Optical properties of the isotropic phase of a liquid crystal in pores


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Investigations were made of the temperature and angular dependences of the intensity of light scattered in the isotropic phase of a liquid crystal impregnating the pores (of typical size $10^3 \, \text{Å}$) in a silicate matrix with a volume porosity 0.38. The intensity of light scattered in this system could not be described (in contrast to a system formed by an isotropic nonmesogenic liquid–porous matrix) by a sum of the intensities representing double scattering, intrinsic scattering by the matrix, scattering because of the difference between the refractive indices of the substance filling the pores and the matrix material, and scattering by fluctuations of the density and order parameter of the liquid crystal. The presence of an excess scattering amounting to 45% of the total scattered-light intensity, its dependence on the wave number, and the temperature dependences were explained on the basis of a single assumption that at temperatures above a certain critical value the liquid crystal in the pores was a pseudobinary medium with an anisotropic layer at the pore walls formed as a result of oriented wetting. The scattering properties of this layer differed from those in the rest of the liquid crystal because of the scattering of light on fluctuations of the local director and because of an anisotropy of the refractive index, both of which were absent from the bulk isotropic phase.

Investigations of condensed media in porous matrices have revealed various new properties and effects not observed in the same media when they are in a free state.\textsuperscript{1,2} The spatial confinement and the existence of a highly developed interphase surface have the strongest influence on phase transitions. It is manifested by a shift and broadening of the temperature of the main phase transitions, and can also be useful in practical applications of disperse liquid crystals.

We investigated the temperature and angular dependences of the polarized component of the intensity of light scattered in the isotropic phase of cholesteryl oleate (which is a cholesteric liquid crystal with the transition to the isotropic phase in the free state at $T = 35 \, ^\circ\text{C}$) introduced into a macroporous silicate glass matrix. The scattering of light in the isotropic phase of free cholesteryl oleate had been investigated earlier.\textsuperscript{3} This liquid crystal was selected because the refractive index $n$ of cholesterics in the isotropic phase is closer to the refractive index $n_e$ of the matrix material than in the case of other liquid crystals. The similarity of the refractive indices of the substance filling the pores and the matrix material makes it possible to minimize the scattering of light due to the difference between $n$ and $n_e$, as observed for any two-component heterogeneous system with different refractive indices of the components.

Our porous glass matrices were formed by through leaching of the sodium borate component from the original sodium borosilicate glass by a method described in Ref. 11. The average size of the pores ($r$) and their volume fraction $\omega$, determined by the method of low-angle x-ray scattering,\textsuperscript{12} were $r = 1000 \, \text{Å}$, $\omega = 0.38$.

Our measurements were carried out on a cylindrical sample 0.3 cm in diameter and 3 cm high; this sample was placed inside a cylindrical cell made of fused quartz (diameter 1.2 cm and height 5 cm), in such a way that the cell and sample were coaxial.

The matrix was impregnated by the investigated material employing a technology which minimized the volume that was not filled by the cholesteric liquid crystal. The matrix was placed in a narrow trough containing a liquid crystal and was kept at $T = 65 \, ^\circ\text{C}$ for 24 h. The area of the contact...
I, ignore the molecular scattering, cholesteric liquid crystal and macroporous glass we could in the investigated system and the corresponding intensity \( I \), scattered in the isotropic phase of the investigated cholesteric in its free state, because sum from the phase transition point in a system comprising a Eq. I,1 was found by measuring the intensity \( I \) of light scattered in the investigated system and the corresponding intensity \( I \), scattered in the isotropic phase of the investigated cholesteric in its free state, because \( I \) was governed by the sum \( I + I \). In the temperature range 45–55°C the experimental results indicated that \( I/I \), negligible compared with the total intensity \( I \), i.e., there was a strong excess scattering \( SI = 0.45I \) ignored in Eq. (1). Consequently, when the scattering angle was \( \theta = 90° \) the scattering of light in the cholesteric liquid crystal–matrix system could not be described by the above assumption of additivity of the contributions to the total intensity. Earlier investigations demonstrated that when the refractive indices of the isotropic liquid filling the pores of a macroporous matrix and of the matrix material itself were equal, the dependence \( I(q) \), where

\[
q = \left( \frac{\pi n \sin \theta}{\lambda} \right) \frac{1}{\lambda},
\]

