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Interaction of LC with a substrate in a system LC-porous glass studied by IR spectroscopy

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Abstract

IR spectra of porous glasses (PG) with a pore diameter of 20, 40 and 100 Å, and those filled with 4-pentyl-4'-cyanobiphenyl (5CB) nematic liquid crystal (LC) were studied at room temperature in 400–13 000 cm⁻¹ spectral range. Incorporation of the LC into the porous glass results in the changes of some fundamental bands, overtones and combination tones in the IR absorption spectra of the porous glass and the liquid crystal. The most essential changes in the spectrum of PG were observed for the bands corresponding to the absorption of the surface OH groups, whereas in the spectra of the LC, for the bands associated with the C \equiv N group of the 5CB molecules. Changes observed in the spectral parameters of the 5CB are more pronounced in the case of microporous glasses as compared to that of macroporous ones. These results indicate the existence of strong interaction between the LC molecules and porous glass matrix. In the case of the 5CB, such interactions are realized through the hydrogen bonds formation between the polar C \equiv N groups of the 5CB molecules and the surface OH groups of the 5CB molecules and the surface OH groups of the 5CB molecules and the surface OH groups of PG. Using the IR spectra of LC–PG system, one can also estimate the degree of the LC molecules penetration into the pores. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vast majority of the applications of liquid crystals (LC) is associated with the use of the mono-domain samples. LC alignment is usually reached by special treatment of the substrates confining liquid crystalline layers. It provides orientational ordering of the LC on the surface of the substrate. Such ordering could be transferred into the LC monolayer contacting with a

surface and then into the bulk of the LC due to the collective orientation of the liquid crystal molecules. So, investigation of the interaction of the LC with a surface of orienting substrate is of great importance for the understanding of the phenomena of the LC alignment.

Investigation of the molecular interaction in the interface layers "LC-substrate" is associated with many experimental difficulties. Using the transparent geometry of investigation of the LC films confined between two substrates, it is quite difficult to separate the signal yielded from the interface against the background of big response from the LC bulk. That is why

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Fig. 1. Differential pore volume as a function of pore width.

the methods associated with the reflection from the interface layers are usually used for the investigation of such systems [1-3].

Situation could be drastically changed by the use of highly porous media as a matrix for liquid crystals. For instance, in the porous glasses, the portion of the molecules contacting the walls of the pore could be comparable with that of those ones located in the center of the pore [4]. One can assume that in such case the response from the interface should be comparable with that from the bulk even if the transparent geometry of the measurements is used. This idea was realized in our work. The IR spectroscopy method was applied to the investigation of the "LC-substrate" interaction in the plates of microporous glasses filled with liquid crystal.

2. Experimental

2.1. Samples

The porous glasses used in our studies were fabricated in the Institute of Technical Chemistry of Martin-Luther-University (Halle, Germany) by the standard procedure described, for example, in Ref. [5]. Original sodium borosilicate glasses were leached in order to remove the sodium borate phase. Through-pore matrices were obtained as the result of this process. The structure of such matrices could be considered as composed from SiO₄ tetrahedrons connected by oxygen atoms. The samples with three different pore diameters (20, 40 and 100 Å) were manufactured by variation of the leaching conditions. Characterization of the mesoporous glasses (20 and 40 Å) was provided by nitrogen adsorption, while the macroporous ones (100 Å) were identified by the mercury intrusion measurements. These results showed narrow distribution of the pore radius in the prepared samples (Fig. 1). The porosity ω and specific surface S/V of the samples with the pore size d =20 Å were 0.14 cm³/g and 200 m²/g, respectively. For the glasses with d = 100 Å, the following values obtained: $\omega = 0.53 \text{ cm}^3/\text{g}$ were and S/V = $34.41 \text{ m}^2/\text{g}.$

Plates of 0.5 mm thickness were divided and polished. Than they were cleaned with toluene and baked at 350°C within 2 h just before the IR measurements.

4-pentyl-4'-cyanobiphenyl (5CB) liquid crystal by Merck with nematic mesophase within 22.5–35°C



Fig. 2. FTIR absorption spectra of porous glasses with different pore diameter: 20 Å (Glass 20), 40 Å (Glass 40), and 100 Å (Glass 100) in the glass transparence region. Vertical line marks the change of the frequency scale.

was used as filling material. Porous plates preliminary aged at 350°C were dipped into the melt of the 5CB at 80°C and kept there for 5 h. Then the plates were removed from the LC and thoroughly cleaned with cotton.

The samples of the 5CB for the IR studies were prepared as the LC films placed between two CaF_2 and RBr plates. Thickness of the 5CB layer was about 3 μ m.

2.2. Equipment

The IR spectra of the 5CB, pure porous glasses and the same glasses filled with the 5CB were measured in the range of $400-4000 \text{ cm}^{-1}$ using UR-20 (Karl Zeiss, Jena) and FTIR Nicolet "Avatar" 360 spectrometers. The spectral slit width was 2–4 cm⁻¹. The "Cary-5E" (Varian) spectrophotometer was used for the measurements in the near IR spectral region 3500–13 000 cm⁻¹ (3000–750 nm). All measurements were carried out at room temperature (Figs. 2–6).

