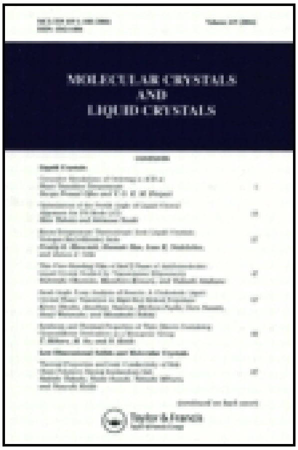

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photodielectric Properties of C_{60} Solution in the Ferroelectric Liquid Crystal

A. V. Koval'chuk [a] & T. N. Koval'chuk [b]

[a] Institute of Physics, NAS of Ukraine, Kiev, Ukraine

[b] Institute for Semiconductor Physics, NAS of Ukraine, Kiev, Ukraine

Version of record first published: 06 Jul 2012

To cite this article: A. V. Koval'chuk & T. N. Koval'chuk (2008): Photodielectric Properties of C_{60} Solution in the Ferroelectric Liquid Crystal, Molecular Crystals and Liquid Crystals, 496:1, 269-277

To link to this article: http://dx.doi.org/10.1080/15421400802451865

Mol. Cryst. Liq. Cryst., Vol. 496, pp. 269–277, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802451865

Photodielectric Properties of C_{60} Solution in the Ferroelectric Liquid Crystal

A. V. Koval'chuk[1] and T. N. Koval'chuk[2]
[1]Institute of Physics, NAS of Ukraine, Kiev, Ukraine
[2]Institute for Semiconductor Physics, NAS of Ukraine, Kiev, Ukraine

Within the range of 10^{-3}–10^{6} Hz, we investigated the frequency dependences of capacity C and resistance R of a 3 wt% solution of C_{60} with attached molecules of 1,8-octanediamine in a ferroelectric liquid crystal (FLC/C60-Ok). The measurements were carried out in darkness and on the exposure to focused white light. The basic feature of the electric properties of solutions of FLC/C_{60}-Oc is a reduction of the ac conductivity σ_{AC} at the transition from the cholesteric to smectic phase. The measurements have shown that the ratio C_P/C_D (the subscripts D and P correspond, respectively, to measurements in darkness and under illumination) has a peak at a frequency of ≈3.5 Hz, and the ratio R_D/R_P increases monotonously up to a constant value within the range of 10^{-3}–10^{3} Hz. These data indicate that the volumetric photoelectric processes are more essential than the near-electrode ones in the solution FLC/C_{60}-Oc as compared with the colloidal mixture $C_{60}+C_{70}$/FLC.

Keywords: dielectric spectroscopy; ferroelectric liquid crystal; fullerene

INTRODUCTION

The polar electrooptical effect (turn of molecule dipoles under action of an electric field) is possible in ferroelectric liquid crystals (FLC), in contrast to the majority of other liquid crystals. For the first time, a practical realization of this effect was offered in work [1], which became a reference point for practical use of FLCs.

The majority of scientific researches of FLCs was directed towards the elucidation of an opportunity to use this material in displays and to

Authors express sincere gratitude to E.V. Basiuk for the availability to use their samples for measurements. The work was financially supported by the budgetary grant 1.4.1 B/134 of the Institute for Physics, NAS of Ukraine.

Address correspondence to A. V. Koval'chuk, Institute for Semiconductor Physics, NAS of Ukraine, 46, Nauki Prosp., Kiev 03028, Ukraine. E-mail: akoval@iop.kiev.ua

improve parameters of these displays [2]. We consider that properties of photosensitive FLCs can be interesting as well. In these materials, the photogenerated charge transport can be efficiently carried out by a turn of molecule dipoles (bonded charges). In this case, the problems caused by the recombination of charge carriers were removed, and at a modulated illumination, the problems concerning contact phenomena were partially removed too.

As the synthesis of photosensitive FLC molecules is not a simple chemical problem, it was concluded to obtain these materials by the introduction of photosensitive molecules into a liquid crystal. We used the fullerenes as such photosensitive impurities.

