

Molecular interaction and ‘memory’ of filled liquid crystals

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Abstract

The dependences of an irreversible response (‘memory’ effect) of 5CB–aerosil suspensions on the chemical composition and concentration of the aerosil and the electric field parameters are investigated. IR-spectra show that hydrogen bonds between the 5CB molecules and aerosil particles play an important role in the occurrence of the ‘memory’ effect. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

The physics of heterogeneous liquid crystals (LC) is one of the most vigorously developing fields of both the applied and the fundamental physics of liquid crystals. Filled nematic LC (suspensions of small silica (usually aerosil) particles in LC) are prospective heterogeneous media from the point of view of their application. Such particles are a source of LC orientation defects and, therefore, such a medium in an initial state scatters the light intensively. On applying an electric field, the system clears up owing to both the orientation of LC molecules along the field and the transformation of defects.

Depending on the applied aerosil and LC, the system can be in the cleared state (‘memory’ effect) [1–3] or can be reset to the initial state very quickly (< 1 ms) [4] by removing the field. As was shown before [5,6], the characteristics of the ‘memory’ effects depend on both the chemical nature of aerosil surface and the LC molecules. The aim of this work

was to study the influence of chemical modification of the aerosil surface as well as its concentration on the molecular organization of the LC–aerosil system and on its ‘memory’ effect.

2. Experimental

2.1. Objects of investigation

4-pentyl-4'-cyanobiphenyl (5CB) $C_5H_{11}-C_6H_4-C_6H_4-CN$ (NIOPIC, Russia), which exists in nematic phase within the temperature range of from 295.5 to 308 K, was used as LC.

Aerosils (DEGUSSA, Germany), both chemically untreated (A) of type A-300, with specific surface of 300–400 $m^2 g^{-1}$, and of type R-202 modified (MA) by introducing hydrophobic molecular fragments – polymethylsiloxanes (PMS) – were used as LC fillers.

Aerosil A consists of complex globules (100–150 Å

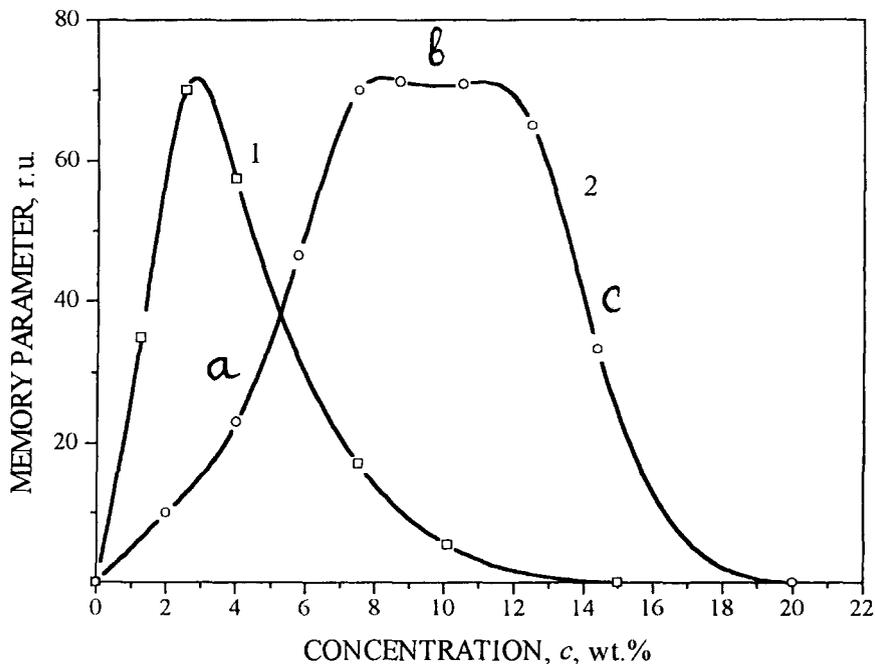


Fig. 1. The dependences of $M(c)$ for the 5CB + A (1) and 5CB + MA (2) systems.

in diameter) formed by Si–O–Si groups joined to each other. On the globule surfaces there are hydroxy OH-groups, both free and connected by hydrogen bonds to each other and to water molecules in associates of complex form. In the liquid medium the aerosil globules form aggregates as well as more complex agglomerated aggregates and three-dimensional

networks. On the surface of the MA aerosil, the number of OH-groups is considerably decreased owing to the substitution of the PMS groups for them.

