
TEMPERATURE DEPENDENCE OF THE IR SPECTRA OF THE SYSTEM LC - AEROSIL

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IR spectra of the suspension of aerosil A300 in a nematic liquid crystal (LC) 5CB are studied in the temperature interval corresponding to the nematic and isotropic state of 5CB. The most considerable changes under heating from the nematic to isotropic state were observed for IR absorption bands sensitive to the interactions between aerosil particles (OH...O bonds) as well as between aerosil particles and LC molecules (OH... π bonds). Crucial decrease of the intensities of some mentioned absorption bands at the transition point T_{NI} could be interpreted as an essential weakening of the LC - aerosil interaction and a strong destruction of the aerosil structure. These results are in good agreement with the earlier proposed mechanism of "memory" effect observed in the system studied.

Introduction

A filled liquid crystal is a suspension of small particles in the LC matrix. As a filling material, aerosil is usually used. The averaged size of primer aerosil particles is about 100 Å. The filled LC suggested in 1990 [1] provokes a big interest because of very promising applications in LC displays, information storage systems, optical shutters, *etc.* Light scattering in the layers of filled LC is sensitive to the applied electric field. Such an electrooptical response could be reversible or irreversible depending on the properties of LC and aerosil and its interaction in a mixture [2].

According to the current conception, the electrooptical response of filled LC depends on structural changes under the applied electric field. The irreversible response ("memory" effect) is supposed to be associated with a strong distortion of the original structure of the aerosil phase. Indeed, LC molecules reorienting in the field can involve the aerosil structure in the reorientation process. It should cause the destruction of the original aerosil structure and formation of a new one in the oriented LC matrix. The new aerosil structure could remain after switching off the electric field stabilizing the oriented state of

LC [2, 3]. However, prior to our investigations, this hypothesis was not proved because of a lack of experimental results.

In [4, 5], we showed that IR spectroscopy is a very useful tool for investigation of intermolecular interactions in filled LC. It was proved that the irreversible electro-optical response of the suspension is associated with the high aggregation rate of aerosil particles and the effective interaction of LC molecules with the surface of aerosil. The interaction between aerosil particles and between aerosil and LC realized, respectively, through the hydrogen bonds between Si-OH groups on the aerosil surface and between these Si-OH groups and LC molecules [4].

As was earlier shown, the oriented state of filled LC may be destroyed by heating of the sample above the clearing point of LC [2, 3, 6]. In the frame of the described above model, it should be connected with the destruction of the aerosil structure and weakening the intermolecular interactions in the system. These questions are studied in the present work using the method of IR spectroscopy.

Experimental

In our studies, we used nematic LC 5CB by Merck (Germany) and industrial aerosil A300 by Degussa (Germany) as the components of the suspension. LC 5CB (4-*n*-pentyl-4'-cyanobiphenyl) has the nematic mesophase in the 18–35 °C temperature range. Its physical properties are well studied. IR spectra of 5CB were investigated, for instance, in [4, 7, 8].

Aerosil A300 consists from ultrasmall silica particles with a size of about 100 Å. A surface of such particles is not chemically modified. It is covered with Si—OH surface groups with a surface density of 2.5 nm⁻² [9, 10]. Before preparing samples, aerosil was dried at 200 °C for 2 h in order to remove water

adsorbed on its surface. Such a procedure diminishes the degree of aggregation of aerosil particles in the suspension. The studied suspension was prepared immediately before the measurement of IR spectra. LC and aerosil were mixed using an ultrasonic disperser. The intensity and frequency of sonication were 4000 W/m² and 22 kHz, respectively. The concentration of aerosil in the mixture was 10% by weight. The suspension was placed between CaF₂ or KBr crystalline substrates. The cell gap was set by teflon strips of 5–60 μm in thickness depended on the measured spectral region.

The IR absorption spectra of 5CB, aerosil, and their mixture have been measured in the 4000–400 cm⁻¹ region using Specord M-80 and FTIR Bruker IFS-88 infrared spectrometers. The spectral slit width was 2–4 cm⁻¹. The spectra were measured at temperatures 20–60 °C corresponding to the nematic and isotropic mesophase of LC 5CB. The temperature was stabilized with the accuracy of 0.1 °C by the use of a home-made temperature stabilizing system.

Results and Discussion

The IR absorption spectrum of the 5CB–A300 mixture at 25 °C is shown in Fig.1. The intensive bands of aerosil, 471 and 1111 cm⁻¹, correspond to Si–O–Si deformation vibrations and Si–O stretching vibrations of the silica skeleton, respectively. The most intensive bands of 5CB are observed in the spectra at the frequencies of 1495, 1606, 2225, and 2928 cm⁻¹. The bands at 1495 and 1606 cm⁻¹ are assigned to stretching vibrations $Q_1(C-C)$ and $Q_2(C-C)$ of the C–C bonds in the benzene rings of 5CB molecule, the band at 2225 cm⁻¹ to the stretching vibration $Q(C\equiv N)$ of the C≡N group, and the band at 2928 cm⁻¹ to asymmetric $q(CH)$ vibrations of the CH₂ groups of alkyl fragments. As was determined earlier in [2], contrary to the $Q(C\equiv N)$ band, the intensities of $Q_1(C-C)$ and $Q_2(C-C)$ vibrations strongly depend on the concentration of aerosil. It was a reason to conclude that the 5CB molecule interacts more likely with aerosil through the benzene rings, forming the H-bonds with the silanol groups of the aerosil surface. This supposition can also explain the changes observed in the IR spectra in the region of OH stretching vibrations (2250–4000 cm⁻¹).