We showed that, by selecting the fullerene concentration, it is possible to obtain photosensitive colloid mixtures "ferroelectric liquid crystal – fullerene" [3,4] rather stable in time. Their dielectric properties were investigated and it was shown that, at temperatures $T > 329\,\mathrm{K}$, the conductivity of these colloidal mixtures is caused by fullerene conductivity. At $T < 329\,\mathrm{K}$, the dielectric properties of the FLC-fullerene system are basically determined by the properties of FLC. This is supported by the fact that the dielectric spectrum of the colloidal mixtures contains the Goldstone mode.

It was also shown that illumination by the focused white light results in a reduction of resistance R and a change of capacity C of the colloidal mixtures. It should be particularly noted that the illumination results in a reduction of the capacity in the isotropic (I), cholesteric (Chol), and smectic A (SmA) phases whereas the capacity of the chiral smectic (SmC^*) phase increases (positive photodielectric effect). The greatest change of the capacity under illumination was observed near the temperature of phase transition $\mathrm{SmC}^* \leftrightarrow \mathrm{SmA}$. This is the exact verification of the fact that, in the processes of the charge phototransport, the bias currents caused by a turn of molecule dipoles around of the helicoidal axis are present.

But it turned out that the colloidal mixtures are stable no more than two months. Therefore, we made decision to obtain and investigate the solutions of photosensitive molecules in FLC. As it was shown in [5,6], the illumination of these solutions can cause a reorientation of molecules. It was one more precondition to that it would be possible to realize no less interesting photoelectric effects in solutions of photosensitive molecules in FLCs than those in the colloidal mixtures. For adequacy of comparison of the expected results with the data in [5,6], we used the soluble fullerene.

Therefore, the aim of this work was to manufacture fullerene solutions in FLC and to research their photodielectric properties.

MATERIALS AND METHODS

The FLC under study was an eutectic mixture of 4-*n*-hexyloxyphenyl 4'-*n*-decyloxybenzoate and 4-*n*-hexyloxyphenyl 4'-*n*-octyloxybenzoate with LUCH-15 polar chiral additive [7]. For a pure FLC, the scheme of phase and the phase transition temperatures (in K) are as follows:

$$I \xrightarrow{358} Chol \xrightarrow{349} SmA \xrightarrow{345} SmC^{*} \xrightarrow{313} Cr.$$

We used fullerene C_{60} with attached molecules of 1,8-octanediamine ($(NH_2\text{-}(CH_2)_8\text{-}NH_2)$ as a photosensitive impurity. It was producted at the Universidad Nacional Autónoma de México. The solution of this modified fullerene in FLC is photosensitive, by starting from a concentration of 2 wt%. We study a solution FLC + 3 wt% C_{60} with attached molecules of 1,8-octanediamine (FLC/C_{60}-Oc). The examination with the use of a polarizing microscope has shown that the phase transition temperatures for a solution of FLC/C_{60}-Oc are the same as those for the pure FLC to within 0.5 K.

The studies were carried out by using sandwich cells. Transparent layers of In_2O_3 deposited on a glass plate were used as electrodes. Each electrode was divided by etching into measuring and protecting sections. The protecting electrode was grounded during the measurements. We used polyamide to create a planar orientation of molecules.

The composite layer thickness *d* lying within the interval of 30–50 μm was obtained by introducing a Teflon film between the glass plates over the protecting electrode. Due to a high viscosity of the FLC/C_{60}-Oc composite, filling the cells was achieved by pressurizing the composite between the electrodes bearing the Teflon film. An empty (composite-free) volume was left, where d was measured by interferometry. The assembled cell was sealed on its perimeter with a glue.

The temperature stabilization with an error below 0.2 K was carried out in a custom-designed thermostat, having a low level of electromagnetic noise. The measurements were performed in a temperature interval of 315–370 K. The capacity *C* and resistance *R* of the sample were measured within the frequency range of 10^{-3}–10^{6} Hz by using the oscilloscopic method [8–10]. The measured signal had the triangular shape. The peak voltage value was $U_0 = 0.25$ V. Based on the obtained data, the frequency dependence of the ε' and ε'' components of complex dielectric permittivity was analyzed.

