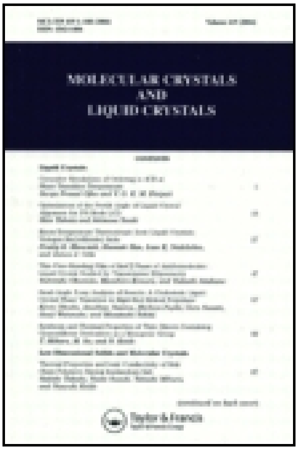

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On the Physicochemical Properties of New Liquid-Crystalline Compositions Exhibiting the Smectic A Phase

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ON THE PHYSICO-CHEMICAL PROPERTIES OF NEW LIQUID-CRYSTALLINE COMPOSITIONS EXHIBITING THE SMECTIC A PHASE

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Abstract The results of some investigations of the physico-chemical properties of smectic-nematic mixtures are reported. Liquid crystalline composition is obtained exhibiting the smectic A phase in a wide temperature range, including room temperatures. The dielectric susceptibility $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, the dielectric anisotropy $\Delta\varepsilon$ (1kHz), the specific conductivities $\sigma_{\parallel}$, $\sigma_{\perp}$ (1kHz), threshold voltage values and the elastic constants of $\bar{B}$.K for the obtained mixtures in the smectic A phase temperature interval are measured. It is determined that the smectic A phase has a negative dielectric anisotropy for all obtained mixtures. The given results show that a mixture of smectic liquid crystals with a nematic can be used to vary their general parameters and to obtain compositions which can be well utilized for a particular application.

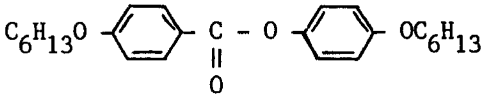
There is a great interest in the smectic liquid crystals due to the following factors. First, the unique layered structure of the smectics permits the observation of peculiar physical phenomena[1,2]. Second, some of these effects which occur under an electric field can be applied with a great success in the display technique. The electrooptic effects in the smectic A depend strongly on the sign of the dielectric anisotropy $\Delta\varepsilon$ ($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$), where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric components parallel and perpendicular to the liquid crystal molecules.

At present the scientific literature gives structural formulae of the liquid crystals exhibiting a smectic A phase at room temperatures and with positive dielectric anisotropy[3,4,5]. The smectic A with negative dielectric anisotropy described until now elsewhere have a high-temperature smectic A phase existence[6,7]. This limits their wide application, and makes difficult the detailed study of their properties.

In this paper we describe our way of obtaining of a liquid crystal composition with a smectic A phase within a wide temperature range including room temperatures and we report the results of the measurements of some of their physico-chemical properties.

In order to prepare suitable mixtures we use liquid crystal of 4-n-hexyloxyphenyl-ethyl-4^1-n-hexyloxybenzoate which exhibits a smectic A phase at a high temperature, and has the following structural formula:

A.

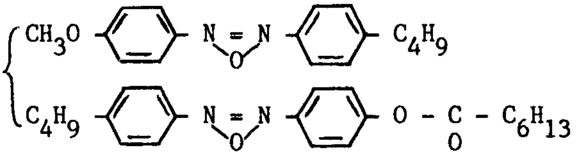


$$C \underset{29^{\circ}C}{\overset{36^{\circ}C}{\rightleftharpoons}} S_A \underset{71^{\circ}C}{\overset{71^{\circ}C}{\rightleftharpoons}} I$$

The liquid crystal molecules have two transversal dipole moments with fragments - NO_2 and C=O (2.3 D). Those two enhance the lateral interaction of the molecules and favor the formation of the smectic phase. The dielectric anisotropy of substance A is high and in the middle of the smectic A phase temperature range is $\Delta\varepsilon = -8.5$.

In order to diminish the phase transition temperatures the given liquid crystal was doped by a low-temperature nematic, which is a mixture of two substances:

B.



66.7%

33.3%

The phase transition temperatures of this binary mixture are the following:

$$C \xleftrightarrow{-15^{o}C} N \xleftrightarrow{75^{o}C} I$$

Fig.1 shows a phase diagram of the mixtures of A and B liquid crystals. It is shown in the Figure that as soon as