The aerosil concentrations in the 5CB + Aerosil systems investigated in the present work are $c = m_a/m_m = 2\text{--}25$ wt.% (m_a and m_m are the masses of the aerosil and the mixture, respectively).

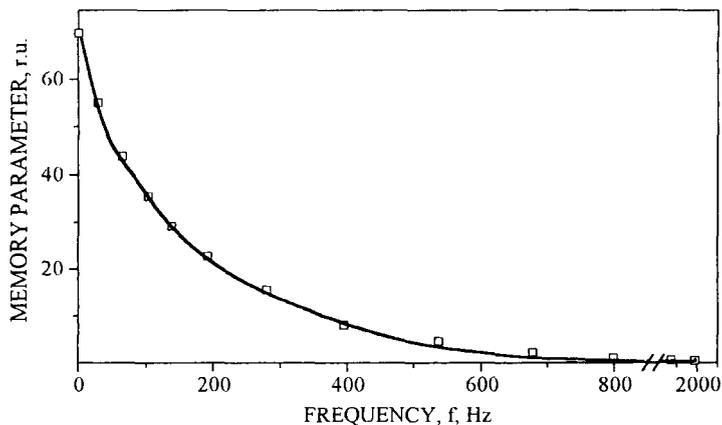


Fig. 2. The dependence of $M(f)$ for the 5CB + MA ($c = 10$ wt.%) system ($U = 50$ V).

A detailed description of the method for preparing suspensions is given in Ref. [5].

2.2. Methods of investigation

2.2.1. Light transmission.

Suspension layers of 10 μm thickness placed between two glass substrates with transmission SnO_2 electrodes on the inner surfaces were investigated. Both the scheme and description of the experimental unit are given in Refs. [4,5]. The intensity of the He–Ne laser light beam ($\lambda = 640 \text{ nm}$, of 1 mWt power) transmitted through the sample, I_{out} , was registered within the cone of 2° . Dependences of the value of ‘memory’ $M = (T_m - T_0)/(T_s - T_0)$ (T_0 , T_s and T_m are the initial transmittance of the sample, the transmittance of saturation in an electric field and the residual transmittance after removing the field, respectively) on the parameters of the suspension components were calculated. The accuracy of determining M is 0.5%. Measurements were carried out at $T = 298 \text{ K}$.

2.2.2. IR spectroscopy.

The IR absorption spectra of the 5CB + A ($c = 2.5, 6$ and $10 \text{ wt.}\%$) and 5CB + MA ($c = 6, 10$ and $15 \text{ wt.}\%$) systems and of the initial components were measured at 298 K in the region of $4000\text{--}400 \text{ cm}^{-1}$ with the aid of spectrophotometers SPECORD M-80 and UR-20. The spectral width of the slit was $2\text{--}4 \text{ cm}^{-1}$. Crystals of CaF_2 with a conducting layer of InSnO_2 ($0.5 \mu\text{m}$ in width) deposited on their inner sides for measurements in the electric field, as well as crystals of KBr, were used as cuvette windows. The absorbing layer widths (b) from 3 to $60 \mu\text{m}$ were set with the aid of teflon spacers.

An electric field of 60 V and 2 kHz frequency set by the acoustic frequency signal generator G3-56/1 was applied to the cuvette with the sample.

3. Experimental results and discussion

3.1. Light transmission.

The results of measuring the concentration dependence of ‘memory’ $M(c)$ for 5CB + A and 5CB + MA suspensions at voltages of $U = 0\text{--}200 \text{ V}$ and a

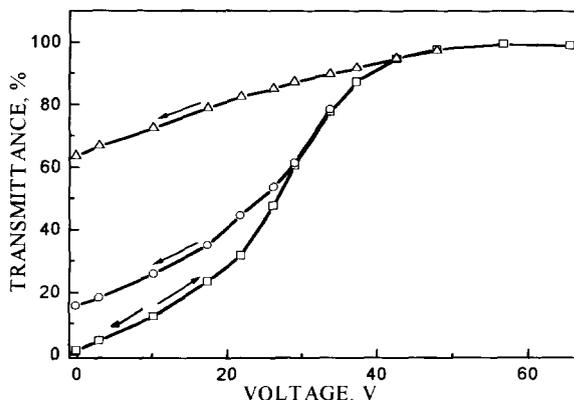


Fig. 3. The voltage contrast curves for the 5CB + MA ($c = 10 \text{ wt.}\%$) system measured by decreasing the applied voltage beginning from $U = 10, 30, 50 \text{ V}$ ($f = 2 \text{ kHz}$).

frequency of $f = 2 \text{ kHz}$ are given in Fig. 1. For both suspensions, three sections may be seen in the curves $M(c)$: a section of increasing value of M (a), a section of ‘effective memory’ (b), and a section of decreasing value of M and transition to a reversibility regime (c).

