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Chr. V. Gutsulyak ^a

^a Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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Processes of Molecular Transformations and Self-Organization of Chromenoacridines in Liquid Crystal Matrices

Chr. V. Gutsulyak

Institute of Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

The thermochromism and the crystallization of bistable chromeno[2,3-q]acridines in liquid crystals are investigated. The dependence of thermochromic properties of the dye and characteristics of the liquid crystal on the dye concentration is revealed.

At small concentrations of the dye, the ordering of the LC matrix stimulates the thermotransformations of the dye and reflects in the increase of the transition temperature from the chromene form to the merocyanine form. At large concentrations of the dye the LC matrix ordering hampers the reversal transition from the merocyanine form to the chromene form, and the transition temperature reduces $(\Delta T = 80^{\circ}\text{C})$.

The ordering of the LC matrix impedes the crystallization of the dye and causes both a modification of the form and a decrease of the size of crystals.

The influence of the dye on the LC properties is exposed in the modification of physical characteristics of the LC (reduction of the crystallization temperature) and in the oriented influence of the dye on the LC (appearance of the texture).

Keywords: concentration; crystallization; dye; liquid crystal; thermochromism

1. INTRODUCTION

The interaction of organic dyes with liquid crystals is a pressing scientific issue from the viewpoint of studying the nature of new physical effects, as well as for development of new technologies and materials. Among the main directions of the investigations of dye-liquid crystal compositions, it is worth to mention the study of the influence of dyes

Address correspondence to Chr. V. Gutsulyak, Institute of Physics, National Academy of Sciences of Ukraine, 46, Nauky Ave, Kyiv 03650, Ukraine. E-mail: gutsul@iop.kiev.ua

on characteristics of liquid crystals [1,2], the research of the dependence of dye properties on parameters of a liquid crystal [3], and the study of the dye—liquid crystal interaction by the guest-host principle [4,5].

The practical interest is caused by the compositions of liquid crystals with bistable dyes, whose properties can be modified by means of different physical factors: light, temperature, electric fields, etc. The processes of thermochromic transformations of bistable organic substances depend on properties of the environment. The peculiarity of liquid crystal matrices is the existence of the ordering, whose parameters change with the temperature, as well as properties of dyes. The character of the interaction between a dye and a matrix in different temperature ranges differs substantially, making an additional factor of the influence on their properties. In this connection, the thermochromism of dyes in liquid crystal matrices can have some special features in comparing with the thermotransformations in solutions [6], gels [7], and in the crystal state [8].

The phase state of a liquid crystal can influence not only the intramolecular thermochromic transformations of a dye, but the creation of supramolecular structures by a dye and the crystallization processes as well. There are a lot of works devoted to the analysis of the influence of the environment, dissolubility, and solvation on the formation of dye crystals [9–12]. The shape of a crystal is determined by the structure of a molecule [13,14]. So, by different additives to the solution, the growing, shape, and sizes of crystals can be managed [15]. The orienting influence of the liquid crystal fosters the growing up of highly organized dye crystals of ultra small sizes [16], being very prospective materials in nanotechnologies.

2. EXPERIMENTAL

The present work is devoted to the research of chromeno[2,3-q]acridines (CA) possessing thermochromic characteristics and existing in two forms – the colorless chromene form and the colored merocyanine form (Fig. 1). There were CA compositions in MBBA, EBBA, ZLI-3145, ZLI-4387 liquid crystals with different ratios of components as well as CA solutions of different concentrations in solvents and polymer matrices used during the studies.

The CA compositions in MBBA and EBBA were prepared via the mixing of a liquid crystal with a dye (2%) accompanied by a further heating of the mixture. CA dissolves while rising a temperature in the isotropic phase of a crystal. In the mentioned concentrations, the investigated compositions were no homogeneous solutions (2% are

