines 1–4, connecting the pairs of these points are the projections of the experimentally studied temperature sections of the phase diagram. The phase-diagram sections by the planes \((T, C_{1-decanol})\) and \((T, C_{water})\) are shown in Figs. 6 and 7, respectively.

The temperature–concentration region studied has five clearly seen states.

The isotropic phase (I) is located in the region of low concentrations <4 wt % of 1-decanol and <30 wt % of KL \((T = 22^\circ C)\). The solution consists of a transparent optically isotropic liquid, with the viscosity being of the same order of magnitude that the viscosity of water.

The nematic phase (N) is located in the domain having a complicated shape (Fig. 2) and, occupies mainly the regions with 5–8 wt % of decanol and 25–32 wt % of KL \((T = 22^\circ C)\). The solution is a transparent optically anisotropic liquid, with the viscosity of the order of magnitude the viscosity of glycerol. The solution in test tubes (thick samples) provides complete depolarization of light; whereas the solution in capillaries and meniscus edge (thin samples) exhibits the structure typical of nematics (Fig. 3). The measurements on oriented samples indicate the positive sign of the optical anisotropy and the uniaxial symmetry of the solution in the state of mechanical equilibrium (i.e., in the absence of hydrodynamic perturbations). The comparison of the defects observed with those known for lyotropic liquid crystals [6] showed that the textures formed in our system at 18–22°C correspond to a lyotropic nematic with the discotic structure-forming units. At the temperatures over the range 30–40°C, we also observed in some samples the formation of defects typical of the nematic calamitic structure.

The hexagonal state (H). The domain of the hexagonal state \(H\) (Fig. 2) is a narrow stripe above the domain.
of the nematic phase. The aggregate state resembles swollen soap showing no flowability. In a polarized light, thick layers have a white color. The liquid-crystal texture of the thin oriented layers (Fig. 5) is similar to that formed in hexagonal lyotropic phases [17]. The 1-decanol concentrations for such textures lie within a very narrow (0.5%) range.

The gellike state (G). The domain of the gellike state is adjacent to those of the isotropic and the nematic states and also to those of the polycrystal and hexagonal structures. Near the boundary with the isotropic phase (denoted as G-1), the sample is a suspension of optically anisotropic droplets within the isotropic medium (Fig. 4). The droplets are anisometric they have mainly disklike shape and are characterized by concentric color rings in the polarized light. The extinction of the fringes in a polarizing microscope indicates the uniaxial optical anisotropy of the droplet substance. In the unpolarized light, thick layers of the G-1 emulsion are turbid. This inhomogeneous system is rather stable.

In the middle of the domain, there is the state denoted on the phase diagrams as G-2. Here, the sample loses fluidity and, rheologically, is very similar to the H phase. The polarization–optical experiments with the thin layers of the G-2 gel revealed no appreciable tendency to orientation. In unpolarized light, the thick specimens are of turbid white color. Close to the boundary with the nematic domain, the system restores its fluidity.

The polycrystalline phase (C). The domain of this phase is adjacent to those of the isotropic, hexagonal, and gellike states. It is determined from the observations on thin layers and looks like the accumulation of numerous small polydomain regions. Inside these regions, the sign of the optical anisotropy can vary, which may be explained by the presence of spherulites and similar formations. The phase C is characterized by the absence of the large-scale structures similar to those observed in the H phase. The aggregate state resembles a swollen soap. Thick layers are of white color in both polarized and unpolarized light.

2.4. Phase transitions. Studying the transition between the isotropic and the nematic phases, we established two types of such transitions, which is most clearly seen on in the \((T, C_{\text{1-decanol}})\) diagrams at the constant KL/water ratio.

The transition from the isotropic to the nematic phase may occur either through the intermediate gel state (for example, at \(T = 35^\circ\text{C}\), see Fig. 6b) or directly (for example, at \(T = 20^\circ\text{C}\)). The transitions themselves occur qualitatively differently. In particular, in the phase transformation G \(\rightarrow\) N, the isotropic one-phase solution, first, laminates to give the stable emulsion (its morphology is illustrated by Fig. 4). With addition of 1-decanol, the droplets of the new optically anisotropic phase gradually increase in size and number. It should be pointed out that the method of the texture analysis used does not allow the reliable determination of a type of the droplet-forming mesophase. Moving along the \(C_{\text{1-decanol}}\) axis, we arrive at the G-2 region, where, most likely, the essential restructuring takes place. The G-1 phase is a liquid, whereas the G-2 phase is a gel with a considerable shear stress. With the further increase of the 1-decanol concentration (approaching the nematic-domain boundary) the system restores its fluidity. The transition to the nematic phase occupying the whole sample volume proceeds within a very narrow temperature or concentration range. The actual width of the transition zones appeared to be less than the accuracy of our measurements. Hence, the boundary between the domains of the G and H states is shown by a line in Figs. 6 and 7.

The G \(\rightarrow\) N transition may occur with the changes in both concentration (1-decanol and/or water) and temperature. Our observations indicate the possibility of the reversible N \(\rightarrow\) G \(\rightarrow\) N transformation depends on the “penetration depth” into the state G. If, the transformation results in the gel state, then it is impossible to return to the nematic state using only the temperature variation. However, repeating the mixing, one can again observe the nematic state at the given temperature. If the system preserves its fluidity, then the nematic state is restored with a decrease of the temperature. In our opinion, the possibility of reversible N \(\rightarrow\) G \(\rightarrow\) N transformation indicates that the nematic is a true phase and not a metastable state. The seeming irreversibility of the N \(\rightarrow\) G-2 transition (with respect to the temperature) is associated solely with the kinetic difficulties of restructuring.
Another scenario of the $I \rightarrow N$ transition involves no droplet formation and the transformation occurs between the homogeneous states. Of particular interest is the pattern of the pretransitional phenomena. An isotropic solution located rather closely to the nematic-domain boundary responds to the small mechanical disturbances (vibration) by the formation of macroscopic regions with the uniaxial optical anisotropy, i.e., with giant orientational fluctuations. In the light transmitted through crossed polaroids, a slight shaking of the test tube results in a bright light flash against the black (in the equilibrium) background. The intensity of the response noticeably increases with an approach to the boundary of the $I \rightarrow N$ transition irrespective of whether it is caused by the change in temperature or concentration. This “fluctuation” interval is denoted by $I_F$ in Figs. 6 and 7. A similar phenomenon was also reported for the lyotropic system sodium dodecyl sulfate–1-decanol–water [11].

