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 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 surface 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.[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 (on the temperature scale) of phase transitions, and can lead to a change of the nature of the transition, give rise to new phases, and produce transitions between these phases. The nontriviality of the physical phenomena that occur in pores is manifested, for example, when a phase transition is studied in a stratifiable binary solution using light-scattering methods.[3–5] It has been shown recently that a major role in the reported phenomena is played by the wetting phase transition.[6] It alters the properties of the solution near the pore walls because of a change in the concentration of one of the substances in the mixture, thereby influencing the scattering properties.

In the case of one-component media such as liquid crystals, an analog of this effect is the orienting influence of the solid surface of a substrate on the molecules in a liquid crystal, so that the physical properties of the layer next to the substrate differ from the properties of the liquid crystal in bulk.[7] Obviously, the effects become stronger on increase in the specific area of the interface between the phases, as is true of porous media. Studies of the intensity of light scattered in disperse liquid crystals have been limited so far to the case of droplets of the isotropic phase of nematics in polymer matrices.[8,9] The smallest dimensions of such drops are limited by the technology used in the preparation of porous samples: they amount to ~1 μm and they exceed the dimensions of the pores in matrices of the kind used in the studies of surface and size effects. Therefore, the role of surface effects in systems of this kind is limited and the temperature dependence of the scattered-light intensity is governed by the bulk properties of a liquid crystal. The influence of the orientational wetting on the scattering properties of a disperse liquid crystal has not been investigated even in the isotropic phase far from the critical point. Therefore, it would be highly desirable to carry out such investigations, because they should yield information essential for the understanding of the characteristics of phase transitions in systems of this kind 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 liquid in the free state at $T = 35$ °C) introduced into a macroporous silicate glass matrix. The scattering of light in the isotropic phase of free cholesteryl oleate had been investigated earlier.[10] This liquid crystal was selected because the refractive index n of cholesterics in the isotropic phase is closer to the refractive index n_m 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_m, 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 $\langle l \rangle$ and their volume fraction ω, determined by the method of low-angle x-ray scattering,[12] were $\langle l \rangle = 1000$ 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 $T = 65$ °C for 24 h. The area of the contact

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between the cholesteric liquid crystal and the matrix represented ~25% of the cylinder surface. In the subsequent measurements the whole free space in the cell was filled with the investigated liquid, which prevented its leakage out of the pores.

Measurements of the scattered-light intensity were made using apparatus described in Ref. 13. Our light source was a He-Ne laser ($\lambda = 6328$ Å). The temperature of the sample was varied from 45 to 55 °C. This temperature was kept constant to within ± 0.05 °C with a thermostat.

It seemed natural to assume that the intensity I of light scattered by a cholesteric liquid crystal inside a porous matrix is described by the following sum of intensities:

$$I = I_m + I_{\Delta n} + I_\rho + I_\eta + I^{(2)}, \qquad (1)$$

where I_m and $I_{\Delta n}$ represent the intrinsic scattering by the matrix and the scattering due to the difference between the refractive indices $\Delta n = n - n_m$; I_ρ and I_η are the contributions due to fluctuations of the density and of the tensor order parameter, respectively; $I^{(2)}$ is the double-scattering intensity. The contributions made to the total intensity were estimated for the scattering angle $\theta = 90°$. The contribution $I_\rho + I_\eta$ was found by measuring the intensity I of light scattered in the investigated system and the corresponding intensity I_{is} scattered in the isotropic phase of the investigated cholesteric in its free state, because I_{is} was governed[10] by the sum $I_\rho + I_\eta$. In the temperature range 45–55 °C the experimental results indicated that $I/I_{is} \sim 10^3$. Consequently, far from the phase transition point in a system comprising a cholesteric liquid crystal and macroporous glass we could ignore the molecular scattering, i.e., the terms I_ρ and I_η in Eq. (1).

The double scattering intensity was determined in a crossed-cylinder geometry using a method described in Ref. 13. The experimental results indicated that $I^{(2)} \approx 0.25I$. The term $I_{\Delta n}$, due to the difference between the refractive indices of the substance filling the pores and the material of the porous matrix, could not be eliminated by a suitable selection of the temperature of the sample, because the refractive index of the cholesteric liquid crystal was identical with n_m at temperatures above 100 °C where cholesteryl oleate could undergo thermal dissociation.

We estimated the contributions I_m and $I_{\Delta n}$ to I by comparative measurements of the scattered light at $T = 52.8$ °C using cholesteryl oleate and the same matrix impregnated with toluene at 20 °C. At these temperatures the refractive indices of toluene and of our cholesteric liquid crystal were identical to within the third decimal point, i.e., if we ignored the temperature dependence of n_m we could assume that the difference between the refractive indices of the substance filling the pores and the matrix material was the same for both systems and, consequently, the contributions n_m should be the same. The intrinsic scattering by the matrix was independent of the nature of the material filling the pores, so that the values of $I_m + I_{\Delta n}$ should be the same for both systems if Δn are the same. The intensity of light scattered in the toluene–porous matrix system was also described by Eq. (1). The experimental results indicated that $I^{(2)}$ for this system was one-third of $I^{(2)}$ for the cholesteric–porous matrix system. Bearing this point in mind and ignoring the molecular scattering in toluene, we used measurements of the total intensity of light scattered in the toluene–matrix system to find the sum $I_m + I_{\Delta n}$ 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: $I^{(2)} = 0.25I$, $I_m + I_{\Delta n} = 0.3I$, and the sum $I_\rho + I_\eta$ negligible compared with the total intensity I, i.e., there was a strong excess scattering $\delta I = 0.45I$ ignored in Eq. (1). Consequently, when the scattering angle was $\theta = 90$ °C 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[14] 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