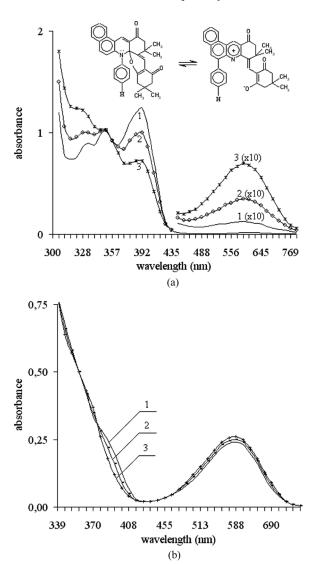


FIGURE 1 CA structure formula (a) and absorption spectra of $1 \cdot 10^{-4}$ M in ethanol (a) and DMFA (b) as a function of the temperature: $1-25^{\circ}$ C, $2-45^{\circ}$ C, $3-65^{\circ}$ C.

only of nominal value). A surplus amount of CA in a liquid crystalline solution exists in the form of the dispersion of small CA polycrystallites in a dissolved CA solution. On the cooling to room temperature, the CA polycrystallites precipitate.

For the preparation of the homogeneous CA in ZLI-3145 and ZLI-4387 liquid crystals, the dye previously had been dissolved in an organic solvent, and afterwards the obtained solutions were added to liquid crystals, i.e., the three-component mixture had been prepared: solvent – liquid crystal – dye. The preparation of the mixture was done using two types of solvents: solvents which dissolve a dye as well as a liquid crystal (acetone, toluene) and solvents dissolving a dye but not mixing with a liquid crystal (ethanol, dimethylsulphoxide). The dye concentration was as maximal as possible: the saturate solutions were prepared at $T=50\,^{\circ}\mathrm{C}$, being filtered before the preparation of compositions. The concentration of dyes depending on a solvent counts from 10^{-4} to $10^{-2}\mathrm{M}$.

While using solvents of the first type, the mixing of a dye solution with a liquid crystal results in the creation of a three-component mixture. On the evaporation of a solvent, the two-component CA composition in a liquid crystal was created. It was inserted into the cell for further investigations or was used for coating the surface of a glass plate. In dependence on the ratio of the amounts of the CA solvent and a liquid crystal, the compositions with different contents of CA in a liquid crystal were created. If the amount of the CA solution considerably exceeds the amount of LC, the concentration of the CA in the liquid crystal after the evaporation of a solvent exceeds the concentration of satiation in a pure solvent. The CA compositions obtained in such a way were homogeneous and had homogeneous coloration.

If a liquid crystal does not mix with a solvent, we get a heterogeneous three-component mixture. In such a mixture, there appears the interface between a liquid crystal and a dye solvent, which disposes, in dependence on the density, over the liquid crystal (for example, in case of dimethylsulphoxide) or under the liquid crystal (for example, in case of ethanol). In case of the mixing and the heating of a three-component mixture, the liquid crystal extracts a dye from a solvent, and the gradual coloration of the liquid crystal takes place. The extraction of a dye is facilitated by the evaporation of a solvent and by the satiation of a solution caused by that. The extracts of CA compositions prepared by such a method were also homogeneously colored and homogeneous.

Absorption spectra were investigated at a spectrophotometer SPE-CORD M-40 (Carl Zeiss, Jena). Transmission spectra were studied by means of the experimental setup with the photoelectric registration of spectra created at the basis of a monochromator SPM-2 (Carl Zeiss, Jena) with the use the filament 25-W lamps as a source of light. In order to measure the spectra of absorption and transmission, we used quartz cuvettes with thickness of 2, 5, and 10 mm. For the

temperature investigations, we used the thermostabilized handle, the temperature being set by the thermostat. Visual surveillances over the velocity and the process of thermochromic transformations of CA in different LC matrices were carried out during the heating (up to 160° C) and the cooling of the compositions CA-LC in quartz cuvettes equipped with a magnetic mixer, and also while cooling the samples down to -15° C in a freezing chamber.

3. RESULTS AND DISCUSSION

CA Thermochromism in Non-Oriented Matrices

The CA compounds are a polycrystalline powder of light-yellow color. CA solutions are practically colorless and are characterized by absorption in UV with maxima near 330, 350, and 390 nm (Fig. 1a). While heating the CA solutions, their coloration into intense blue color takes place, and the additional band in the visible range of the spectra with maximum near $\lambda=580$ nm appears in the absorption spectrum. In the UV-range of the spectra, the intensification of a band at $\lambda=330$ nm and a decrease of the absorption at $\lambda=390$ nm are observed hereby. The existence of the isosbestic point indicates the existence of two CA forms. The transition temperature depends on the nature of a solvent (approximately 50°C). The further cooling of CA solutions leads to their discoloration and the renewing of the initial spectra. The process can be repeated many times.