Visually, the $N \rightarrow H$ transition and $I \rightarrow G-I$ the transition are quite similar. The former transition is also reversible. Each time, the formation of a new phase starts from the appearance of the nucleation centers, which looks like the regions with smectic-like (lamellar) order.

3. DISCUSSION AND CONCLUSIONS

Nematic order in a lyotropic system is a fine effect [1]. This is indicated by the narrow region of the nematic domain in Fig. 2 in comparison with the entire concentration plane and the strong dependence of the polymorphism on the conditions of the compound preparation. In the Sections 1 and 2, a number of rules was formulated, whose thorough fulfillment provided the preparation of lyotropic compounds with the reproducible phase diagrams. The reproduced properties were observed at both concentration and temperature variations. Because of pronounced orientational–optical effects, the liquid crystal phases and transitions between them can readily be observed even using a simple polarization cell.

The study of the systems prepared provided: (1) the precise localization of the nematic phase $N$ in the three-dimensional space of the thermodynamical variables of the system (the temperature and the concentrations of any two components), (2) the demonstration of the possibility of the first- and the second-order $I \rightarrow N$ phase transitions and the establishment of the qualitative differences between them, (3) the determination of the two-phase domain (G), in which the system has the form either of a gel or an emulsion, and the study of its morphology, (4) the demonstration of the fact that, in addition to the temperature and partial concentrations, an important parameter characterizing the state of the lyotropic solution is also pH.

The present study is the first one, which considers the problem of reproducibility (and, thus also, the possible standardization) of the properties of the lyotropic solutions. As far as we know, all the preceding publications [7, 8, 11, 12] implied the reproducibility as a natural fact, because none of them had any detailed description of the synthesis of a lyotropic system. At the same time, the experimental results reported by various authors are inconsistent. Thus, comparing the representative points of the ternary diagrams of the systems KL–1-decanol–water, the data of [7, 8, 12] differ within 1 wt %. With the widths of the phase domains under discussion ranging from 0.1 to 1 wt %, this contradiction seems to be quite serious.

The above quantitative approach to the synthesis of the lyotropic system KL–1-decanol–water opens the way for studying the nematic state, for which many serious problems should be solved. For example, until now the problem of the “fine structure” of this phase remains open. Thus it was concluded [7, 18] that the nematic domain (N) has several modifications which are characterized by different micelle shapes. These are the discotic $N_d$, the calamitic $N_c$, and biaxial $N_{bn}$ phases with the elementary units in the shape of a disk, a cylinder, and a biaxial ellipsoid or a parallelepiped, respectively.

Studying the existence domain of the nematic phase, we found out the transitions through its external borders are of a complicated nature (see diagrams in Figs. 2, 6, and 7). In particular, either the transformation from the isotropic to the nematic state can be implemented only by the mechanism with obvious features of the first-order transition, the phases N and I, are separated by a rather wide domain G, where both these phases coexist or else the $I \rightarrow N$ transition occurs, which is very close to second-order phase transition and is accompanied by a drastic increase in the orientation fluctuations with an approach to the boundary (region $I_F$ in Figs. 2, 6, and 7). The character of the transition changes at the point of intersection of the boundaries of the I, G, and N domains. It should also be indicated that not far from the point indicated, above in the phase N the conoscopic observations showed the biaxiality. Although all the biaxial textures were formed under the action of mechanical perturbations and then relaxed to the uniaxial configuration, their formation signifies that it is in the vicinity of the intersection point mentioned above that the lines separating the still hypothetical $N_b$, $N_c$, and $N_{bn}$ phases pass.

It is worth noting to indicate some characteristic features of the two-phase domain G that separates the nematic and the isotropic phases. In particular, the “entering” into this domain from the side of any of the homogeneous phases results in an abrupt phase segregation. In our observations at the spacial resolution not exceeding $10^{-2}$ cm at the time scale of $\geq 1$s, the appearance of droplets (Fig. 4) was observed at once in the amounts comparable with the volume of the initial homogeneous phase. This fact points to the unconventional shape of the spinodal in our system. So far, we do
not have enough data for a detailed description of the domain G and the constituting states (their division into G-1 and G-2 only reflects the difference in their rheologies). The detailed study of this domain is the objective of future studies.

In this connection, it should be indicated that the kinetic effects substantially hinder the implementation of the “cyclic” transition \( N \rightarrow G \rightarrow N \) with respect to temperature. As an example, consider Fig. 3c. Heating of the nematic to the temperatures characteristic of the region G-2 does not directly lead to gel formation. The gel is formed with a time lag of 5–10 min. Prior to gel formation, a decrease of the temperature “returns” the “overheated” nematic to the domain N. If the gel had enough time to be formed, a decrease in the temperature provides only the “freezing” of this state and the time necessary for the return to the nematic state, indefinitely increases. Thus, the supercooled gel, being, in fact, metastable, behaves in practice as the stable one.

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REFERENCES


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