

Memory effect in filled nematic liquid crystals

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(Received 19 November 1996; in final form 14 March 1997; accepted 15 March 1997)

The irreversible electro-optical response (memory effect) of 'liquid crystal-aerosil' suspensions under the influence of an electric field is investigated. Thereby, the influence of the aerosil concentration on the efficiency of the memory effect is studied. The experimental results are discussed in the frame of a model where the filled nematic is considered as a system of aerosil agglomerates in a liquid crystal matrix stabilized by the forces of liquid crystal orientational elasticity.

1. Introduction

The physics of heterogeneous liquid crystals (LCs) is of interest for both applied and fundamental physics [1]. One version of such systems is provided by filled nematic LCs consisting of suspensions of aerosil particles in a LC matrix. Thereby the solid particles generate defects in the liquid crystalline phase. As a result, such a medium scatters light intensively in the initial state. By applying an electric field, the system clears due to both reorientation of the LC molecules and transformations of defects. The system can remain in the cleared state (memory effect) [2–4] or relax back very quickly ($\tau < 1$ ms) [5–6] to the initial state on removing the field. As noted before [5, 7], the characteristics of the memory effect depend upon the chemical nature of both the aerosil surface and the LC molecules. The aim of this work was to study the influence of chemical modification of the aerosil surface, of aerosil concentration and of electric field parameters on the memory effect.

2. Experimental

2.1. Samples and measurements

Samples of 4-pentyl-4'-cyanobiphenyl (5CB) (NIOPIK, Russia) with a dielectric anisotropy $\Delta\epsilon = 7$, and of nematic liquid crystalline mixtures ZhKM-1285 (NIOPIK, Russia) with $\Delta\epsilon = 11.8$ and ZLI-4801 (Merk, Germany) with $\Delta\epsilon = 5.1$ were used in the experiments.

Liquid crystals 5CB and ZhKM-1285 contain molecules with cyano groups, which can form hydrogen bonds. Such a special interaction is not possible for ZLI-4801. In order to prove the importance of hydrogen bonds on the memory effect, 0.5 weight per cent of a proton accept, di-*n*-nonyl 4-(4-cyanobenzoyloxy)benzylidenemalonate (HA) was added to ZLI-4801.

Aerosils A300 and R812 (pyrogenic silica of DEGUSSA, Germany) were used as solid components [8]. The surface of aerosil A300 contains about 5 OH groups nm^{-2} , whereas for aerosil R812 which is modified with hydrophobic polymethylsiloxane fragments, a density of only 0.29 OH groups nm^{-2} was measured [9].

Suspensions with various aerosil concentrations $c = 2\text{--}25$ wt % ($c = m_a/(m_a + m_m)$, where m_a and m_m are the weight of the aerosil and the mixture, respectively) were prepared by mixing the components in an ultrasonic mixer. Films of the suspensions of 10 μm thickness placed between two glass substrates equipped with transparent ITO electrodes, were investigated. Observations of the suspensions by polarized light microscopy showed the chaotically disordered texture of the LC containing aerosil agglomerates with sizes up to several microns.

The experimental set-up for our investigation has been described in previous papers [5–7]. The intensity of the HeNe-laser light beam transmitted through the sample, I_{out} , is measured within a cone of 2° . From these data, the sample transmittance, $T = I_{\text{out}}/I_{\text{in}}$, is calculated (I_{in} is the intensity of the incoming beam). Based on these

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data, the transmittance–voltage ($T(U)$) and transmittance–frequency ($T(\nu)$) characteristics were obtained for various LC–aerosil systems with varied aerosil weight concentrations. For the description of the memory effect, a memory parameter $M = (T_m - T_o)/(T_s - T_o)$ was introduced. Here T_o , T_s and T_m are the initial transmittance of the sample, the saturation value of the transmittance at high voltage and the residual transmittance after removing the field, respectively.

2.2. Dependence of memory parameter on suspension composition

The dependence of $M(c)$ for the various LC–aerosil combinations at a frequency of 2 kHz is given in figure 1. Three parts can be distinguished in the curves: (a) an increasing value of M with increasing concentration, (b) a maximum in the memory effect, and (c) a decrease of M and transition to a reversibility regime.