obtained for our macroporous glass–isotropic nonmesogenic liquid system revealed that the scattered-light intensity depended strongly on the modulus of the scattering vector \( q \) and had a broad maximum at \( q = 2.7 \times 10^4 \text{ cm}^{-1} \). Therefore, in order to determine whether the excess intensity \( SI \) exhibited by the liquid crystal–matrix system was due to the difference between the dependences \( I(q) \) for the liquid crystal–matrix and toluene–matrix systems, we had to study the scattering indicatrices of these two systems for the same values of \( \Delta n \). The \( I(q) \) dependences with allowance for the double scattering and assuming that \( \Delta n = 0.026 \) were determined and are shown in Fig. 1 (curves 1 and 2). Clearly, these dependences were of the same shape and this shape was identical with that of the curve described by a correlation function governing the structure of the matrix. It is clear from Fig. 1 that the excess scattering \( SI \) was observed for all values of \( q \) (curve 3) and that \( SI(q) \) was similar in shape to the dependences 1 and 2. Two main features of the scattering of light by the liquid crystal–matrix system were the excess scattering \( SI \) and the dependence \( SI(q) \), and they could be both explained by the following assumption. We assumed that a surface layer with its scatterings of the total intensity of light scattered in the toluene–matrix system to find the sum \( I + I \) equal in this case to the sums of all the contributions in the cholesteric–matrix system. This value was found to be 30% of the total intensity \( I \) in the liquid crystal–matrix system.

We found thus that a system comprising a cholesteric liquid crystal and a porous matrix was characterized by the following values deduced from our experiments: \( S_{1} = 0.52I \), \( I + I \), and the sum \( I + I \) negligible compared with the total intensity \( I \), i.e., there was a strong excess scattering \( SI = 0.45I \) ignored in Eq. (1). Consequently, when the scattering angle was \( \theta = 90° \) the scattering of light in the cholesteric liquid crystal–matrix system could not be described by the above assumption of additivity of the contributions to the total intensity. Earlier investigations demonstrated that when the refractive indices of the isotropic liquid filling the pores of a macroporous matrix and of the matrix material itself were equal, the dependence \( I(q) \), where

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The nature of the orienting properties differing from the properties of the bulk cholesteric liquid crystal in pores; 2) toluene in pores. FIG. 2. a) Dependence of the scattered-light intensity on $\Delta n$: 1) scattered-light intensity obtained for toluene in pores in a wide range of and by the structure of the matrix, which determined the longing to different pores were governed by the pore shape and by the structure of the matrix, which determined the nature of the $\Delta n$ dependence.

The hypothesis of a layer appearing at the interface between glass and liquid crystal, i.e., at the pore walls, was supported by the temperature dependence of the scattered-light intensity. We plotted in Fig. 2a the dependences of the scattered-light intensity for the investigated systems on the temperature dependence of the $\Delta n$. $I$ was practically independent of temperature in the investigated range $\Delta T$.

The appearance of such a layer and the difference between its properties and those of the bulk liquid crystal were due to the orienting influence of the solid surfaces of the pores, which (at distances of $-10^2$ Å) resulted in an anisotropy and surface ordering of a cholesteric liquid crystal even at temperatures corresponding to the isotropic phase of a free liquid crystal. Therefore, the distinct scattering properties of the surface layer of the cholesteric liquid crystal were not only due to a change in the refractive index because of the orientation of the molecules by the surface, but also due to an additional mechanism in the form of fluctuations of the local director, governing the preferential orientation of the molecules imposed by the pore walls.

We thus found that the absence of the $I( T)$ dependence, together with the existence and nature of the dependence $I(q)$, suggested the existence (at temperatures corresponding to the isotropic phase of a free cholesteric) of an orientationally ordered surface layer, which governed largely the optical properties of the liquid crystal inside the pores.

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Note added in proof (April 2, 1991): F. M. Aliev [JETP Lett. 41, 314 (1985)] reported earlier a temperature dependence of the transmission coefficient of a heterogeneous system formed by a macroporous glass in a liquid crystal at temperatures in the range corresponding to the isotropic phase of the liquid crystal. As correctly pointed out in Ref. 8, this dependence was not only related to the contribution of the term $I_m$, to the total scattered-light intensity, but also to other physical phenomena specific to the experiments in question, including possible leaking of the liquid crystal out of the pores.