With aerosil hydrophobization, the bell-shaped form of curve $M(c)$ remains without any essential decrease of the maximum values of M , but these values are achieved at higher concentrations with a broadening of the ‘effective memory’ area at the same time. It should be noted that a very large switching contrast, $k = T_s/T_0$ ($1:100\text{--}150$ or more) is observed in these cases, which makes these systems especially attractive for practical applications.

The ‘memory’ of the 5CB + Aerosil system depends not only on the properties and ratio of components, but on the external field parameters as well, i.e., its frequency and voltage. While the frequency of the external field f decreases, the ‘effective memory’ area (b) of curve $M(c)$ is broadened (Fig. 2).

Fig. 3 shows the voltage-contrast curves for 5CB + MA suspension ($c = 10 \text{ wt.}\%$) measured while decreasing the applied voltage beginning from $U = 10, 30, 50 \text{ V}$ at $f = 2 \text{ kHz}$. It is seen that the ‘memory’ effect appears on achieving the saturation voltage of the voltage-contrast dependence. Such a result is also observed for system 5CB + A. Under the low frequencies ($f < 50 \text{ Hz}$) the ‘memory’ of the system can be observed on applying lower voltages.

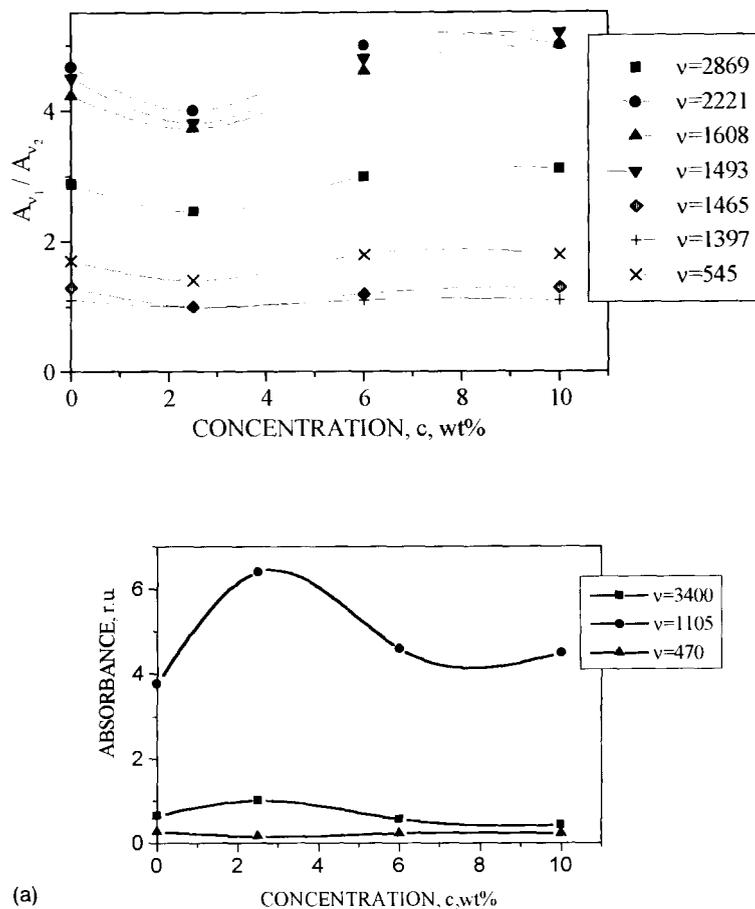


Fig. 4. The dependences of normalized absorbances corresponding to IR -bands of the 5CB + A (a) and 5CB + MA (b) systems on the aerosil concentration ($b = 3 \mu\text{m}$).

3.2. IR-spectroscopy.

The frequencies of some characteristic absorption bands of the systems under investigation and their assignments made on the basis of literature data [7–10] are given in Table 1.