The largest memory parameter ($M > 70\%$) is observed for the suspension A300–5CB, for which the components can form hydrogen bonds (curve 1)†. The curve $M(c)$ is shifted to higher aerosil concentrations and broadened as a result of the decrease in hydrogen bond concentration on the aerosil surface (R812–5CB suspension, curve 2). We did not detect a memory effect for the suspension A300–ZLI–4801, where the LC has not the ability to create hydrogen bonds (curve 3). The addition of an initiator of hydrogen bonds, HA, to ZLI–4801

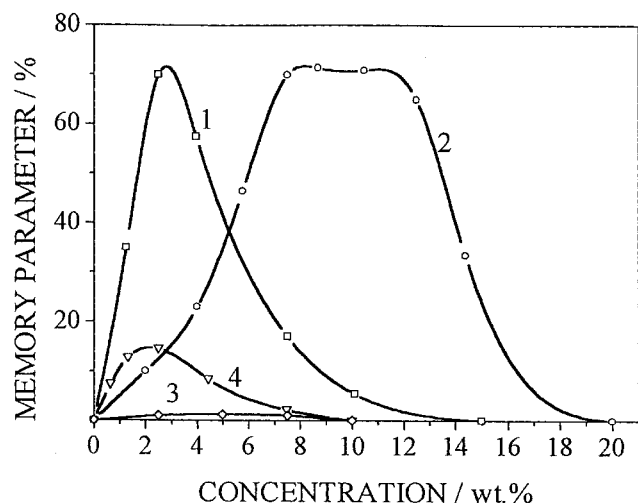


Figure 1. The dependences $M(c)$ for various pairs of LC–aerosil. 1 = 5CB–A300 (unmodified, hydrophilic aerosil); 2 = 5CB–R812 (hydrophobic aerosil); 3 = ZLI–4801–A300; 4 = ZLI–4801 with H-dopant–A300. The frequency of the applied field $\nu = 2$ kHz; the saturation value T_s corresponds to the applied voltage, $U = 200$ V.

†The dependence of $M(c)$ for the unmodified aerosil–ZhKM–1285 pair is similar to that given by curve 1; therefore, this is not shown in figure 1.

results in the appearance of the essential memory effect; the corresponding $M(c)$ -dependence curve (curve 4) has a similar shape to that for the suspension A300–5CB (curve 1).

2.3. Dependence of M on electric field parameters

To investigate the influence of further parameters on M , the frequency and voltage of the applied electric field were varied. The electro-optical response differed drastically between low ($f \leq 50$ Hz) and high ($f > 100$ Hz) frequencies of the electric field. At low frequencies the electric field caused the occurrence of flow and separation of the suspension components. Microscopic observation showed that on switching on the electric field, turbulent flow of the LC occurred, together with motion of the aerosil particles. Increasing the voltage at a fixed frequency resulted in an increase of the turbulence and involved bigger agglomerates in the motion. Furthermore, break-up of the largest agglomerates was observed. With increase of field frequency (at a fixed voltage), motion of the aggregates ceased, starting with the biggest aggregates. Concurrently the memory parameter M decreased (figure 2).

The time required for the appearance of the hydrodynamic effect is several seconds. The ‘boiling’ of the suspension occurs all the time under the electric field action and does not prevent relaxation to the transparent state of the cells after the field is switched off.

Observations by polarized light microscopy show that the transparent state of the cells is caused by both the orientation of the LC and separation of the phases. The effect of the phase separation is especially strong for the unmodified aerosil and can be observed after a few seconds of action by the electric field. A much longer time is needed for separation in this case of the modified