$$q = \left(4\pi n \sin\frac{\theta}{2}\right)\frac{1}{\lambda},$$

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 $q = 2.7 \times 10^5$ cm^{-1}. Therefore, in order to determine whether the excess intensity δI 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 Δn. 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.[14]

It is clear from Fig. 1 that the excess scattering δI was observed for all values of q (curve 3) and that $\delta I(q)$ 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 δI and the dependence $\delta I(q)$, and they could be both explained by the following assumption. We assumed that a surface layer with its scatter-

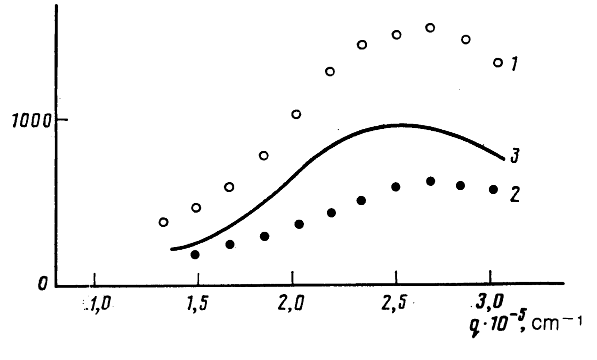

FIG. 1. Dependences of the scattered-light intensity on the modulus of the wave vector: 1) cholesteric liquid crystal in pores ($T = 52.8$ °C); 2) toluene in pores ($T = 20$ °C); 3) excess scattering δI.

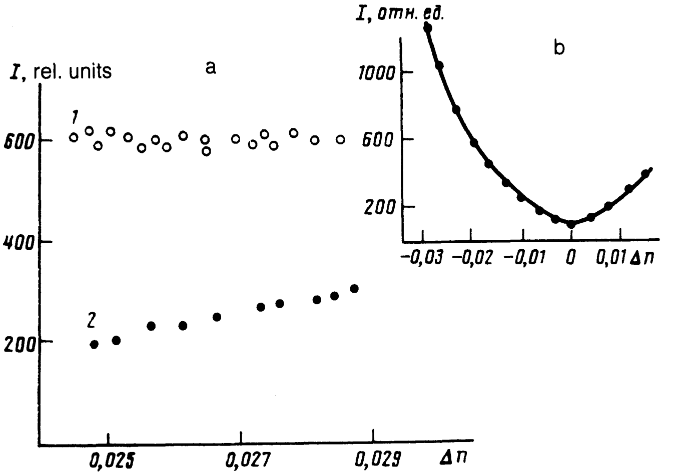

FIG. 2. a) Dependence of the scattered-light intensity on Δn: 1) cholesteric liquid crystal in pores; 2) toluene in pores. b) Dependence of the scattered-light intensity obtained for toluene in pores in a wide range of Δn.

ing properties differing from the properties of the bulk cholesteric liquid crystal formed at the pore walls and was responsible for the excess scattering δI. The shape of the layer in each pore and the relative distribution of the layers belonging to different pores were governed by the pore shape and by the structure of the matrix, which determined the nature of the $\delta I(q)$ 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 difference between the refractive indices Δn of the substance filling the pores and the matrix material. The range of Δn from 0.025 to 0.029 for the liquid crystal–matrix system corresponded to a change in T within 55–45 °C, whereas for the toluene–matrix system it corresponded to 22–13 °C. In the case of toluene the $I(T)$ dependence could be approximated by the expression $I = I_m + I_{\Delta n}$ in accordance with Eq. (1), where $I_{\Delta n} = \text{const} \cdot (\Delta n)^2$, as expected for an isotropic liquid (Fig. 2b). It is clear from Fig. 2 that, within the limits of the experimental error, there was no temperature dependence of I for the liquid crystal in the pores. This was in agreement with the earlier assumption of the existence of a surface layer of a cholesteric liquid crystal within the pores. The optical (and consequently, structural) properties of this layer were practically independent of temperature in the investigated range ΔT.

If a pore is regarded as a sphere of radius $R \sim \langle l \rangle /2$ and if it is assumed that the linear size of the molecule with the investigated liquid crystal is ≈ 40 Å, then even for a surface layer of thickness $\sim 10^2$ Å, representing several molecular lengths, a considerable part of the cholesteric liquid crystal ($\sim 50\%$) in the pores should be within the surface layer. 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 $\sim 10^2$ 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 $\delta I(q)$, 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 $I_{\Delta n}$ 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.

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