The spectral decomposition of the broad $q(OH)$ band of the suspension 5CB–A300 shows that, in comparison to the pure 5CB, new bands emerge with the peak positions at 3750, 3614, 3540, and 2500 cm⁻¹, respectively [4]. According to [9], the first band corresponds to free OH groups. The

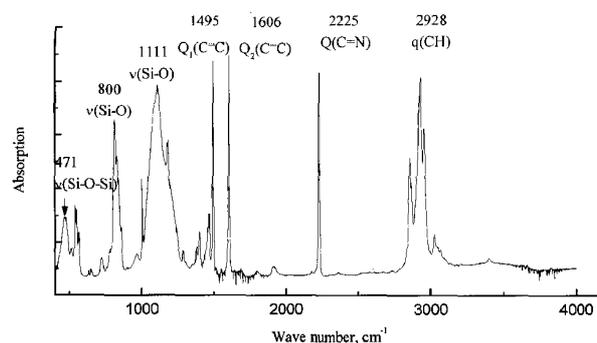


Fig.1. IR absorption spectrum of the suspension LC 5CB–aerosil A300 measured at 25 °C. Thickness of the suspension layer is about 15 μm

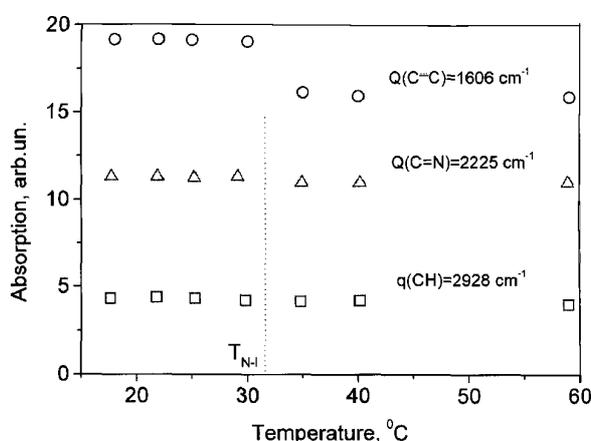


Fig.2. Temperature behavior of some characteristic bands of LC 5CB

consequent two bands correspond to the OH groups forming new weak OH–π bonds. In our system, they could be assigned to the interaction of Si–OH groups of the aerosil surface with the benzene rings of 5CB molecule. The last component with a maximum at 2500 cm⁻¹ corresponds to the polymer-like bonds of OH groups [10]. We assigned this band to the aggregation of aerosil particles in LC.

In the present study, we use the bands $Q_2(C-C) = 1606$ cm⁻¹, $Q(C\equiv N) = 2225$ cm⁻¹, and $q(CH) = 2928$ cm⁻¹ as characteristic bands of different fragments of 5CB molecule, while $q(OH-O) = 2500$ cm⁻¹ and $q(OH-\pi) = 3614$ cm⁻¹ bands are used as characteristic bands of the aerosil surface. We did not observe any noticeable changes in the position of the selected absorption bands under heating. In contrast, the intensities of some characteristic bands demonstrate considerable changes. Temperature dependences of the intensities of the LC bands located at 1606, 2225, and 2928 cm⁻¹ are presented in Fig.2. It is evident that

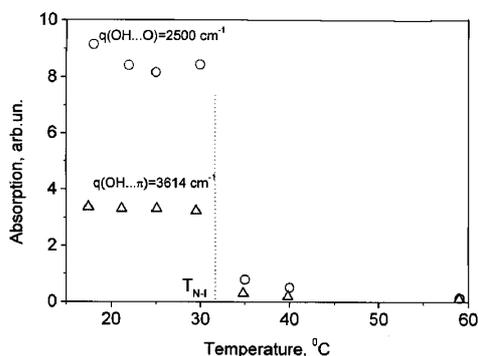


Fig.3. Temperature behavior of Si-OH characteristic bands of the aerosil surface

the intensities of the $q(\text{CH})$ and $Q(\text{C}\equiv\text{N})$ bands do not suffer critical changes, while the intensity of the $Q_2(\text{C}-\text{C})$ band considerably decreases in the isotropic state demonstrating the critical behavior at the transition point. This could be due to an essential decrease in the number of $\text{OH}\cdots\pi$ bonds between 5CB molecules and Si-OH groups of aerosil. The same could be concluded from the temperature behavior of the intensity of the $q_2(\text{OH}\cdots\pi)$ band, which is similar to the behavior of $Q_2(\text{C}-\text{C})$ (Fig.3.).

As is evident from Fig.3, the shape of the $q(\text{OH}\cdots\text{O}) = 2500\text{ cm}^{-1}$ band undergoes the most drastically changes at the transition point from the nematic to isotropic state. Since this band corresponds to aggregation of aerosil, this result could reflect a crushing of aerosil aggregates.

It should be noted that the intensities of all selected bands change very slightly in the nematic and isotropic state suffering jump-like changes only at the transition temperature T_{NI} . It means that the structure of the studied system is quite stable in the nematic and

isotropic state and changes drastically only at the phase transition point.

Conclusions

Heating of the suspension LC 5CB - aerosil A300 causes a drastic decrease in the number of hydrogen bonds of the $\text{OH}\cdots\pi$ type between LC and aerosil as well as between aerosil particles at the transition point 'nematic - isotropic state'. It results in a weakening of the anchoring of LC with aerosil particles and the destruction of the aerosil structure. It means that the oriented state of filled LC could be destroyed by heating of the system to the isotropic state of the liquid crystalline matrix. Thus, the obtained results confirm the model of the memory of filled LCs earlier suggested.

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