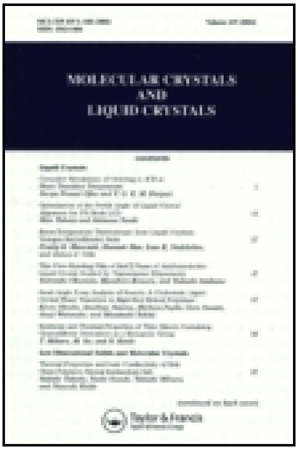

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Arif Nesrullaev [a] & Farhad Rustamov [a]
[a] Physical Department, Azerbaijan State University, Azerbaijan SSR, Baku, USSR

To cite this article: Arif Nesrullaev & Farhad Rustamov (1987): The Change of Mesomorphous Properties and the Shift of Phase Transitions in the Lyotropic Liquid Crystalline System, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 152:1, 421-434

To link to this article: http://dx.doi.org/10.1080/00268948708070970

Mol. Cryst. Liq. Cryst., 1987, Vol. 152 pp. 421-434
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Printed in the United States of America

THE CHANGE OF MESOMORPHOUS PROPERTIES AND THE SHIFT OF PHASE TRANSITIONS IN THE LYOTROPIC LIQUID CRYSTALLINE SYSTEM

ARIF NESRULLAEV and FARHAD RUSTAMOV
Physical Department, Azerbaijan State University,
Azerbaijan SSR, Baku, USSR

Abstract The article gives the results of a study of the influence of inorganic salt additives on the capacity of Potassium Caprylate to form lyotropic phases as well as of some micro- and macroscopic properties of Potassium Caprylate + Water lyotropic liquid crystalline systems.

INTRODUCTION

Recently intensive investigations of the physical properties of lyotropic liquid crystals, having a wide practical application, have been carried out. The investigations of multicomponent systems containing amphiphile, water, inorganic salt and/or alcohol are of particular interest. Every component of such a system, with a different degree of freedom, can modify not only the types and structures of phases but also their different physical properties, e.g. electrical conductivity, birefringence, viscosity etc.[1-5]. After adding certain additives into a binary amphiphile + water system, a nonuniform distribution of their molecules takes place within the system volume depending on their hydrophilicity or oleophilicity. These molecules can affect both the short range intramicellar interactions determining the micellar shape and sizes and the long range intermicellar interactions determining the mutual orientation of the micelles.

Thus, studying the effect of certain additives upon the phase states of lyotropic systems and on their properties, one can reveal the intermolecular interaction type, and determine its influence on the formation of lyotropic liquid crystal.

In this respect, the investigation of the effect of inorganic salt additives on the lyotropic liquid crystalline systems is of particular interest, due to the formation of new types of mesophases that are not present in the regular amphiphile + water systems. And this in its turn leads to gross changes of the physical parameters of those systems and to the occurrence of additional phase transitions. At present, there are some available papers[2,6-9] concerning the effect of inorganic salts on lyotropic systems. However, the data reported in these works is ambiguous and often inconsistent.

Therefore, in order to study the effect of inorganic salt both on the susceptibility to form lyotropic phases and on some properties of these phases, e.g. the electrical conductivity, viscosity and orientation, investigations of binary lyotropic liquid crystalline Potassium Caprylate (PC) plus Water system with different potassium chloride (KCl) concentration have been carried out.

MATERIALS AND EXPERIMENTAL TECHNIQUE

The amphiphile ($C_8H_{15}O_2K$) of the system studied was cleaned by multiple overcrystallization process followed by a filtration with a Büchner funnel. Its purity determined chromatographically was better than 99.5%. The water used as a solvent was simultaneously distilled and deionized twice. The potassium chloride was a pure compound used for analysis. In order to obtain the systems to be studied, the following was done: first, the salt solutions with a certain concentration were prepared, and then the corresponding amount of amphiphile was added. This order was needed to secure the total dissolution of the amphiphile and the salt. To obtain homogeneous solutions, after the vessel with the system was sealed it was heated to isotropic state, kept in that state and then cooled gradually down to a temperature of 290 K.