3. Results and discussion

3.1. Spectra of PG

The IR spectra of the 0.5 mm thickness plates of pure PGs with different pore diameter in the regions of 1900–4000 and 4000–8000 cm⁻¹ are presented in Figs. 2 and 3, respectively. In the spectra shown in Fig. 2, one can see a transparence window between 2000 and 3000 cm⁻¹ which is limited from the low frequency side with the absorption bands of the SiO₄ matrix and from the another side with the strong broad absorption corresponding to vibrations of surface OH groups of the pores [6,7]. The PGs are also transparent in the near IR region. This makes the PG useful for spectral studies of the various materials in the confined geometry.

According to Ref. [7], the tetrahedron SiO₄ (T_d symmetry) has the following fundamental modes: $\nu_3(F_2)$ at 1075 cm⁻¹, $\nu_1(A)$ at 800 cm⁻¹, $\nu_2(E)$ at 457 cm⁻¹ and $\nu_4(F_2)$ at 615 cm⁻¹. Lowering of site symmetry of these structural units in the lattice of the PG matrix may remove the degeneracy of F₂ and



Fig. 3. NIR absorption spectra of bare porous glasses with different pore diameter 20 Å (Glass 20) and 40 Å (Glass 40).

E normal modes and allow to reveal the silent modes (symmetry A and E) in the IR spectra of the PG. The above mentioned SiO₄ modes were not detectable in our measurements due to high absorption of thick PG plates in the corresponding spectral regions. However, the bands of the weaker intensity assigned to overtones and combination tones of the fundamental modes of SiO₄ were clearly detected at 2290, 2545 and 2780 cm^{-1} (Fig. 2) as well as at 4450, 5150 and 5350 cm^{-1} (Fig. 3). For example, the band at 2290 cm⁻¹ is more likely to be the $2\nu_3$ overtone, the band at 2545 cm⁻¹ corresponds to the $(\nu_3 + 3\nu_2)$ combination, and the band observed at 2780 cm^{-1} is related to $(\nu_3 + 2\nu_1)$ combination. The bands observed in the spectra shown Fig. 3, are related to overtones and combination tones of SiO₄ of higher order. All these bands have a complex shape, which is nearly the same for all the glasses with different sizes of pores.

The broad intensive band centered at 3440 cm^{-1} and the narrow one at 3747 cm^{-1} , which are observed in the spectra of the PG, are assigned to the stretching vibrations of the hydroxyl groups on the surface of pore walls. The broad band centered at 3440 cm^{-1} corresponds to the $\nu_{as}(OH)$ vibrations of OH groups connected by hydrogen bonds of the Si–OH…OH– type with each other or with the water molecules adsorbed onto the pore surface. The narrow band $\nu_{\rm free}$ (OH) at 3747 cm⁻¹ corresponds to the vibrations of "free" (non-interacting) OH groups. The overtones of the mentioned bands were observed at 7120 and 7326 cm⁻¹, respectively. It should be noted, that the ratio of the intensities of $\nu_{\rm as}$ (OH) and $\nu_{\rm free}$ (OH) bands as well as that one of their overtones was different for the glasses with the different pore size.

3.2. Spectra of porous glasses filled with 5CB

The IR spectra of the plates of the PG with different pore diameter filled with 5CB are presented in Figs. 4 and 5. The contiguity of the LC and the PG results in the changes in spectral parameters of some fundamental bands of both interacting components. In the case of porous glasses, the bands corresponding to the stretching vibration of free OH groups located on the pore surface become essentially weaker or completely disappear after the PG filling with LC. As it can be seen from Fig. 4, the $\nu_{\text{free}}(\text{OH})$ band at 3747 cm⁻¹ completely disappears in the glass specimens with the pore diameter $d \ge 40$ Å. In the spectra of the PG (with the pore diameter d = 20 Å) filled with 5CB, the weakened $\nu_{\text{free}}(\text{OH})$ band still is observed



Fig. 4. FTIR absorption spectra of pure 5CB liquid crystal and porous glasses filled with 5CB in the glass transparence region. Vertical line marks the change of the frequency scale.



Fig. 5. FTIR absorption spectra of pure 5CB liquid crystal and porous glasses with different pore diameter filled with 5CB in the region of Q(C=N) stretching vibrations.



Fig. 6. NIR absorption spectra of bare Glass 40 porous glass and that one filled with 5CB liquid crystal.

at 3747 cm^{-1} . This fact shows that the LC molecules do not completely fill the pores with the diameter of 20 Å. Similar behavior is observed for the $2\nu_{\text{free}}$ (OH) overtone of this band at 7326 cm^{-1} (Fig. 6). The next important peculiarity of the spectra of filled PG, which is observed in the region of the stretching OH vibrations as compared to the spectra of bare PG, is the red shift of the broad band ν_{as} (OH). The value of the shift, which was measured by the displacement of the highfrequency edge of the band at its half-height, for different PG samples varies from 30 to 40 cm^{-1} . These two facts could be attributed to the interaction between the surface OH groups and the LC molecules penetrated into the pores and to the changes in it the uniform H-bond network resulting in the formation of stronger H-bonds [8]. So, the measurement of the intensity and frequency shift of the bands corresponding to the vibrations of the "free" and associated OH groups could provide a test for the determination of the degree of penetration of the LC molecules into the porous matrix.