The measurements were carried out in darkness and on the exposure to focused white light of a halogen incandescent lamp. The density of light energy equals 1.5 W/cm^2.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Dielectric Properties

In Figure 1, the frequency dependences of imaginary component of dielectric permittivity ε'' for planar oriented FLC/C_{60}-Oc (curve 1) and FLC (curve 2) are presented. In the first and second cases, the measurements were carried out at close values of temperatures which corresponded to the SmC*-phase of FLC.

First, we analyzed features of the dielectric spectrum of FLC. In the investigated range of frequencies, two dispersion areas can be distinguished: low-frequency (10^{-3}–10 Hz) and high-frequency (10^2–10^4 Hz) ones. As we have shown earlier [8–10], the low-frequency dispersion area manifests itself in all liquids and caused by the near-electrode phenomena. The high-frequency area of the dispersion ε' and ε'' in pure FLC arises only in the SmC*-phase and is caused by a turn of molecules around of a helicoidal axis (the Goldstone mode).

It follows from Figure 1 that, in the solution of FLC/C_{60}-Oc, the low-frequency dispersion area ε'' is observed, whereas and the high-frequency one disappears. As the presence of the high-frequency dispersion area ε'' is caused by the SmC*-phase, from the obtained data it follows that only the addition of 3 wt% C_{60}-Oc results in the essential

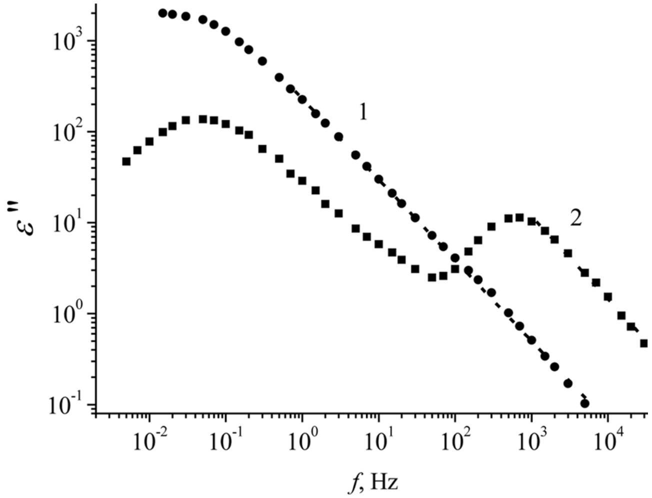

FIGURE 1 Frequency dependences of ε'' for the planar oriented FLC/C_{60}-Oc solution (1) and pure FLC (2) at the temperatures of 313.5 and 314.2 K, respectively.

change of the parameters of samples down to disappearance of ferroelectric properties.

Examining with the use of a polarizing microscope has shown that, in LC phases, the textures of pure FLC and a FLC/C_{60}-Oc solution did not differ from each other. From the preceding, it is possible to make the assumption that the nonchiral phase SmC-phase is realized in the solution instead of the SmC*-phase. Blocking the chirality in the SmC-phase of a FLC/C_{60}-Oc solution most likely occurs because of the formation of a polymeric network between molecules C_{60}. As shown in work [11], this "polymeric" network can essentially affect the LC structure.

The molecule of 1,8-octanediamine (NH_2-$(CH_2)_8$-NH_2) is symmetric. Therefore, it can be attached with its two ends directly to two molecules C_{60}. As to one molecule C_{60}, from 4 up to 8 molecules of 1,8-octanediamine can be attached to it according to the chemical analysis, which is a direct confirmation of forming the polymeric network of molecules C_{60}-Oc in a FLC/C_{60}-Oc solution. One more confirmation of this assumption may be a substantial increase of the viscosity of a FLC/C_{60}-Oc solution in comparison with that of pure FLC. This may be concluded from the analysis of the process of filling of a capillary with a FLC/C_{60}-Oc solution or pure FLC when manufacturing the samples.