As is evident from Table 1, the changes of the 5CB vibration frequencies in various suspensions are insignificant (within the range of the experiment error). But for concentrations of 2.5 wt.% in the 5CB + A system and 10 wt.% in the 5CB + MA system (concentrations corresponding to the maximum value of the ‘memory’ – see Fig. 1) a decrease in frequency of $3\text{--}6 \text{ cm}^{-1}$ is observed for most bands. This can be interpreted as evidence of changes of electronic density in the 5CB molecule.

More sensitive to the charge rearrangement in the molecule are the intensities of the IR-bands. To characterize the changes of intensities we used the ratio of absorbance A_{ν_1}/A_{ν_2} for two bands of the same spectrum. The concentration dependences of vibration band intensities in the 5CB + Aerosil systems are given in Fig. 4. As can be seen, the greatest changes of the intensities of vibration bands of 5CB for the 5CB + A system are observed for the concentration of 2.5 wt.% (band intensities decrease by 10–15% as compared with 5CB). At concentrations of aerosil A in 5CB equal to 6 and 10 wt.%, the intensities are increased by 3–10% as compared with 5CB. In the case of the 5CB + MA system, concentrations of 10 wt.% also correspond to the minimum value of the intensity (5–7% decrease as compared with 5CB),

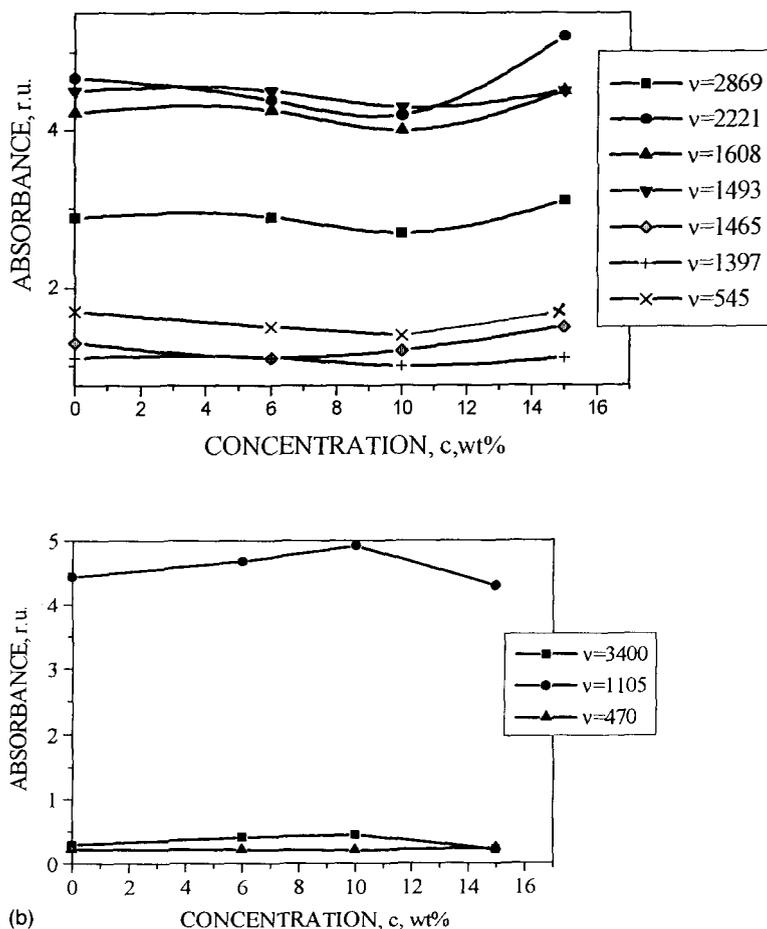


Fig. 4. Continued.

and in the case of the concentration of 15 wt.% (where $M \approx 0$), the intensity is 6–8% greater as compared with that of 5CB.

Let us consider changes of parameters of the IR-absorption bands of the aerosil under investigation. As was shown earlier in Ref. [11], a wide band of complex form with a maximum of 3400 cm^{-1} corresponds to OH-group absorption of aerosil A. The shape of this band changes in the 5CB + A system. Graphical decomposition of this band made it possible to identify bands with frequencies of 3669, 3404 and 3160 cm^{-1} in the aerosil spectrum, corresponding to the vibrations of hydrogen-bonded OH-groups. In the IR spectrum of the 5CB + A system, the additional bands at 3750, 3614, 3540 and 2500 cm^{-1} appear, of which the first corresponds to free OH groups, the next two

bands to OH groups forming weak hydrogen bonds of $\text{OH} \cdots \pi$ type, and the last to OH groups forming bonds of the polymer type $\text{OH} \cdots \text{OH}$ [11].