The characteristics of the environment can substantially influence the balance of two CA forms. In solvents with strong basic properties (dimethylformamide), the colored merocyanine form is stabilized at room temperature, while the solution is colored in dark blue. At the further heating, the spectral characteristics of the solution demonstrate quite little changes (Fig. 1b). However, these changes completely correlate with temperature changes of the spectra of colorless CA solutions: an increase of the absorption near $\lambda = 580\,\mathrm{nm}$ and a decrease in the region of $\lambda = 390\,\mathrm{nm}$.

The preceding investigations of dyes showed [17] that the thermochromic properties are displayed by CA at its insertion into a polymer matrix. Along with that, the temperature of transition rises to 60–90°C by depending on the polymer type, while the kinetic characteristics of the transmutation of both forms are slowed down. The coloration appears not instantly. At holding the films at the transition temperature for 1–5 min, the process of coloration lasts up to 10 minutes. One of the specific features of the thermotransformations of CA in polymer matrices is the interaction of the dye with some polymers (for example,

with polyvinylchloride) at high $(>100^{\circ}C)$ temperatures accompanied with irreversible chemical processes.

The existence of two CA forms is confirmed by the thermal sputtering of substances in vacuum. The polycrystalline films obtained at an evaporator temperature of 230–240°C are of yellowish color. At higher evaporator temperatures (270°C), the films are of dark blue color, while the band with a maximum near 600 nm appears in their spectra. Unlike solutions and polymer films, the polycrystalline CA films obtained at different evaporator temperatures maintain their color unchangeable regardless further temperature changes.

CA Thermotransformations in LC

The investigations of the CA thermotransformations in liquid crystals are of peculiar interest as, in such environments, not only CA properties are dependent on the temperature, but the properties of liquid crystals as well. The CA-LC compositions as well as the solutions of these compositions in different solvents are characterized by the effect of thermochromism: along with rising the temperature, the coloration of compounds changes reversibly from yellow to dark blue. The influence of LC on intramolecular CA transformations is manifested in an increase of the temperature of transition to the colored form in comparison with that for liquid solvents. Along with that, for a number of liquid crystals of one type, the CA transition temperature increases with the temperature of the nematic – isotropic phase transition of LC. For example, the thermochromic properties are displayed at temperatures $> 50^{\circ}\text{C}$ for MBBA $(T_{N-I} = 42^{\circ}\text{C})$ but at temperatures $> 80^{\circ}\text{C}$ for EBBA ($T_{N-I} = 77^{\circ}C$). Thus, the existence of the ordering in a LC matrix restrains thermotransformations of CA. This effect correlates with the peculiarities of thermochromism of CA in hard polymer matrices and sputtered films.

Due to the substantial dispersion of light by the LC matrix and the own LC absorption in the range of CA absorption, the comparison of changes in CA absorption spectra in solvents and in LC seems to be impossible. In view of the detection of peculiarities of the thermochromic CA transformations in compositions with LC, the changes of the comparative absorption at $\lambda = 580\,\mathrm{nm}$ for the CA solution in ethanol, the CA-MBBA composition, and CA in polyvinylchloride were investigated (Fig. 2).

It was revealed that the thermotransformations of CA in ethanol are a totally reversible process: at the heating and the cooling of solutions, the changes of the transmission are practically identical. For CA-MBBA compositions, the thermotransformations of CA begin only

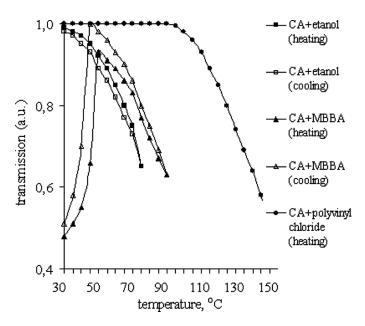


FIGURE 2 Temperature dependence of the relative transmission at 580 nm (absorption band of the merocyanine form of CA): $1 \cdot 10^{-4}$ M CA in ethanol, 2% CA in MBBA, 3% CA in polyvinylchloride.

in the isotropic phase of the liquid crystal when the factor of ordering is removed. The curve of thermochromic transmission changes of CA-MBBA compositions is shifted to the higher temperatures in comparison with those for ethanol, but completely reproduces the pace of transmission changes in a liquid solution. The thermochromic transitions in polymer films take place at still higher temperatures, but the pace of changes remains the same.