Both, the studying of the phases under consideration and the determining of the temperature-concentration phase diagrams were carried out using polarization microscopy methods.

The concentration dependence on the electrical conductivity were investigated using the bridge method, with an external generator and an external indicator. It allowed us to carry our the investigations at frequency of 20 kHz, in order to avoid possible errors caused by near electrode processes.

EXPERIMENTAL RESULTS

First of all the binary system PC + water was investigated. The investigations showed that the given system is monomorphous and has a simple hexagonal mesophase E, revealed as fan and angular textures, in a wide temperature and concentration regions.

When KCl in small concentration was added into the binary PC + water system, the typical textures and concentration regions of phase existence changed considerably. Figure 1 represents a part of the PC + water + KCl phase diagram, including the region of the phase transition from an isotropic micellar solution L_1 to a simple hexagonal mesophase E at 290 K. This diagram shows

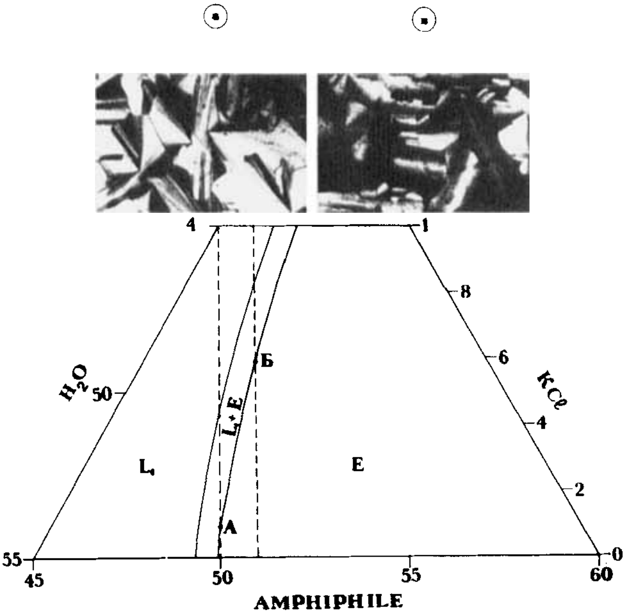

FIGURE 1. A part of the phase diagram of Potassium Caprylate + Water + Potassium Chloride lyotropic system

that the electrolyte causes a shift of the boundaries of the two-phase regions of the isotropic micellar phase L_1 plus the anisotropic mesophase E and hence of the boundary of the mesophase E itself. In other words, the addition of electrolyte into the binary lyotropic liquid crystalline system gives as a result a change of the amphiphile - water concentration ratio necessary for each phase to be formed. From the comparison of the two systems with different KCl concentration (point A corresponds to 1%, B denotes 5.4%) it is obvious that a PC/water concentration ratio of 50:50 is needed for the E phase to be transformed into point A, whereas for the formation of the same phase in point B this ratio must be equal to 51:49. Thus, the adding of the inorganic salt into the binary system of amphiphile + water gives as a result the shift of the boundaries of $L_1 \rightarrow L_1 + E \rightarrow E$ phase regions towards the higher amphiphilic/water concentrations. It is seen from this diagram that when the added amount of KCl increases in a system with a constant amphiphile/water concentration ratio (the lines of constant ratios are denoted as dashed lines) the system tends to the micellar solution L_1 .