The introduction of aerosil A into 5CB ($c = 2.5 \text{ wt.}\%$) does not change the position of the wide OH band, but the intensity at the maximum increases approximately 1.6 times (Fig. 4). At concentrations of 6 and 10 wt.% the values of frequencies and intensities are close to the values of the corresponding parameters of pure aerosil A.

In the MA aerosil spectrum, the intensity of the band with the maximum at 3400 cm^{-1} which corresponds to vibrations of hydrogen-bonded OH groups decreases by approximately 2.3 times as compared with the spectrum of aerosil A, but does not disappear, which shows that the surface OH groups have been

Table 1

Some absorption frequencies (cm^{-1}) of 5CB in the nematic phase and in the 5CB + A and 5CB + MA systems with different aerosil concentrations (wt.%) and their assignment

5CB in nematic phase	5CB + A			5CB + MA			Group modes
	2.5	6	10	6	10	15	
3028	3022	3025	3028	3030	3024	3030	CH aromatic stretching, $\nu(\text{C-H})$
2932	2925	2928	2935	2933	2925	2933	CH_2 asymmetric stretching, $\nu_{\text{as}}\text{CH}_2$
2861	2855	2855	2858	2863	2855	2863	CH_2 symmetric stretching, $\nu_{\text{s}}\text{CH}_2$
2221	2221	2221	2221	2221	2221	2221	$\text{C}\equiv\text{N}$ stretching, $\nu(\text{C}\equiv\text{N})$
1608	1601	1601	1608	1605	1603	1605	ring C–C stretching, $\nu(\text{C-C})$
1493	1490	1490	1495	1493	1492	1493	ring C–C stretching, $\nu(\text{C-C})$
1465	1463	1462	1465	1465	1463	1466	CH_3, CH_2 asymmetric deformation, δ_{as} CH_3, CH_2
1397	1394	1396	1397	1395	1395	1396	CH_3 symmetric deformation, $\delta_{\text{s}} \text{CH}_3$
1376	1375	1376	1377	1376	1373	1375	CH_2 symmetric deformation, $\delta_{\text{s}} \text{CH}_2$
856	856	856	856	856	856	856	CH aromatic out-of-plane deformation, $\gamma(\text{CCH})$
830	828	828	828	828	828	828	CH aromatic out-of-plane deformation, $\gamma(\text{CCH})$
813	810	810	812	810	809	810	CH aromatic out-of-plane deformation, $\gamma(\text{CCH})$
568	567	567	567	567	567	567	Benzene ring out-of-plane deformation, $\gamma(\text{CCC})$
555	554	554	554	554	554	554	Benzene ring out-of-plane deformation, $\gamma(\text{CCC})$
545	544	545	545	545	544	545	Benzene ring out-of-plane deformation, $\gamma(\text{CCC})$

incompletely substituted by PMS-groups. In the 5CB + MA system, when changing the MA concentration, the most prominent changes of intensity of this band are observed for a concentration of 10 wt.% (see Fig. 4). Under these conditions the frequency of this band does not change.

In the spectra of aerosils and their suspensions in 5CB, two intense bands with frequencies 1100 and 470 cm^{-1} are assigned to asymmetric and symmetric vibrations, respectively, of Si–O–Si groups within the cyclic system. In the MA and 5CB + MA spectra, in addition, absorption at the frequencies 1030 and 450 cm^{-1} appears, corresponding to Si–O–Si vibrations within the open chain PMS, and bands 1260 cm^{-1} (δCH_3), 800 (νSiC), as well as weak bands in the area of $3000\text{--}2900 \text{ cm}^{-1}$ ($\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{s}}\text{CH}_3$), corresponding to the vibrations of the PMS group.

The intensities and forms of Si–O–Si group vibrations in the 5CB + Aerosil systems depend also on the concentrations of the components (Fig. 4), the changes for these as well as for other vibrations

being maximal for concentrations which correspond to the region of 'efficient memory'. The change of the form of these bands, which includes the growth of absorbance on the low-frequency wing, may be evidence for a change of structure of aerosil aggregates in 5CB.

