EXPERIMENTAL STUDY OF THE TEMPERATURE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY OF CERTAIN NEMATIC LIQUID CRYSTALS AND THEIR MIXTURES

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Results of an experimental study are presented pertaining to the temperature dependence of the magnetic susceptibility of three different nematic liquid crystals and two different mixtures of these crystals, in either the isotropic state or in the mesophase. For the substances in the mesophase, moreover, this dependence is also described by analytical expressions.

The magnetic susceptibility of mixtures can, according to Wiedeman's additive law, be expressed by the relation

$$X = X_1 P_1 + X_2 P_2 + \cdots + X_k P_k, \tag{1}$$

where X is the magnetic susceptibility of the mixture and X_k are those of the components, with P_k denoting the weight fractions of the respective components. This law has been verified more than once and found to be exactly true for mechanical mixtures, according to Selwood [1], any departures from linearity being due to chemical or physical changes. Studying the magnetic properties of nematic liquid crystals and their mixtures should, therefore, help reveal whether or not such changes have occurred.

Already available data on the magnetic susceptibility in the isotropic state and in the mesophases, on the assumption that the mean magnetic susceptibility in the mesophase is equal to the magnetic susceptibility in the isotropic state and that the molecules are similar in shape, can be used for calculating the anisotropy of magnetic susceptibility in the mesophase [2, 3]

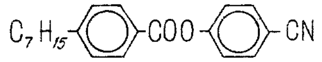
$$\Delta X = 3/2\,(X_{\parallel} - \bar{X}), \tag{2}$$

where $\bar{X}$ is the magnetic susceptibility in the isotropic state and $X_{\parallel}$ is the magnetic susceptibility in the mesophase with molecules oriented parallel to the magnetic field. With the anisotropy of magnetic susceptibility (ΔX_0) in a single crystal known, the degree of ordering can be calculated according to the relation [2, 3]

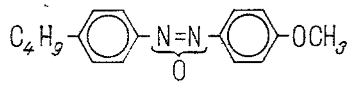
$$S = \Delta X / \Delta X_0. \tag{3}$$

This quantity is one of the most important parameters characterizing a nematic liquid crystal and counts in several theories of the liquid-crystal state [4].

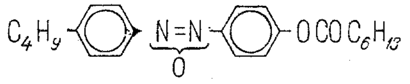
This study deals with the temperature dependence of the magnetic susceptibility in the mesophase and in the isotropic state, under consideration being the three nematic liquid crystals



(ZhK-489),



(ZhK-434),



(ZhK-439),

and their mixtures

$$\text{ZhK-400} = \begin{cases} 2/3 \text{ wt. fraction of ZhK-434} \\ 1/3 \text{ wt. fraction of ZhK-439} \end{cases}$$

or the ternary mixture of 88% ZhK-440 + 12% ZhK-489.

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TABLE 1. Nematic-to-Isotropic Transition Temperatures and Magnetic Susceptibility in the Isotropic State of the Test Substances

Substance	ZhK-489	ZhK-434	ZhK-439	ZhK-440	Ternary mixture
T_t, °C	56,6	74,8	80,4	73,1	70,4
$-\bar{X}\cdot 10^6$ cm^3/g,	0,6496	0,6240	0,6404	0,6287	0,6310

The magnetic susceptibility was measured by the relative (Gouy) method, in the test stand and according to the procedure described in earlier reports [5, 6]. Deaerated and twice-distilled water served as the reference substance. Its magnetic susceptibility at 20°C was taken as equal to $0.720\cdot 10^{-6}$ cm^3/g. A double-wall glass beaker with a heat carrier fluid pumped between the walls by a thermostat served as the thermostatic vessel. The temperature was checked precisely within 0.05°C. The relative error in a determination of the magnetic susceptibility was within 0.2-0.5%. A test tube was filled with a specimen of liquid-crystal substance under vacuum. The temperature dependence of the density of the substance, a necessary relation needed for calculation of its magnetic susceptibility, had been determined in an earlier study [7].

Measurements were made beginning at 5-10°C above the nematic-to-isotropic transition point and ending at room temperature or at the crystallization point. The temperatures T_t of transition from isotropic to nematic state and from nematic to isotropic state were then determined from the readings, also visually verified, and found to almost agree with earlier data [7]. The substances in this study were diamagnetic, their magnetic susceptibility in the isotropic state remaining within 0.1-0.2% independent of the temperature. The magnitudes of their magnetic susceptibility in the isotropic state as well as their nematic-to-isotropic transition temperatures are given in Table 1.

A jump of magnetic susceptibility occurs as these substances pass from the isotropic to the nematic state. With these substances in the mesophase, the absolute value of their magnetic susceptibility decreases monotonically with decreasing temperature.