Fig.1 includes the micrograph of the E mesophase textures observed in the ternary system studied. The photo "a" presents a general fan texture observed also for binary PC + water systems. The photo "b" shows a new lyotropic liquid crystalline texture, i.e. the bulk-mosaic texture with separate domains of fan texture. In this texture the

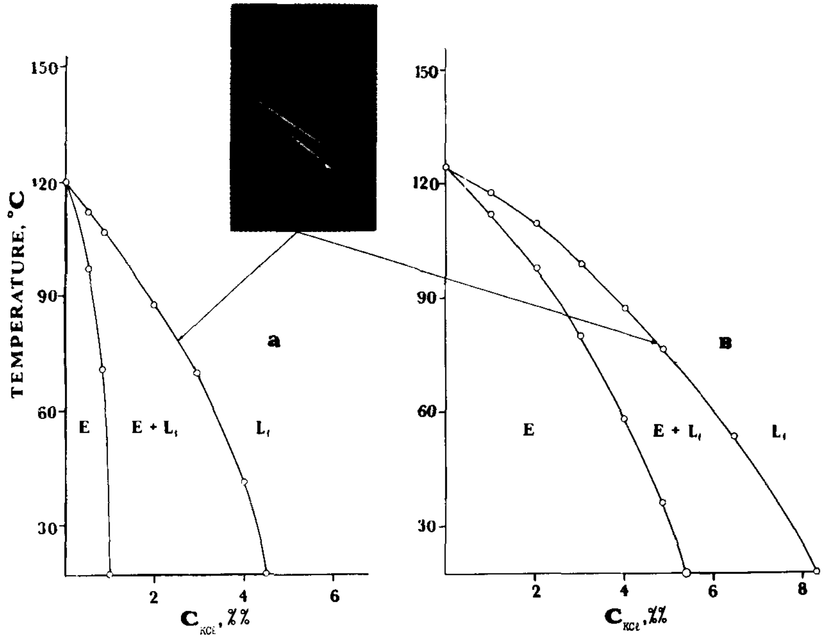

FIGURE 2. $L_1 \rightarrow L_1 + E \rightarrow E$ phase transition regions and temperature regions of the phases for two compounds with amphiphile/water ratio 50:50 and 51:49.

bulk-mosaics are less birefringent in comparison with the fan formation.

The temperature variations of $L_1 \rightarrow L_1 + E \rightarrow E$ phase transitions and temperature regions, where the phase can exist have also been investigated. The results obtained are given in Fig.2 (a,b) as an example of two compositions with different component concentrations at amphiphile/water ratio of 50:50 and 51:49, respectively. These dependences show that: 1) with the increasing of temperature, the E phase region and the region of dynamic coexistence of $L_1 + E$ appear in a narrower concentration range; 2) the temperature phase transitions from the E mesophase take place at lower temperatures. Thus, with the adding of inorganic salt into an amphiphilic - water binary system the control of the temperature transitions and the obtaining of lyotropic liquid crystal becomes possible.

The specific property of the given system is the appearance of structures with rotational symmetry, which follow the cooling of the system, when an evolution from L_1 phase to L_1+E region takes place (Fig.2). When rotating the table of the microscope each of these formations was found to darken and lighten as a whole. With the cooling of the system these formations grow in size and amount, came in contact with one another and with the surface of the capillaries. Micellar layers perpendicular to the formation axis were twisted into Dupin cyclides that brought about the formation of general fan texture (photo "a" of Fig.1) when the system was cooled to the temperature of the transition to mesophase E. The textures with rotation figures were monotropic and were found not to occur when heating the system.

When a PC + water + KCl ternary system was analyzed an influence of the electrolyte on the system's viscosity was also found, consisting of a considerable decrease of this viscosity. This fact has been reported earlier[2,10]. A similar decrease of the viscosity of these systems can facilitate considerably the methods of investigation, and allow the use for the orientation of such systems of the classical methods of thermotropic liquid crystal orientation which cannot be applied for lyotropic liquid crystals, which are too viscous.

Moreover, the inorganic salt additives themselves may promote the occurrence of orientation. Thus, the orientation effect of KCl on the binary system studied was accompanied by the formation of homogeneous textures in which the longitudinal axes of the cylindrical micellar aggregates are parallel to capillar surfaces.