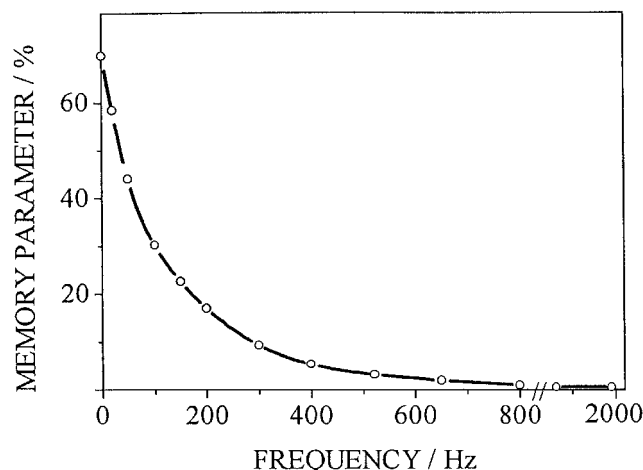


Figure 2. The dependences $M(\nu)$ for the 5CB–hydrophobic aerosil suspension: $c = 10$ wt.%, $U = 10$ V.

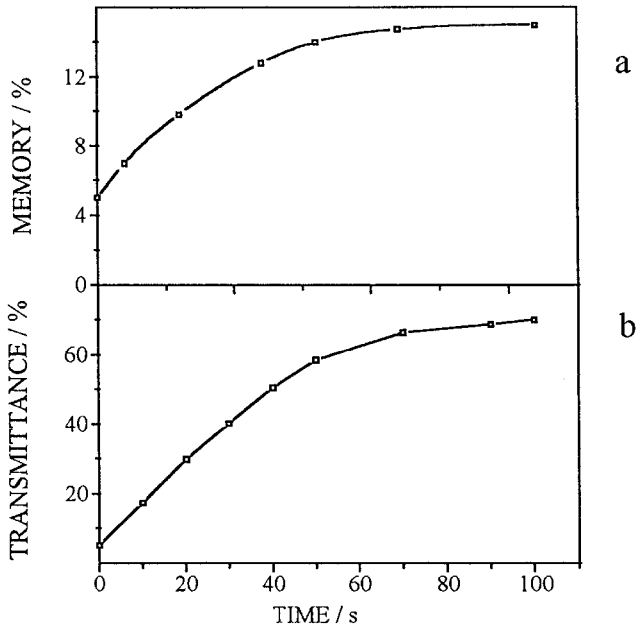


Figure 3. The dependences $M(t)$ (a) and $T_{ch}(t)$ (b) for the 5CB-unmodified aerosil suspension: $c = 15 \text{ V}$, $\nu = 20 \text{ Hz}$.

aerosil. The observed phase separation, as well as the hydrodynamic effect, is accompanied by the interesting effect of a 'swinging' of the system which can be observed with frequencies $\nu < 50 \text{ Hz}$ just after the electric field is switched on. In this case a slow increase in the value of M with time is found (figure 3 (a)). Simultaneously, the amplitude of the variable component of the transmitted light, T_{ch} , also increases (figure 3 (b)).

The instability of the systems makes it difficult to obtain reproducible transparency-voltage characteristics in the low frequency region. The phase separation causes irreversible changes in the starting parameters for each measurement cycle; this leads to the strong dependences of T_{ch} and M upon the number of measurements.

There are no hydrodynamic effects in the high frequency region. Moreover, we did not find any phase separation for all the suspensions investigated. The transparency of the cells is caused by the reorientation of the LC molecules due to the electric field. Figure 4 shows the transmittance-voltage curves for 5CB-R812 (hydrophobic aerosil) suspension ($c = 10 \text{ wt } \%$) measured with decreasing voltage. The saturated value $T_s \approx 90\%$ does not depend on concentration, but the saturation voltage increases with increasing concentration of aerosil. Such results are common for all suspensions investigated. There is no 'swinging' effect in the high frequencies region. Here characteristic switching times of the system from transparent to dark are a few milliseconds (figure 5 (a)). The time for development of the memory effect is of the same order of magnitude (figure 5 (b)).