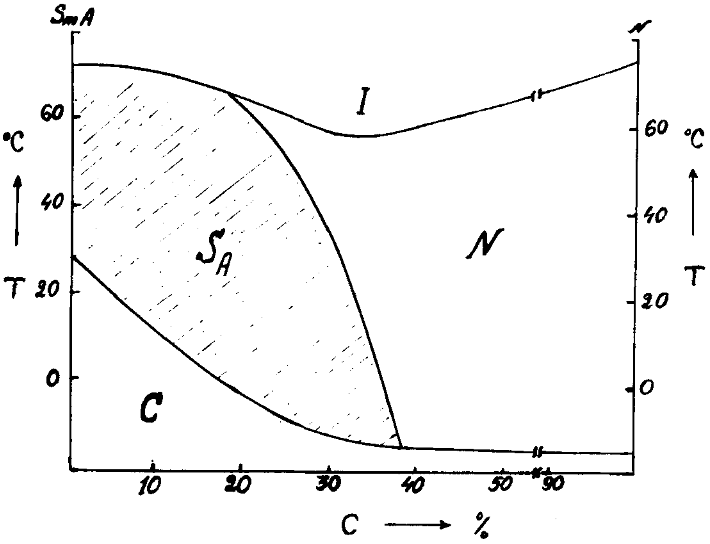


FIGURE 1. The phase diagram of A + B liquid crystal mixtures.

the amount of B in the mixture increases, the temperature range of the smectic A phase shifts to the low-temperature region and for C≥7% it passes the room temperatures. The temperature interval of the S_A phase is sufficiently wide and the given mixtures can be recommended as a working medium of electrooptic devices. It is important to note that mixtures can be used manifesting phase transitions both of the first-order S_A-I (0<C<18%), and of the second order S_A-N (20<C<38%). Further on, the characteristics of the prepared triple mixture were studied. In Figure 2 dielectric anisotropy temperature dependence of the mixture with the ratio 70:30 (A:B) is shown. Δε was measured by an a.c. bridge. The effective area and the cell thickness were equal to S=0.4 and d=7 μm, respectively. ε was measured with high accuracy. The liquid crystal had an homeotropic orientation obtained through the cooling from the nematic phase, which allowed us to measure ε in the direction of the long axis of molecules ($\varepsilon_{\parallel}$).

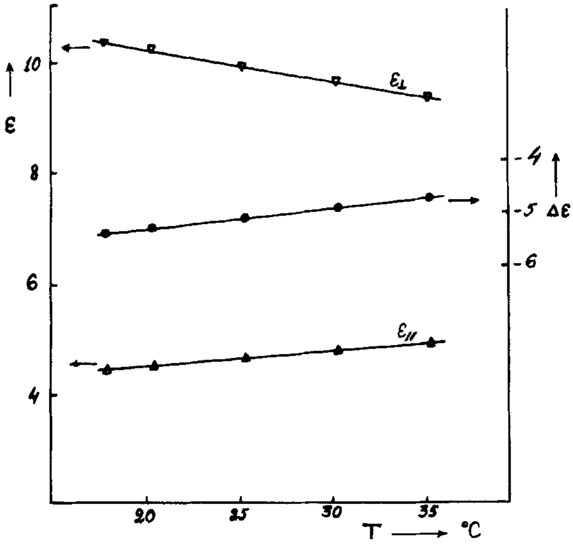


FIGURE 2. The dielectric anisotropy temperature dependence for 30% mixture.

In order to measure $\varepsilon_{\perp}$ a high quality planar texture was obtained through the homeotropic planar transition[6,7].

It is shown in Figure 2 that $\varepsilon_{\perp}$ decreases with the increasing of the temperature while $\varepsilon_{\parallel}$ increases at the same time. As a result the dielectric anisotropy $|\Delta\varepsilon| = |\varepsilon_{\parallel} - \varepsilon_{\perp}|$ decreases. Fig.3 shows the dependence of $\Delta\varepsilon$ on the temperature both for the pure substance and the mixtures having different concentration of B.

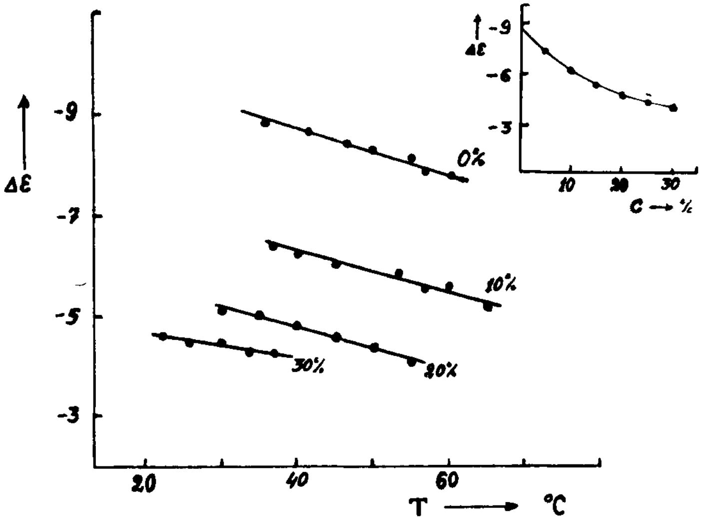


FIGURE 3. The dielectric anisotropy ($\Delta\varepsilon$) temperature dependence of mixtures. The concentration dependence of $\Delta\varepsilon$ is presented in the insertion.