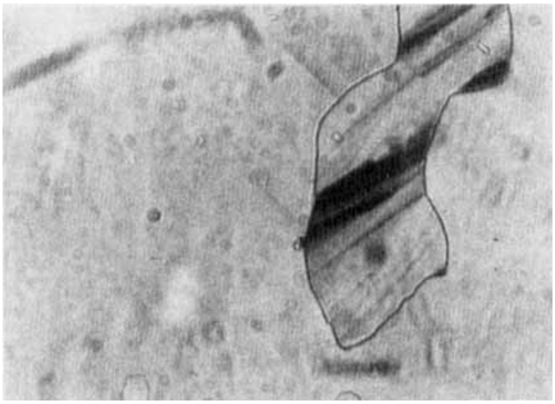

FIGURE 3. A micrograph of a homogeneously oriented texture.

Figure 3 shows a micrograph of such a homogeneous texture whose background has the nonoriented part. The longitudinal shift of the sample has broken the separate polycrystalline formations, if they were present in the specimen at all, and formed the more ordered homogeneous texture. Thus, the adding of inorganic salts into the lyotropic liquid crystalline system serves as one of the technological methods for the formation of oriented textures.

The present paper shows the results of the investigation of the concentration dependences of the electroconductivity σ of the PC + water system with different KCl additives at the constant frequency of 20 kHz. These dependences are shown in Fig.4. The amphiphile concentrations of the amphiphile + water system are plotted on the abscissa. It is seen from the curve "a" that when the concentration of KCl

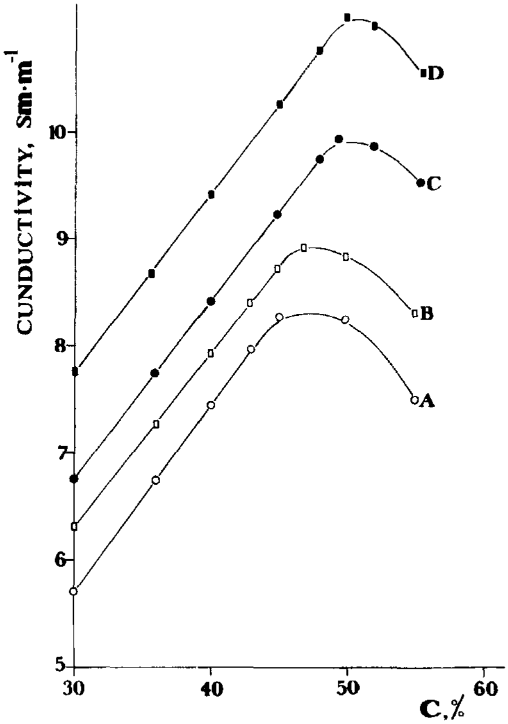

FIGURE 4. Concentration dependence of electroconductivity of PC + water system with different amount of KCl: "a" - 0%; "b" - 1%; "c" - 2%; "d" - 4%.

is equal to zero, the concentration dependence of σ in that part, which corresponds to isotropic phase L_1, increases in a linear fashion up to concentrations corresponding to L_1 + E region where the phase transition to E mesophase takes place. Then the value of σ decreases. The PC + water systems with different KCl additives (curves "b", "c", "d") have similar types of concentration dependence of electroconductivity. Fig.4 shows, however, that the absolute values of the electroconductivity increase with increasing potassium chloride concentration. The concentration dependences of σ in this case is observed in higher amphiphile concentrations which is in agreement with the shift of $L_1 \rightarrow E$ phase transition towards a higher amphiphile/water concentration ratio (Fig.1).

DISCUSSION

It is known[6,11] that a succession of phases observed in lyotropic liquid crystalline systems can be explained in terms of the phenomenological R-theory based on the analysis of the effect of the change of the system composition and of the temperature on the counteracting intramicellar forces. In order to characterize these forces determining the shapes and the sizes of the micellar aggregates and the lyotropic phase stability, a parameter R is introduced as the ratio between the tendency of the amphiphile layer (C) to blend with the oleophilic medium (O) and the tendency of the amphiphile layer (C) to blend with the polar medium (W). With different effects on the system as well as with different additives, the R parameter can be changed with respect to the changes of the hydrophilic and oleophilic interactions in the system in the following way[6,11]:

$$R = \frac{A_{co} - A_{oo}}{A_{cw} - A_{ww}} \qquad (1)$$

where A_{oo} is the interaction characterizing the clustering of oleophilic (O) molecules and the entire phase separation; A_{ww} is the interaction characterizing the clustering of hydrophilic (W) molecules and an entire phase separation; A_{co} and A_{cw} are the energies at C/O and C/W boundaries, respectively.