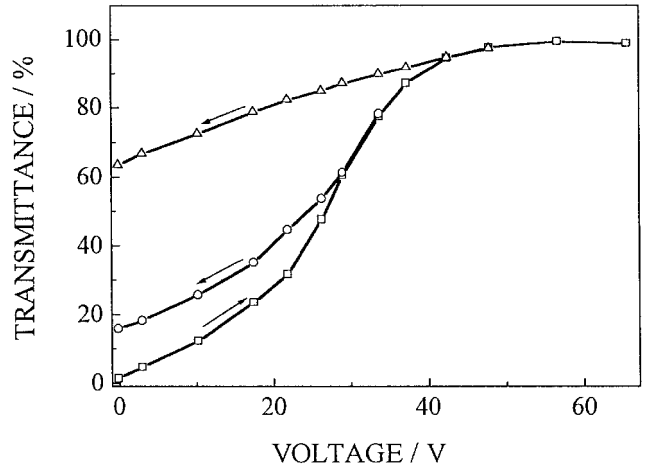


Figure 4. The voltage-contrast curves for suspension '5CB-hydrophobic aerosil' ($c = 6.6\%$) measured by decreasing applied voltage beginning from $U = 35.50 \text{ V}$ ($\nu = 2 \text{ kHz}$).

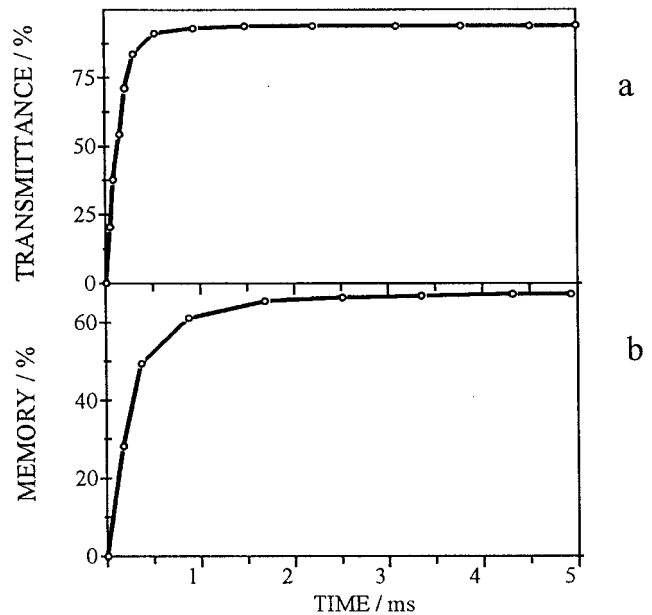


Figure 5. The dependences of $M(t)$ (a) and $T(t)$ (b) for the 5CB-unmodified aerosil suspension ($\nu = 2 \text{ kHz}$).

3. Discussion

The microscopic mechanism of the memory origin was proposed by Eidenschink, Kreuzer *et al.* [3-4]. They supposed that aerosil forms a network structure in a LC matrix with the individual aerosil particles connected through hydrogen bonds. On applying the electric field, the LC molecules orient toward the field direction and involve the aerosil network in the reorientation process. The original aerosil structural network is broken and a new stable network is formed. The resulting network has an anisotropic structure, being oriented in the direction of the electric field, and keeps

the director of the LC parallel to the vector \mathbf{E} , resulting in the transparent state of the system. Thus, the LC orientation is stabilized by the aerosil network in the transparent state.

It is reasonable to suppose that in some region of aerosil concentration, the suspension can be represented as a LC matrix with the insertion of separate aerosil agglomerates. Our own tentative studies by ultrasonic spectroscopy have shown that up to $c = 10$ wt %, the filled nematic LCs have indeed such a structure [10]. The structure and size of the agglomerates is dependent upon the value of c . The estimation showed [7, 10] that the typical average size of agglomerates is about 1000 Å at $c = 5$ –10 wt % and the distance between the agglomerates is of the same order.

We believe that the structure of the agglomerate suspension might be stabilized by the elastic forces of the LC. Certainly, the aerosil agglomerates are in an anisotropic environment. Therefore, it is to be expected that the agglomerates also have to be anisotropic. Reorientation of the anisotropic agglomerates from the equilibrium state is prevented by the elastic torque exerted by the surrounding LC. In turn, the agglomerates can be considered as a spatially-distributed aligning surface stabilising the LC alignment. Thus, it is just the elasticity of the LC that maintains the transparent state while the electric field is switched off.