Influence of Dye Concentration

The kinetic courses of thermotransformations for CA-MBBA, CA-EBBA, and CA-ZhK-1282 compositions differ substantially. It could be logical to presume that these distinctions are concordant with the temperature of phase transition of LC, but such a correlation was not revealed. For the investigation of the process of thermotransformations, all the compositions were placed in quartz cuvettes with a thickness of 10 mm, were simultaneously heated from 25 to 100°C under the action of a magnetic mixer, and then simultaneously were cooled. The rate of the thermotransformations was estimated by the

time of appearance/disappearance of the color. For CA-MBBA $(T_{N-I}=42^{\circ}C)$ compositions at heating, the fast transition to the colored form and the slow renewing of the colorless form at cooling are observed. The kinetics of the process is opposite for CA-ZhK-1282 $(T_{N-I}=62^{\circ}C)$ compositions: the slow creation of the colored form and the fast renewing of the initial colorless state. The rate of thermotransformations in the CA-EBBA composition $(T_{N-I}=77^{\circ}C)$ takes the middle place between those for two previous compositions. It was revealed that the rate of thermotransformations of CA depends on the solubility of CA in LC: the worse the solubility of the dye in a liquid crystal, the slower the rate of thermotransformations, the less the intensity of coloration of a high-temperature solution and the faster the renewing of the colorless form of CA.

The methodology of the preparation of samples of CA-MBBA, CA-EBBA, and CA-ZhK-1282 for these investigations foresaw a surplus amount of the dye in a composition due to the disperse polycrystallites (at cooling, it partially precipitates). Consequently, the different solubilities of CA in LCs caused different actual concentrations of the dye in a liquid crystal at the nominal identical 2% amount of CA in a composition. The increase of the CA concentration in a composition was accompanied with the faster transition of molecules of CA to the colored form and with a deceleration of the inverse process.

The increase of the dye concentration in CA-LC compositions is terminated by means of the additional solution of disperse polycrystallites at every heating of the composition to a temperature higher than that of the LC phase transition. The solubility of the dye in CA-ZhK-1282 composition is insignificant, and the CA concentration in this composition practically remained the same, while those in CA-MBBA and CA-EBBA compositions increased drastically. For concentrated CA-MBBA and CA-EBBA compositions, the loss of the CA capability to renew the initial colorless form is observed. The greater the concentration of CA, the less the number of cycles of thermotransformations is observed. The balance is shifted to the stabilization of the merocyanine form, while the CA stays colored at the temperatures typical of the colorless form. Most clearly, it is displayed for CA-EBBA composition: after three cycles of heating-cooling, the merocyanine form stays stable and does not disappear at room temperature and even at a decrease of the temperature down to 5°C. The properties of EBBA and CA are changing collaterally. EBBA at the mentioned temperature stays in the liquid state, though it is a solid substance without adding the dye at room temperature. Only at the cooling of the composition down to -15° C, EBBA returns to the solid state, while CA becomes colorless. However, at increasing the temperature to room one, EBBA becomes again liquid, while CA becomes colored. Hereby at high dye concentrations in CA-EBBA compositions, the temperature of the CA transition to the colorless form shifts to the range of temperatures below zero. All these transformations concern only CA in the molecular form, while the coloration of precipitated polycrystallites stays invariable (light yellow) and corresponds to the initial coloration of the dye in all investigations.

Unlike CA-EBBA composition, only the insignificant residual darkening is observed for CA-MBBA composition after 5 cycles of thermal transitions at room temperature; while, at the heating, the intense coloration takes place again. For CA-ZhK-1282 composition, thermochromic transitions of CA are kept invariable at any number of cycles.