It is seen on the same Figure that for all studied mixtures $|\Delta\varepsilon|$ decreases with the increasing of the temperature. $|\Delta\varepsilon|$ decreases also with the increasing of concentration of B substance (the insertion in the Fig.3). For the mixture with a ratio of (70:30) $\Delta\varepsilon$ takes a value of $\Delta\varepsilon$=-5.5 which is sufficiently large for a dielectric moment of

$\simeq\Delta\varepsilon E^2$. Both the threshold voltage of the electrooptic effects and ε and $\Delta\varepsilon$ depend on the electroconductivity and on the anisotropy. The electroconductivity was measured with a bridge at a frequency f=1kHz (Fig.4). It is known that

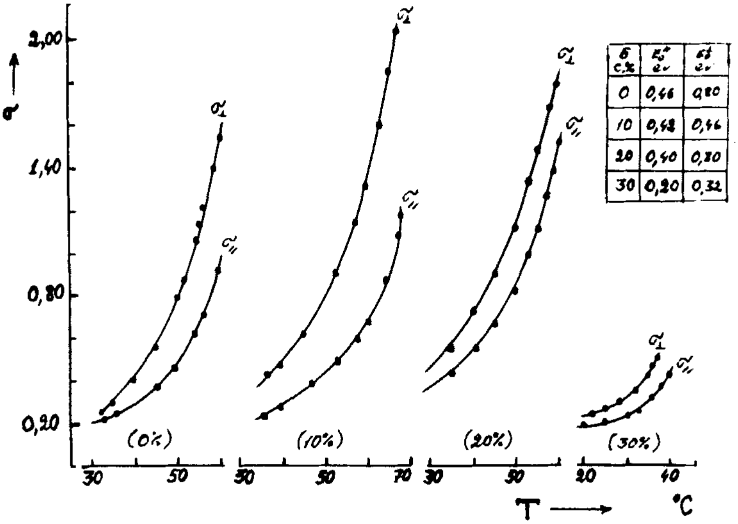


FIGURE 4. The electroconductivity temperature dependence at f=1kHz. The values of the electroconductivity activation energies are shown in the insertion.

both for the homeotropic ($\sigma_{\parallel}$) and the planar ($\sigma_{\perp}$) textures electroconductivity temperature dependences satisfy the Arrenius law $\sigma=\sigma_o e^{(-E_o/kT)}$. In the insertion in Fig.4 four values of the electroconductivity and the connected with it activation energy E are given for different mixtures. The obtained experimental results show that $\varepsilon_{\perp}$ differs for the homeotropic texture and for the planar texture, $E_o^p > E_o^h$. Moreover, the activation energy decreases with the increase of the concentration of B for both textures.

Fig.5 shows the electroconductivity anisotropy $\sigma_{\perp}/\sigma_{\parallel}$

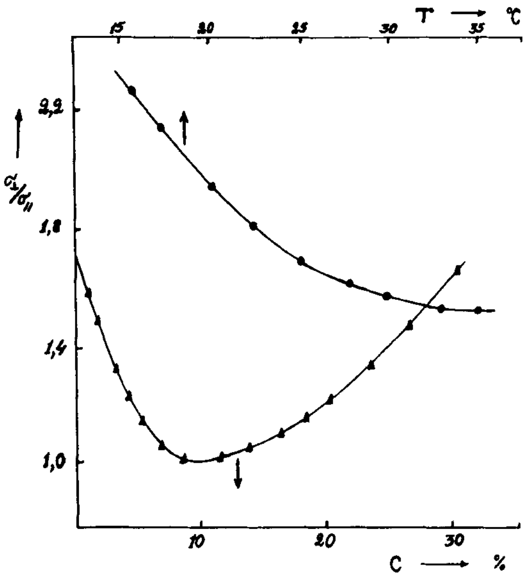


FIGURE 5. Temperature and concentration dependence of the electroconductivity for 30% mixtures.

dependence on the temperature and on the concentration for the 30% mixture. It is shown in the Figure that $\sigma_{\perp}/\sigma_{\parallel}$ decreases monotonously when increasing the temperature.

It is seen from Fig.5 that the minimal values of the electroconductivity anisotropy are reached for the 8% concentration of the nematic. All prepared mixtures have negative dielectric anisotropy. That is why the observed general electrooptic effect is a homeotropic-planar transition.