It is seen from this equation that when the O and W phases are given the parameter R increases with increasing of the A_{co}/A_{cw} ratio. In other words when distinguishing the hydrophilic (A) and oleophilic (L) types of interactions, the behaviour of the parameter R can be determined by the following relation[6,11]:

$$R = \frac{A_{Lco} + A_{Hco}}{A_{Lcw} + A_{Hcw}} \qquad (2)$$

The present paper deals with the study of the effect of inorganic salt on the character of the micellar formation and the consequent possibility for ternary system amphiphile + water + inorganic salt to form a lyotropic liquid crystalline system. Therefore, in this case it would be necessary in terms of the R-theory to take into account the hydrophilic type of interactions.

As it was mentioned above, the increase of the KCl concentration brings about the destruction of the liquid crystalline mesophase E and the phase transition of the system to isotropic micellar solution L_1. The fact was observed in the system with constant amphiphile/water concentration (dashed lines in Fig.1, denoting the amphiphile/water concentration ratio of 50:50 and 51:49, respectively). A similar behaviour of the system ionic SAC + water with inorganic salt additives has been reported elsewhere[7,9,10]. The analysis of that phenomenon on the basis of the R-theory clearly shows that the addition of inorganic salt into the potassium caprylate + water binary system leads to decrease of the parameter R that is needed for the phase transition $E \longrightarrow L_1$. That conclusion contradicts the data given by other authors[2,6,11], which reveal an increase of the parameter R when inorganic salt is added into the binary system amphiphile + water. This contradiction is due to the following fact. As it was mentioned above, the inorganic salt additives affect the hydrophilic interactions caused by the presence of dipoles and ionic charges. Furthermore, the physical nature of water and its properties as a solvent are known to be determined mainly by electrostatic forces due to $O^- - H^+$. Therefore, the inorganic salt additive is expected to change the interaction magnitudes both at the amphiphile - solvent interface and in the solvent itself. This is due to the decrease of the C-layer polarity and the decreasing ionization (the effect of the common ion) and partially due to the inorganic salt additive which causes breaking up of the water - amphiphile and water - water hydrogen bond[6,11,12]. Therefore, one can expect the decrease both of the A_{Hcw} and A_{ww} interactions. In this connection, when analyzing the effect of inorganic salt on the parameter R (i.e. on the ability to form the lyotropic liquid crystalline state) on the base of the R-theory the decrease of A_{Hcw} and A_{ww} should be necessarily taken into account. The argument so far, proves that the use of (2) instead of (1), with not taking into account the interaction change of the A_{ww} type, is not entirely correct when studying the effect of inorganic salt on the parameter R and can give as a result ambiguous treatment of the experimental results. Hence, according to equation (1), the interaction change of A_{cw} and A_{ww} can be a cause both for the increase and the decrease of the difference between A_{cw} and A_{ww} ($A_{cw} - A_{ww}$), and hence for the decrease or increase of the parameter R. Thus, it is obvious that in our case the adding of potassium chloride into the potassium caprylate + water system leads to higher decrease of the water - water interaction, compared to the water - amphiphile interaction, which in its turn leads to the change of the parameter R, i.e. to the phase transition to an isotropic micellar solution.