It follows from Figure 1 that the linear dependence ε'' on the frequency f is revealed at high frequencies. This enables one to find the conductance σ_{AC} from the equation

$$\sigma_{AC} = \varepsilon_0 \, \varepsilon' \omega, \tag{1}$$

where ε_0 is the dielectric permittivity in vacuum, and $\omega = 2\pi f$ is circular frequency.

B. Electric Properties

In Figure 2, the temperature dependences σ_{AC} of planar oriented FLC/C_{60}-Oc (curve 1) and FLC (curve 2) are resulted. Comparison of these data shows that presence of C_{60}-Oc changes cardinally a course of its temperature dependence of σ_{AC} relative to that of pure FLC. The basic difference of the electrical properties of FLC/C_{60}-Oc solutions from those of pure FLC is a reduction of σ_{AC} at the transition from the cholesteric phase to smectic one. In [12], we have shown that, in pure FLC, at the transition from cholesteric phase to the smectic one, the value of σ_{AC} increases because of nonlinear dielectric properties of the SmC*-phase. In this case at such a phase transition, the change of conductivity $\Delta\sigma_{AC}$ enters into the term quadratic in

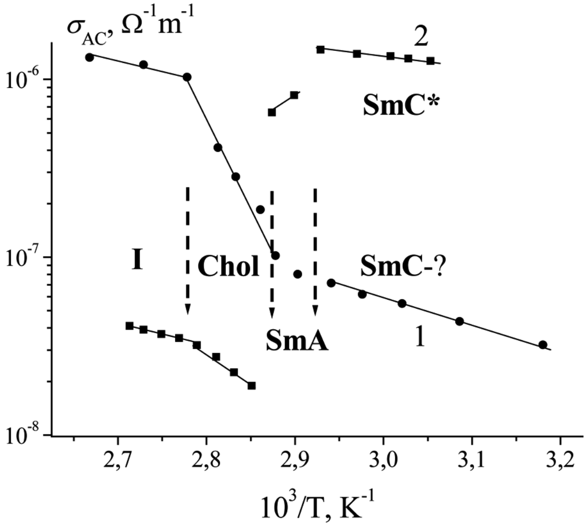

FIGURE 2 Temperature dependences of ac conductivity for the planar oriented FLC/C_{60}-Oc solution (1) and pure FLC (2). Pointers mark the temperatures of phase transitions.

the electric field member in the nonlinear dependence of the polarization P on the applied electrical field E

$$P(t) = \varepsilon_0(\varepsilon' - 1)E(t) + \frac{\Delta\sigma_{ACd}}{4U_0 f}E^2(t). \qquad (2)$$

Therefore, the temperature dependence of σ_{AC} for the solution FLC/C_{60}-Oc which is opposite relative to that of pure FLC confirms once again that the introduction of C_{60}-Oc into FLC results in the SmC*-phase blocking. As a consequence of this fact, which is characteristic of most of the liquid crystals, is observed at the transition from the cholesteric phase to the smectic one, rather than an increase of σ_{AC} (which is characteristic for pure FLC).

It is worth to note that the analysis of the temperature dependences σ_{AC} of a FLC/C_{60}-Oc solution and pure FLC allows us to draw conclusion that the presence of C_{60}-Oc does not influence the temperatures of phase transitions.

C. Photodielectric Properties

In Figure 3, we give the frequency dependences of the ratios of the capacities, C_P, of a FLC/C_{60}-Oc solution (curve 1) and a colloidal mixture $C_{60} + C_{70}$/FLC (curve 2) under illumination by focused white