The threshold voltage U_{th}^{h-p} of this transition depends strongly on the temperature and decreases with its increasing (Fig.6). The concentration dependence of U_{th}^{h-p} draws attention:

First the threshold increases with the increasing of B, then it decreases monotonously (see the insertion in Fig.6).

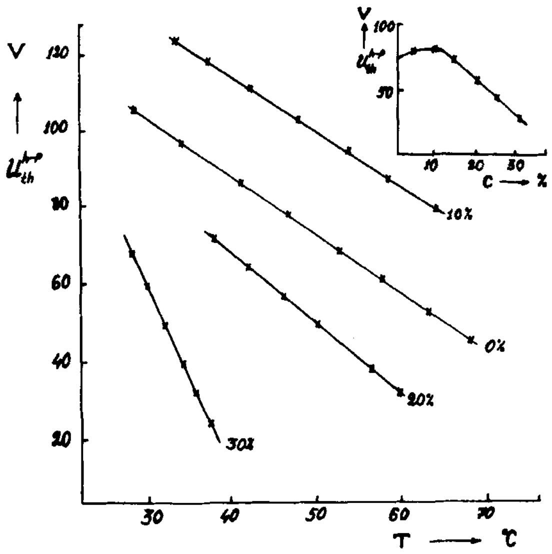


FIGURE 6. Dependence of the homeotropic-planar transition voltage on the temperature.

It has recently been established[7], that the homeotropic-planar transition mechanism can be described by the Geurst-Gussens' theory, according to which the effective threshold is expressed through the equation[8]:

$$E_n^2 = 2q^2K_{11}\,\frac{\varepsilon_\perp}{\varepsilon_\parallel(\sigma_\perp-\sigma_\parallel)\hat{\tau}}\,\frac{1+\omega^2\hat{\tau}^2}{1-\omega^2\hat{\tau}\hat{\tau}_\alpha} \tag{1}$$

The effective threshold is determined by such material parameters as ε, $\Delta\varepsilon$, σ, $\sigma_\perp/\sigma_\parallel$, $\bar{B}.K$. $\bar{B}.K$ is a product of the smectic A elastic constants and it characterizes a system's rigidity. The equation (1) allows for $\bar{B}.K$ to be determined using known expressions for ε, $\Delta\varepsilon$, σ, $\sigma_\perp/\sigma_\parallel$ and U_{th}^{h-p}. Fig.7 shows that the elastic constants of the mixture decrease significantly when the A liquid crystal nematic concentration increases.

This fact is an effective tool for the regulation of the smectic A liquid crystal parameters. The results help to explain the dependence of the threshold voltage of the homeotropic-planar transition on the concentration, and the monotonous decrease of $|\Delta\varepsilon|$ and $\bar{B}$.K with the increasing of the B concentration. The former increases the threshold and the latter decreases it.

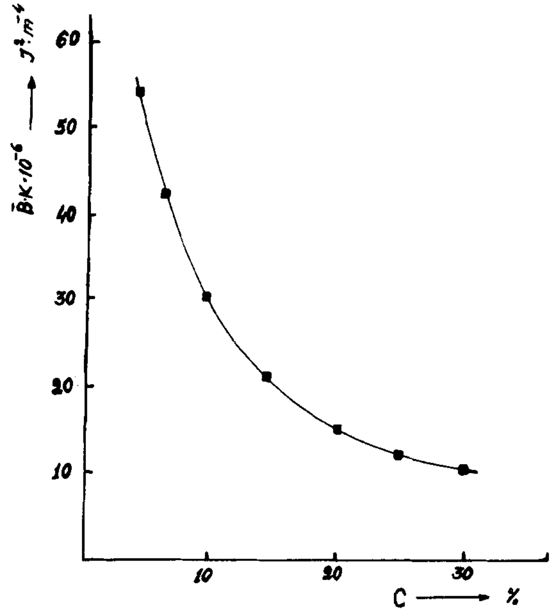


FIGURE 7. The dependence of the smectic A elastic constant on the nematic concentration.

Moreover, the threshold depends strongly on $\sigma_{\perp}/\sigma_{\parallel}$ and decreases with its increasing. That is why the whole concentration influence on the threshold is determined by the competition of different factors. The threshold maximum value observed at C≈8% (Fig.6), is correlated with the fact that the anisotropy takes a minimal value for the same concentration (see the Fig.5). When the concentration is further increased, $\bar{B}$.K changes as compared to the changes of

$\Delta\varepsilon$ and $\sigma_{\perp}/\sigma_{\parallel}$, (Fig.7), and which determines the further decrease (Fig.6).

The obtained results, thus, show that the smectic liquid crystals mix with the nematics, and this mixtures allows us to vary their general parameters and to obtain compositions which can be utilized for a practical application.

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