When an electric field is applied to 5CB + Aerosil systems, the dependence of the relative intensities of the 5CB vibration bands on the aerosil concentration is almost the same as in the starting state (Fig. 5). In this case, the molecule orientation effect and the clearing in the electric field play a role in the change of the absolute intensity values and the vibration forms [11].

4. Conclusions

From the above considerations it is seen that in the 5CB + Aerosil systems changes of the parameters of the IR spectra of 5CB molecules and aerosil OH-groups take place, these changes being maximal at

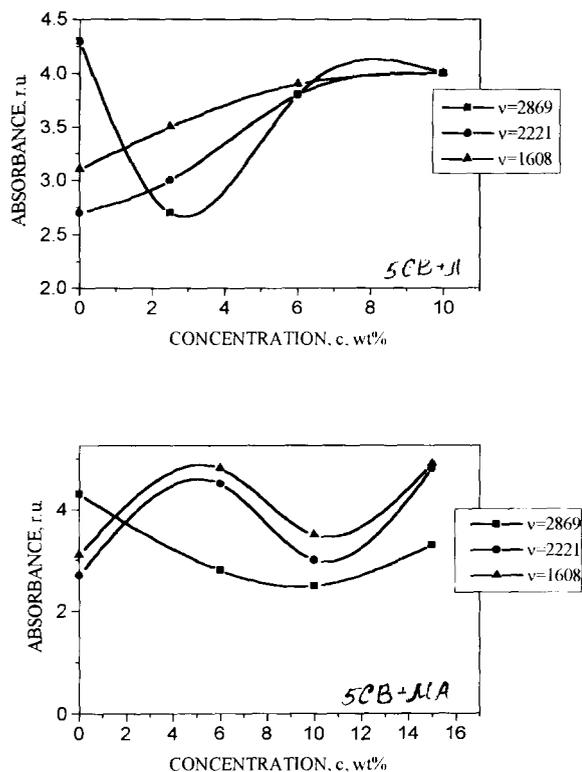


Fig. 5. The dependences of normalized absorbances corresponding to IR bands of the 5CB + A and 5CB + MA systems ($b = 5 \mu\text{m}$) on the aerosil concentration in an electric field.

the concentration at which the 'memory' is maximal. This may be a result of the specific interaction of 5CB molecules with aerosil OH-groups. The important role of aerosil OH-groups is also indicated by the fact that the concentration dependences of the parameters of the IR spectra of the 5CB + MA system are not so pronounced as for the 5CB + A system (see Fig. 4). With many of the 5CB molecule vibrations being delocalized, it is hardly likely that one would find the structure elements of 5CB taking part in the interaction with the surface.

One can suppose that the aerosil concentrations for which the 5CB + Aerosil systems show an 'efficient memory' (the b region on Fig. 1) approximately correspond to the filling of the surface with a monolayer of 5CB molecules. The content of OH-groups in the aerosil MA being less than in aerosil A, such a monolayer in the 5CB + MA systems is formed at a

concentration of aerosil MA which is greater than the corresponding concentration of aerosil A in the 5CB + A system.

When the electric field is applied to the 5CB + Aerosil systems at concentrations which correspond to monolayer formation, the 5CB molecules become oriented with respect to the field, their interaction with the surface remaining. Such an orientationally ordered state of the 5CB + Aerosil system can be retained after removing the electric field, which is the reason for the 'memory' effect.

At low concentrations of aerosil in 5CB (i.e. at polymolecular filling of the surface), the field of the absorbent is to a great extent shielded, and the interaction of 5CB molecules with one another tends to their interaction in the nematic phase. This leads to the partial compensation of the action of the aerosil surface on the 5CB molecules adsorbed immediately onto the aerosil surface. The properties of these molecules, including spectral ones, become close to properties of the mesophase.

At great concentrations of aerosil in 5CB (i.e. at comparatively little filling of the surface with rarefied monolayer of 5CB molecules) the properties of the 5CB + Aerosil system are almost fully determined by the properties of the aerosil.

The increase of the 'memory' effect with the decrease of field frequency (Fig. 2) is probably caused by a more effective involvement of the adsorbed 5CB molecules in the reorientation process under low frequencies. The reorientation of all adsorbed 5CB molecules is achieved at a certain voltage of the applied electric field (Fig. 3).

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