The formerly described effect of stabilization of the merocyanine form by analogy with the properties of liquid solvents was explained by the appliance of MBBA and EBBA to the Schiff base as well as by the basic environment which displaces the equilibrium to the CA colored form [18]. This statement cannot be considered as comprehensive, as it does not explain the following regularities: 1) the merocyanine form of CA in solvents with basic properties is created immediately at the moment of dissolution, and further changes of the temperature do not practically influence it (Fig. 1b); 2) unlike liquid solvents, there exists a low-temperature shift ($\Delta T = 80^{\circ}$ C) of the range of CA thermal transitions; 3) the changes of physical properties of an EBBA liquid crystal are observed.

The reason for the described dependences of CA thermotransformations on concentrations could be the bipolarity of the CA merocyanine form leading to the additional stabilization of the colored form due to the electrostatic interaction of molecules. In liquid organic solvents, such an influence of the concentration on the stabilization of the merocyanine form at photo- and thermointramolecular transformations is typical of bistable molecules.

The existing of ordering in a liquid crystal matrix is an additional factor of stabilization of the merocyanine form in concentrated CA-LC compositions, and this factor will be more important as the LC phase transition temperature increases. First, at increasing the temperature, the thermodynamic equilibrium is shifted to the creation of the colored CA form, and the less amount of colorless CA molecules is present in the composition. Second, at increasing the temperature of the LC transition from the isotropic state to the mesophase over the temperature typical of the thermochromic transformations of single CA molecules (50°C), the ordering of LC starts, when all CA molecules are in the colored form. And *vice versa*, if the temperature of the LC transition from the isotropic state to the mesophase is lower than the temperature of the CA

transition, the part of CA molecules already transit to the colorless form at the moment of the appearance of the LC ordering, and the concentration of the merocyanine form is not sufficient for the emergence of the described effects. The good confirmations of this mechanism are the distinctions of the thermochromic behaviors of the dye in CA-MBBA and CA-EBBA compositions containing LC of the same type. We note the difference in the temperatures of the phase transition: for EBBA, the temperature of the mesophase appearance is higher than that of the CA transformations, whereas it is less for MBBA.

On the investigation of the influence of LC on thermal transitions of CA, the following conclusion was made in [18]: the transition from chromene to the colored merocyanine form is restrained by the LC ordering, while the isotropic phase of MBBA and EBBA facilitates this transformation. As it was revealed in our investigations, the LC ordering restrains analogously the inverse transition from merocyanine to the chromene CA form and evidently is the cause of the discovered effect of a decrease of the temperatures of CA thermochromic transitions at high concentrations of the dye in LC matrices. However, the clarification of this process needs additional investigations.

Dye Crystallization in Anisotropic Environments

The performed experiments have shown not merely the LC influence on characteristics of CA, but the impact of the dye on LC properties as well, namely on the temperature of the EBBA crystallization. Additional confirmations of such an influence were revealed at researching the processes of CA self-organization in LC.

The investigation of the processes of self-organization of the dye in liquid solvents revealed that, at the evaporation of a solvent, the crystallization of CA takes place, and monocrystals of approximately 0.1 mm in size are created. A form and dimensions of monocrystals depend on a type and a rate of evaporation. For example, from the CA solution in toluene, tetrahedral crystals grow up (Fig. 3a), while flat stick-shape crystals emerge in the CA solution in acetone (Fig. 4a). The less the rate of evaporation, the greater the size of crystals.

The crystals are transparent and are of light-yellow color typical of the initial substances. A complete coloration homogeneity in crossed polarizers of the created monocrystals testifies to their high quality. Unlike CA polycrystallites which do not display thermochromic properties and sputtered films not changing their properties at changes of the temperature, the monocrystals become colored at increasing the temperature to 80°C, while returning to the colorless form at the cooling.

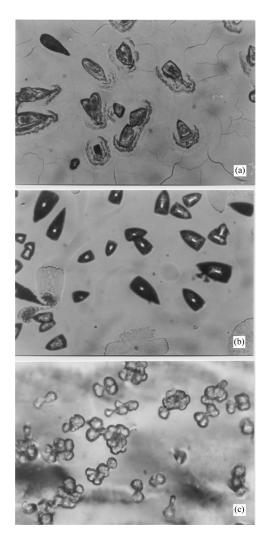


FIGURE 3 Formation of CA crystals from a solution of CA in toluene (a,b) and from CA-ZLI-4387-toluene composition (c); $a,c-25^{\circ}C, b-80^{\circ}C$.