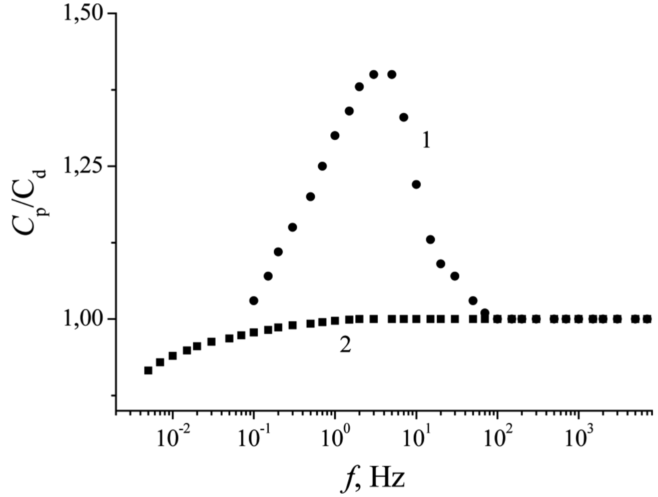

FIGURE 3 Frequency dependences of the ratios of the capacities C_P/C_D for the FLC/C_{60}-Oc solution at the temperature of 362 K (1) and colloidal mixtures $C_{60}+C_{70}$/FLC at the temperature of 360 K (2) measured in darkness (D) and on exposure to the focused white light capacity of 1.5 W/cm^2 (P).

light with a power of 1.5 W/cm^2 to the capacity C_D when measuring in darkness at the temperature that corresponds to phase I. It is clearly seen that the ratio C_P/C_D for a FLC/C_{60}-Oc solution is more or equal to unity. That is, the frequency-dependent capacity of samples either increases or is not changed in general under the action of light. As follows from Figure 3, the ratio C_P/C_D has the peak at a frequency of about 3.5 Hz. It follows from the analysis of the frequency dependences of ε' and ε'' that the frequencies, at which the peak of C_P/C_D is observed, correspond to a segment demonstrating the sharp increase of both components of the complex dielectric permittivity with decrease in the frequency *f*. As was marked already earlier, this segment of the dielectric spectrum is caused by the near-electrode phenomena. Therefore, an increase in the capacity of a FLC/C_{60}-Oc solution under the exposure to light can be explained by changes of the near-electrode layer parameters. The frequency dependence of the ratio C_P/C_D for a colloidal mixture $C_{60}+C_{70}$/FLC (curve 2) differs from the same dependence for a FLC/C_{60}-Oc solution (curve 1) only at low frequencies ($f < 10^2$ Hz). This distinction consists in that the ratio C_P/C_D has the peak for a FLC/C_{60}-Oc solution, and this ratio for a colloidal mixture $C_{60}+C_{70}$/FLC decreases monotonically with a reduction of the frequency.

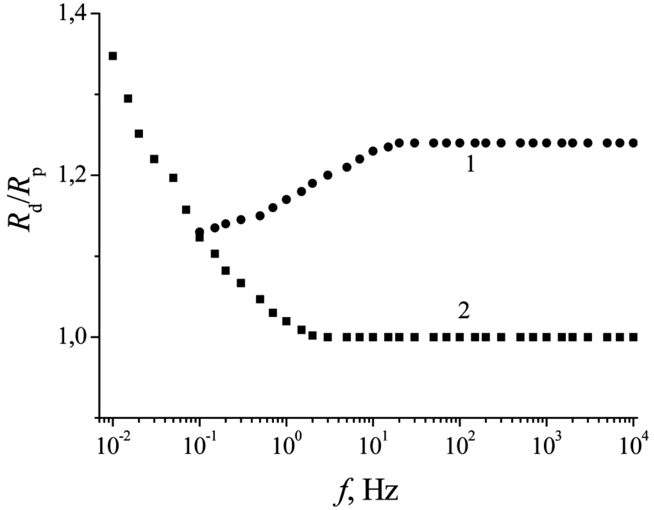

FIGURE 4 Frequency dependences of the ratios of the resistances R_P/R_D for the FLC/C_{60}-Oc solution at the temperature of 362 K (1) and colloidal mixtures $C_{60}+C_{70}$/FLC at the temperature of 360 K (2) measured in darkness (D) and on exposure to the focused white light capacity of 1.5 W/cm^2 (P).

In Figure 4, we present the frequency dependence of the ratios of the resistances of a FLC/C_{60}-Oc solution (curve 1) and a colloidal mixture $C_{60}+C_{70}$/FLC (curve 2) when measuring in darkness, R_D, to the resistance under the exposure by focused white light, R_P, at the temperature that corresponds to phase I.