As it was mentioned in the previous section the inorganic salt additives in the amphiphile - water system were found to influence the phase transition temperatures of $E \rightarrow E + L_1 \rightarrow L_1$. The effect can be explained considering the decrease of the hydrophobic interactions A_{cw} and A_{ww} responsible for the micellar aggregate formation and leading to a decrease in the parameter R as it was mentioned above. In the given E mesophase this means that the decrease of the geometrical sizes of the cylindrical micellar aggregates results in the decrease of the experimentally observed phase transition temperature. Then it should be noted that the decrease of the micellar aggregate sizes causes also the observed decrease of the typical viscosity of the lyotropic system.

The concentration dependence of the electroconductivity with different addition of inorganic salt obtained experimentally (Fig.4) can also be explained when taking into account the discussion above. It is known[1,13,14] that the changes in the behaviour of the concentration dependence of σ occur at the phase transition from the isotropic micellar solution L_1 to the mesophase. Therefore, the shifts of electroconductivity maxima at different inorganic salt concentrations observed at the curves (Fig.4) can be considered as a result of the shift of the phase transition $L_1 \rightarrow L_1 + E \rightarrow E$ (Fig.1).

Thus, the comparison of the obtained and experimental results give further information about the interaction of the macro- and microscopic properties in lyotropic liquid crystalline systems.

CONCLUSION

The addition of potassium chloride into the binary system potassium caprylate + water system results in the following:

1. a transition of the system from the E mesophase to isotropic micellar solution L_1 at a constant amphiphile/water concentration ratio;
2. a shift of the concentration phase transitions $L_1 \rightarrow L_1 + E \rightarrow E$ towards a higher concentration ratio between amphiphile/water;
3. a shift of the temperature phase transitions $L_1 \rightarrow L_1 + E \rightarrow E$ towards the lower temperatures and the narrowing both of the E mesophase and of the L_1 + E biphase region;
4. an occurrence of a new type of lyotropic liquid crystalline texture, a bulk-mosaic texture;
5. a decrease in the typical viscosity of the whole system;
6. oriented homogeneous texture formed spontaneously;
7. an increase in the electroconductivity absolute value and a shift of the electroconductivity maximum towards the higher concentration ratios amphiphile/water.

REFERENCES

1. P. A. Winsor, *Trans.Faraday Soc.*, *46* 762 (1950).
2. D. M. Chen, F. Y. Fujivara, and L. W. Reeves, *Can.J.Chem.*, *55*, 2396 (1977).
3. K. Radly and A. Saupe, *Mol.Phys.*, *35*, 1405 (1978).
4. P. Ekwall, *Adv. in Liq.Cryst.*, *1*, 1 (1975).
5. K. A. Miller, in *Lyotropic Liquid Crystals and Structure of Biomembranes*, edited by S. Friberg, Washington, *Amer.Chem.Soc.*, *Adv. in Chem.Series*, *152*, 1 (1976).
6. P. A. Winsor, in *Liquid Crystals and Plasic Crystals*, edited by G. Gray and P. Winsor (Ellis Horwood, Chichester, England, 1974).
7. D. G. Hall and G. J. T. Tiddy, in *Anionic Surfactants*, edited by E. H. Lucassen-Reynders, (New York - Basel, 1981), p.55.
8. G. J. T. Tiddy, *Phys.Reports*, *57*, 1 (1980).
9. F. B. Rosevear, *J.Soc. Cosmetic Chemists*, *19*, 582 (1968).
10. H. Hoffman, H. Nüsslein, and W. Ulbricht, in *Micellization, Solubilization and Microemulsions*, edited by K. L. Mittal (Plenum Press, New York, 1977) p.263.
11. P. A. Winsor, *Chemical Reviews*, *68*, 1 (1968).
12. G. J. T. Tiddy and M. F. Walsh, in *Aggregation Processes in Solutions*, edited by E. Wyn-Jones and T. Gormally (Amsterdam - Oxford - New York, 1983) p.151.
13. I. Francois and A. Scoulios, *Kolloid-Z. und Z. fur Polymere*, *219*, 144 (1967).
14. Y. Shinichi, T. Kenji, and A. Koichito, *Mol.Cryst.Liq.Cryst.Lett.*, *92*, 99 (1983).