CA Self-Organization in LC

On studying the influence of LC on the self-organization of a dye with the purpose to avoid uncontrolled admixtures of CA polycrystallites, the homogeneous molecular CA compositions in ZLI-3145 and ZLI-4387 liquid crystals were prepared by the above-mentioned methodology. Two-component CA-LC compositions

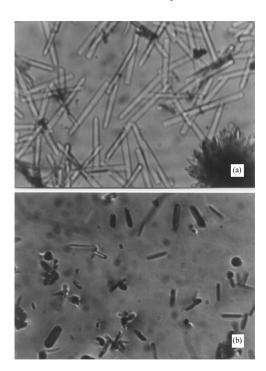


FIGURE 4 Formation of CA crystals from a solution of CA in acetone (a) and from CA-ZLI-3145-acetone composition (b).

as well as three-component CA-LC-solvent compositions display thermochromic properties.

On covering the surface of a glass plate after the evaporation of a solvent by a homogeneous three-component CA-LC-solvent composition, the crystallites of 0.1 mm in size were created. These crystallites fall out from the liquid crystal on the surface of a plate. Herewith, the form of crystals and their size depend on the concentration of components, type of a solvent, and rate of its evaporation. The form of crystals in comparison with that for the CA solution in a pure solvent is totally different.

On the evaporation of the solvent from CA-ZLI-4387-toluene, crystals of the barbell shape (Fig. 3c) are created. But, without LC, the tetrahedral crystals are created (Fig. 3a). The existence of several forms of crystals can be due to the influence of environment, the existence of two stable CA forms, or the incorporation of molecules of a solvent into the crystal. In order to clarify how the factor of ordering of the environment influences the self-organization of CA, the crystal

of ZLI-3145 with a wide area where the mesophase exists (from -40° C to $+94^{\circ}$ C) was used. It is apparent that the domination of the factor of ordering of the environment leads to the creation of identical small stick-shape crystals from CA-ZLI-3145-toluene composition, as well as from CA-ZLI-3145-acetone composition (Fig. 4b). Hence, the ordering of the environment restrains the self-organization of dyes. This conclusion was confirmed while investigating two-component CA-LC compositions, where the influence of a solvent is completely levelled.

Two-component CA-ZLI-3145 and CA-ZLI-3145 compositions are created via the evaporation of a solvent from the three-component composition or via the extraction of the dye from a solvent. The characteristics of these compositions substantially depend on the dye concentration, which can be modified and controlled strictly by the methodology mentioned above. For the concentration of CA in LC lower than 10^{-4} M after the covering of the composition on the surface of a glass plate, the homogeneous layers are created. At increasing the concentration, the dye crystallization takes place, but the sizes of crystals are far less than those in the case of three-component compositions.

Modification of LC Characteristics

While researching two-component compositions, both the influence on the self-organization of CA and the inverse influence of the dye on the characteristics of LC at concentrations in the range of $2\cdot 10^{-5}\,M-4\cdot 10^{-3}\,M$ have been revealed. A 20-µl drop of CA-ZLI-3145 composition was dripped on a non-oriented glass plate, and it was covered with another glass. The thickness of the film was 1 µm.

At high concentrations of CA $(4\cdot 10^{-3}\,\mathrm{M}-4\cdot 10^{-4}\,\mathrm{M})$, the sample includes a huge number of small crystals. The texture of a recently prepared sample is not evinced. At the heating of a sample to $100^{\circ}\mathrm{C}$, the crystals partially dissolve, and the marbled texture appears. The texture is created at the place of dripping the drop and gradually expands centrifugally. The greater the concentration, the more the crystals are in the initial sample, and the better the formed texture is observed. At a decrease of the concentration to $2\cdot 10^{-4}\,\mathrm{M}-1\cdot 10^{-4}\,\mathrm{M}$, M, no crystals are formed, and, after the heating, the texture is formed only at the place of dripping. At the further decrease of the concentration $(4\cdot 10^{-5}\,\mathrm{M})$, the texture is formed after the heating only at the place of dripping for a short period of time and then disappears. For the greatly diluted CA-ZLI-3145 composition $(2\cdot 10^{-5}\,\mathrm{M})$, the