Some fundamental absorption bands of the 5CB are located in the PG transparence window. In the region of 2800–3150 cm⁻¹, one can see a group of the intensive bands corresponding to the ν^{s} (CH) and ν^{as} (CH) stretching vibrations of the CH₂ and CH₃ groups of alkyl tail and ν^{ar} (CH) vibration of the benzene rings [9]. In the case of filled PG, the transmission in the above mention spectral region equals to zero. Fortunately, the overtones of these bands are located in the range of 5650–6000 cm⁻¹ (Fig. 6). Under the incorporation into the PG, they do not change either their positions or shapes. Therefore, the interaction of alkyl tails and the CH groups of benzene rings with the PG active centers could be neglected.

The intensive band at 2227 cm^{-1} was assigned to the stretching vibration of the polar $C \equiv N$ group of the 5CB molecule [9]. As it is well known, this group is very sensitive to any changes in the environment and intermolecular interaction [10]. The dependence of the absorption in the $2200-2270 \text{ cm}^{-1}$ range versus the PG pore diameter is presented in Fig. 5. As one can see from the figure, the decreasing of the pore diameter leads to the Q(C=N) band shift towards the higher frequencies. The value of these shifts in the spectra of the filled PG with pore diameter of 20 and 40 Å is about 6 cm⁻¹, whereas in the case of the PG with the pore diameter of 100 Å, it equals only 1 cm^{-1} . Besides, the introduction of the 5CB in the pores leads to the inhomogeneous broadening of the $Q(C \equiv N)$ band which is more pronounced in the case of mesoporous glasses. Similar features have to be observed for the overtone or combination tone of the C≡N vibration in the NIR spectral region. It is difficult to find the unperturbed position of these vibrations because the anharmonicity parameter of the vibration of the C=N group is unknown. The band at 3830 cm^{-1} is more likely to be the combination tone of the basic $Q(C \equiv N)$ band with the $Q(C \equiv C)$ band of benzene ring at 1604 cm⁻¹. Indeed, the shape and the peak position of this band in the spectra of the filled PG, as compared to that in the spectra of bulk 5CB, undergo similar changes as the $Q(C \equiv N)$ band. In the spectra of mesoporous glasses, this band shifts by 7 cm^{-1} towards the higher frequencies and becomes wider by $5-6 \text{ cm}^{-1}$. Note that recently we have observed similar shift and band broadening of the $Q(C \equiv N)$ band in the case of the 5CB encapsulation in other porous material (molecular sieves of the MCM-41 type) [11].

Taking into account essential changes of the vibrational bands corresponding to the free OH-groups of porous glass and the C≡N groups of the 5CB, it is reasonable to assume that the LC molecules interact with the glass matrix forming the hydrogen bonds of the Si–OH····N=C – type in the interface layer of the pore walls. From the one side, such interaction can cause the decrease in the intensity of $v_{\text{free}}(\text{OH})$ band and the displacement of the $v_{as}(OH)$ band of the PG. From the other side, it could be a reason for displacement and broadening of the $Q(C \equiv N)$ band of the 5CB in the case of filled PG. Indeed, in the spectra of the 5CB LC film, only bulk component is presented, whereas in the spectra of porous glasses both components (bulk and that interacting with the wall surface) contributed to the IR absorption. The increasing of the above-mentioned spectral changes with the decrease of the pore diameter confirms our model. It is worth to note that the interaction of the 5CB with the substrate through the hydrogen bonds of the Si-OH…N≡Ctype is not a common feature for all silica materials. As we have shown earlier, in the case of the 5CBaerosil mixture, the 5CB molecules interact with the aerosil particles forming hydrogen bonds of the Si–OH··· π type [12].

4. Conclusions

Thus, the transmission IR spectra of the LC

5CB-PG system were measured in the wide spectral region. Such spectra contain the bands corresponding both to the porous glasses and LC, because of the "windows" of transparency of porous glass in the middle and near IR regions. Filling of the PG with LC leads to the spectral changes related both to porous glasses and liquid crystal. Such changes are especially strong for the IR bands corresponding to the surface OH groups of the pore walls and polar $C \equiv N$ groups of the 5CB molecules. The strongest changes in the 5CB spectrum were observed in the glasses with the smallest pore size. These facts provide evidence for the essential interaction of the LC molecules with the pore surface. In the case of 5CB, the LC molecules form the hydrogen bonds with the surface OH groups of the Si–OH…N≡C– type. The spectra of LC-PG systems could also be used for estimation of the degree of penetration of liquid crystal molecules into the porous matrix.

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242

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