Let us consider an anisotropic aerosil agglomerate in a homogeneously oriented nematic LC matrix and try to estimate the energy needed to turn the agglomerate in the homogeneously oriented LC. One can describe the aerosil agglomerates as elongated dielectric rods with length L and transverse size R . Both L and R are presumed to be much greater than the dimensions of the molecules of the LC; therefore the agglomerates are macroscopic objects. Since the typical size of LC molecules is about 20 Å and $R > 300$ Å, this assumption is valid.

It is very problematical to find a general solution to the problem of elongated dielectric rods turning in a LC. Therefore we restrict ourselves to two particular cases which have been considered in the literature [11, 12]. In the one elastic constant approximation, the free energy of a system of long dielectric rods (relative geometrical anisotropy $d_a/L = (L - R)/L \approx 1$) providing both parallel and homeotropic anchoring of a surrounding LC with the finite anchoring energy W has a form [9]

$$F \approx \pi K L \frac{\xi}{1 + \xi}, \quad \text{where } \xi = \frac{W R}{K} \quad (1)$$

For typical values $K = 10^{-6}$ dyn, $W = 10^{-2}$ erg cm $^{-2}$ and minimal size $R = 3 \times 10^{-6}$ cm, the anchoring parameter

$\xi \approx 3 \times 10^{-2} \ll 1$. In this case the free energy needed to turn the agglomerate from the equilibrium state is

$$\Delta F \approx \pi K L \xi \approx 3 \times 10^{-13} \text{ erg} \quad (2)$$

This value is an order larger than the energy of thermal fluctuation in the system $k_B T = 4 \times 10^{-14}$ erg.

Expression (2) shows that the larger the size of the agglomerate, the more stable is the transparent state. To estimate the influence of agglomerate anisotropy on the stability of the system, let us explore the model of infinitely strong anchoring of the LC to the anisotropic rod [12]. The energy needed to turn such a rod in a homogeneously oriented LC is proportional to the geometrical anisotropy d_a and θ^2 :

$$F \approx K d_a \theta^2 \quad (3)$$

For $K = 10^{-6}$ dyn, this formula also leads to the value $F \approx 10^{-13}$ erg $\gg k_B T$ at the extremely small anisotropy $d_a = 10^{-7}$ cm. So, the transparent state of the suspension containing non-interacting aerosil particles should be stable, and moreover the ensemble of interacting agglomerates should be stable. Let us estimate the agglomerate concentration when the regions of the director field distortion caused by the agglomerates begin to overlap.

In ref. [11] it is shown that the characteristic effective distance of the director distortion around a particle with radius R is about $3R$. Therefore the critical concentration of agglomerates per unit volume can be estimated as follows:

$$c \sim \frac{1}{(4/3\pi)(3R)^3} \approx 10^{-2} \frac{1}{R^3} \text{ cm}^{-3} \quad (4)$$

The size R of the agglomerates is assumed to be $(3-10) \times 10^{-6}$ cm. In this case cooperative effects should be essential at a concentration of agglomerates $c = 10^{13}$ – 10^{14} cm $^{-3}$. This corresponds to the most effective memory effect observed.

Thus, the above estimations show that the main parameters determining the stability of the transparent state are the size and the anisotropy of the agglomerates, the distance between the agglomerates and the anchoring strength of the LC at the agglomerate's surface. Increase in agglomerate size and anisotropy, as well as aerosil concentration should stabilize the transparent state. The same effect should be provided through increase of the anchoring strength. Let us consider how these tentative conclusions correspond with the experimental results obtained.

The size of aerosil agglomerates usually increases with an increase of c in the liquid matrix [13]. This should lead to stabilization of the transparent state and the amplification of memory parameter with increase of c , corresponding to the initial part of the $M(c)$ curves (figure 1). Nevertheless, one can see that at high concen-

tration, the memory parameter falls. There may be some reasons for this effect. It could be a result, for example, of a non-monotonic dependence $d_a(c)$. For example, close packing may lead to a decrease of agglomerate size and anisotropy at high concentrations (the suspension is supposed to convert to quasi-spheres of aerosil agglomerates in the LC matrix). Another factor could be the creation of a continuous aerosil network which cannot be destroyed by the electric field (the basic concept of Eidenschink, Kreuzer *et al.* [3, 4]).