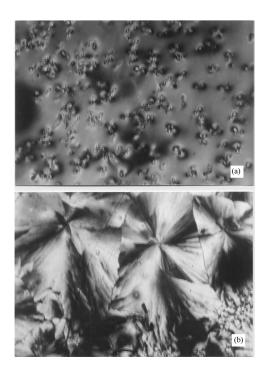


FIGURE 5 Formation of a texture of LC: initial CA-ZLI-4387 composition (from toluene) (a) and CA-ZLI-4387 composition (from toluene) after heating and cooling.

texture is not appeared even at the heating. Analogous regularities are observed for CA-ZLI-4387 composition, though the type of a texture is different: it is fan-shaped (Fig. 5).

Thus, the orienting influence of CA on LC at high concentrations of CA is experimentally observed. The reason for the revealed formation of a texture of LC on the non-oriented surface can be the creation of a thin film of the dye on the plate, which sets the orientation of LC. The formation of such a film on the plate at the creation of crystals from highly concentrated CA-ZLI-4387 compositions is clearly seen in Figure 3. Though, taking into account the factor of the creation of a texture only after the heating of a composition and only at large concentrations of the dye, it can be suggested that a mechanism of the influence of CA on the creation of a texture of LC is the same as that revealed on studying the thermochromic transformations of CA in LC matrices.

CONCLUSIONS

In the present work, the processes of intramolecular thermochromic transformations and intermolecular self-organization of bistable chromeno[2,3-q]acridines (CA) in liquid crystal matrices with different ratios of components have been investigated. The properties of the dye existing in two forms (colorless chromene form and colored merocyanine form), as well as the characteristics of liquid crystals such as the existence of orderings, depend on the temperature. Thus, the features of the interaction of a dye and a matrix in different temperature ranges are substantially different, which presents the additional factor allowing our to influence their properties.

It has been revealed that thermochromic properties of CA and LC matrices depend not only on the temperature, but also on the ratio of components in the CA-LC composition as well. The thermochromic properties are drastically changed at large concentrations of the dye.

At small concentrations of the dye, the influence of the ordering of LC on the thermochromic CA transformations evinces in an increase of the temperature of transition from the chromene to the merocyanine form in comparison with that for liquid solvents. For a number of LCs of the same type (MBBA, EBBA), the temperature of transition of CA increases with the temperature of the nematic – isotropic LC transition. The CA thermal transitions are completely reversible, and the influence of LC on them is not revealed. Hence, the existence of an ordering in the LC matrix plays the role of a stimulator for the thermotransformation of the colorless form of CA to the colored form. This effect correlates with the peculiarities of the CA thermochromism in solid polymer matrices.

At large CA concentrations, the ordering of LC restrains the reversible transition from the merocyanine form to the chromene CA form. The thermochromic equilibrium shifts to the stabilization of the merocyanine form, and CA stays colored at temperatures typical of the colorless form. The temperature of the thermochromic transitions reduces below zero, and $\Delta T = 80^{\circ}\mathrm{C}$ for CA-EBBA compositions. The reason for such an effect involves several factors: 1) ordering of the LC matrix (the higher the LC phase transition temperature, the more important is this factor); 2) bipolarity of the merocyanine form, which leads to the appearance of an additional stabilization of the colored form due to the electrostatic interaction of molecules in the concentrated solutions; 3) the basic properties of EBBA (Schiff base) fostering a shift of the equilibrium to the colored CA form. The clarification of that mechanism needs additional investigations.

It was also revealed that the ordering of LC matrices impedes the processes of intermolecular self-organization of CA and causes a modification of the form and a decrease of the size of crystals of the dye.

The executed experiments have revealed that, at large concentrations of the dye, not merely LC influences CA characteristics, but the dye influences LC properties as well, which is manifested in both the modification of physical characteristics of LC (for example, a reduction of the EBBA crystallization temperature) and the orienting influence of the dye on LC (for example, the appearance of a texture in CA-ZLI-3145 and CA-ZLI-4387 compositions).

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