The experimental data on the magnetic susceptibility in the mesophase have been evaluated by the least-squares method, with the aid of a computer, and the following analytical expressions have been obtained as a result:

$$X_{\parallel} = (-0.620 + 0.0153\,\tau^{0.284})\cdot 10^{-6}\ \mathrm{cm^3/g}\ (\mathrm{ZhK\text{-}489}),$$

$$X_{\parallel} = (-0.599 + 0.0252\,\tau^{0.251})\cdot 10^{-6}\ \mathrm{cm^3/g}\ (\mathrm{ZhK\text{-}434}),$$

$$X_{\parallel} = (-0.615 + 0.0154\,\tau^{0.316})\cdot 10^{-6}\ \mathrm{cm^3/g}\ (\mathrm{ZhK\text{-}439}),$$

$$X_{\parallel} = (-0.600 + 0.0176\,\tau^{0.308})\cdot 10^{-6}\ \mathrm{cm^3/g}\ (\mathrm{ZhK\text{-}440}),$$

$$X_{\parallel} = (-0.610 + 0.0220\,\tau^{0.271})\cdot 10^{-6}\ \mathrm{cm^3/g}\ (\text{ternary mixture}),$$

$$\tau = T_t - T.$$

The calculated values, according to these expressions, do not deviate from measured values by more than 0.1-0.2%. The extrapolated values of $X_{\parallel}$ at $\tau = 0$ are slightly lower than those obtained by measurement in the isotropic state, which corresponds to the jump of magnetic susceptibility during nematic-to-isotropic transition. From expression (2) are easily derived analogous expressions for the anisotropy of magnetic susceptibility. Unavailability of experimental data on the anisotropy of magnetic susceptibility in single crystals of the substances in this study makes it impossible to calculate the degree of ordering. On the basis of experimental data pertaining to compounds which do not form a mesophase [8], however, one can assume for our substances here that ΔX_0 is the same in each case and equal to the anisotropy of one benzene ring ($60\cdot 10^{-6}$ cm^3/mole). This value agrees with the experimentally determined anisotropy of magnetic susceptibility in a single crystal of n-azoxyanisole [9]. The temperature dependence of the degree of ordering, calculated on the basis of this assumption for our test substances here, is shown in Fig. 1. As the temperature decreases, the degree of ordering increases. It increases somewhat slower in the case of ZhK-489 than for all the other liquid crystals. This could be due to differences between the respective end groups as well as center groups in molecules of these substances. The degree of ordering in the ternary mixture near the T_t temperature is lowest of all and indicates that the additive law does not apply here.

The magnetic susceptibility of the binary mixture and of the ternary mixture in the isotropic state, calculated according to expression (1), is, respectively, $-0.6295\cdot 10^{-6}$ and $-0.6319\cdot 10^{-6}$ cm^3/g, which agrees closely with its experimentally determined values (Table 1). When calculating the magnetic susceptibility in

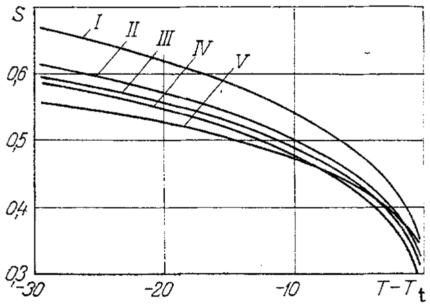

Fig. 1. Temperature dependence of the degree of ordering: I) ZhK-439; II) ZhK-440; III) ZhK-434; IV) ternary mixture; V) ZhK-489.

the mesophase according to expression (1), one must use the values of X_k at a definite temperature, inasmuch as X_k of each component varies with the temperature. The jumps of magnetic susceptibility during nematic-to-isotropic transition and the different transition temperatures for each of our substances provide clear evidence that the additive law does not hold true in the mesophase. Molecules of ZhK-434 and of ZhK-439 in our binary mixture at temperatures above the transition point for the latter do not have an orientational long-range order, e.g., although each of the components separately forms a mesophase at temperatures slightly above the transition point. The situation is analogous in the case of our ternary mixture. Calculation of the magnetic susceptibility at $\tau = T_t - T$ according to expression (1) indicates that, as long as $\tau > 0.2$, the additive law holds true for our binary mixture in the mesophase. Consequently, the degree of ordering can then also be calculated on the basis of the additive law. Our ternary mixture departs from the additive law, the discrepancy decreasing with lower temperatures and remaining within the limits of experimental error at $\tau > 14$ (which corresponds to the difference between the phase transition points of the mixture and of ZhK-489, respectively). An apparent explanation for this can be that molecules of ZhK-489 in the mixture at $\tau < 14$, although they are oriented by molecules of other components, are prevented by thermal motion from attaining the same degree of ordering as in ZhK-489 alone at the same τ. It thus appears that in a mixture with the nematic-to-isotropic transition point below those of its components the degree of ordering complies with the additive law. When the transition point of the mixture is above the transition point of any one of its components, however, then the additive law does not hold true.

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