Our experimental results show that the treatment of the surface of the aggregates, that is the anchoring strength, is very important for the memory effect. Certainly, the efficiency of the memory effect strongly depends on the presence of hydrogen bonds in the system, and this has two main causes. Firstly, an effective interaction of the LC molecules with the aerosil particle surface, that is a high anchoring strength, is possible due to hydrogen bonds. Secondly, the ability to create hydrogen bonds promotes an agglomeration of the aerosil particles that also enhances the stability of the transparent state. In fact, the most effective memory is realized with the suspension A300–5CB. This suspension is characterized by greatest number of hydrogen bonds between the aerosil surface OH groups and the aromatic 5CB molecules [14]. This results in the effective anchoring of the LC molecules with the aerosil particle surface and promotion of the memory effect.

Hydrophobic treatment of aerosil—effectively reducing the number of surface OH groups—decreases the probability of hydrogen bonding between the aerosil particles and also between the aerosil and the LC molecules. This results in a decrease of the memory parameter of the suspension and a shift of the curve $M(c)$ to larger concentrations c (compare curve 1 with curves 2 and 3 in figure 1). Conversely, addition of a hydrogen bond initiator leads to an effective memory parameter increase (curve 4, figure 1).

To change from the scattering state to the transparent state, the system must overcome the stabilizing field of the LC elasticity. Let us estimate whether the driving electric fields are enough to control the orientation state of a suspension. At a small agglomerate concentration, we can use the standard formula for the Fréedericsz threshold [15].

$$\frac{1}{8\pi} E^2 \bar{\varepsilon}_a \geq F_{\text{elastic}} \frac{1}{V} \quad (5)$$

Here $\bar{\varepsilon}$ is the anisotropy of the effective dielectric tensor of the heterogeneous system and V is the volume of the LC director distortion. At small agglomerate concentration, one may consider $\bar{\varepsilon}_a \approx \varepsilon_a$ and estimate $V \approx \pi L (3R)^2$. This approximation leads to the following expression

for the applied voltage needed to make the director turn:

$$U \approx Ed \geq \frac{d}{3R} \left[\frac{8\pi K \xi}{\varepsilon_a (\xi + 1)} \right]^{1/2} \quad (6)$$

For $\varepsilon_a = 10$, $K = 10^6$ dyn and $\xi \approx 10^{-1}$, the value $U \approx 10$ V which is of the same order as that observed experimentally.

It should be noted that the direct reorientation torque from the electric field to the LC is the main, but not the only cause allowing us to disturb the system from the initial polydomain state. The liquid crystal flow, involving the aerosil agglomerates in motion, is the additional factor promoting a destabilization of the initial polydomain structure [16]. This factor is effective in the low frequency region and quickly diminishes with increase in the frequency (see figure 2).

4. Conclusions

The memory effect in filled nematic LCs depends on the modification of aerosil, the aerosil concentration and the parameters of the electric field (frequency and voltage). Hydrogen bonds between the aerosil particles and the liquid crystal play an important role in the memory effect.

The results obtained can be described qualitatively in the frame of a model where the filled nematic is considered as a system of aerosil agglomerates in a liquid crystal matrix. The initial scattering state is due to the polydomain structure of the LC matrix caused by the aerosil agglomerates. Their geometrical anisotropy and sizes and the inter-particle distances depend upon the total concentration of aerosil in the matrix as well as on the properties of the matrix and aerosil surface. Under the action of the electric field the LC molecules orient towards the field direction and involve the aerosil aggregates in the reorientation process. The efficiency of the aerosil motion is determined by the LC anchoring at the agglomerate surfaces. The transparent state produced is stabilized by the elastic forces of the liquid crystal.

The authors thank Audrey Iljin for useful discussions and assistance. The research was supported in part by Grant No. U5 W200 from the International Science Foundation and by Grant GR/J88111 from EPSRC (U.K.).

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