It is seen that $R_D/\mathrm{R}_P \geq 1$ within the full frequency range. For a FLC/C_{60}-Oc solution (curve 1) in the full frequency range, the illumination results in a reduction of the resistance. At low frequencies, the ratio R_D/R_P increases with the frequency by reaching the value of 1.25 for $f = 10$ Hz. For $f > 10$ Hz, the ratio R_D/R_P does not depend on the frequency.

For a colloidal mixture $C_{60}+C_{70}$/FLC (curve 2), the ratio R_D/R_P is equal to unity and did not depend on the frequency for $f > 10$ Hz. For this frequency range, the illumination did not influence the resistance of samples. For $f < 10$ Hz, we observed the opposite behavior of the properties of a FLC/C_{60}-Oc solution: a reduction of R_D/R_P with increase of the frequency. From the comparison of these data, it is possible to draw the important conclusion that photoprocesses occur basically in volume of samples in a FLC/C_{60}-Oc solution and in the near-electrode areas in a colloidal mixture.

CONCLUSIONS

1. The photosensitive solution FLC + 3 wt% C_{60}-Oc is produced, and it is shown that, in its dielectric spectrum, there is no high-frequency region caused by rotation of molecules around of a helicoidal axis (the Goldstone mode).

2. The basic feature of the electric properties of solutions FLC/C_{60}-Oc is a reduction of the ac conductivity at the transition from the Chol to SmC* phase.

3. We assume that the presence of a solution results in a significant increase in the rotary viscosity and to the blocking of the ferroelectric state. One of the possible mechanisms of this phenomenon can be the formation of a polymeric network between C_{60} molecules.

4. The measurements have shown that the ratio C_p/C_D has the peak at a frequency of $\approx$3.5 Hz, and the ratio R_D/R_P increases monotonically up to a constant value within the range from 10^{-3} to 10^3 Hz. The photoprocesses occur in the near-electrode region in the colloidal mixture $C_{60} + C_{70}$/FLC and in volume of a sample for the FLC/C_{60}-Oc solution.

REFERENCES

[1] Clark, Noel A. & Lagerwall, Sven T. (1980). *Applied Physics Letters*, *36*, 899.
[2] Musevic, I., Blinc, R., & Zeks, B. (2000). *The Physics of Ferroelectric and Antiferroelectric Liquid Crystals*, World Scientific, Singapore.
[3] Koval'chuk, A. V., Golovataya, N. M., Shevchuk, A. F., Naiko, D. A., & Basiuk. E.V. (2004). *Nanotubes, Fullerenes and Carbon Nanostructures*, *12*, 681.
[4] Shevchuk, A., Naiko, D., Koval'chuk, A., & Basiuk, E. (2004). *Ukr. J. Phys.*, *49*, a21.
[5] Vlahakis, Jason Z. & Lemieux, Robert P. (2004). *J. Mater. Chem.*, *14*, 1486.
[6] Maly, Kenneth E., Zhang, Peng, Wand, Michael D., Buncela, Erwin., & Lemieux, Robert P. (2004). *J. Mater. Chem.*, *14*, 2806.
[7] Loseva, M., Chernova, N., Rabinovich, A., Pozhidaev, E., Narkevich, J., Petrashevich, O., Kaszachkov, E., Korotkova, N., Schadt, M., & Buchecker, R. (1991). *Ferroelectrics*, *114*, 357.
[8] Koval'chuk, A. V. (1998). *Functional Materials*, *5*, 428.
[9] Koval'chuk, A. V. (1998). *J. Chem. Phys.*, *108*, 8190.
[10] Koval'chuk, A. V. (2001). *J. Phys. Condens. Matter*, *13*, 10333.
[11] Eidenshink, R. & de Jeu. W. H. (1991). *Electron. Lett.*, *27*, 1195.
[12] Koval'chuk, A. V., Pivnenko, M. N. (2002). *Ukr. J. Phys.*, *47*, 154.