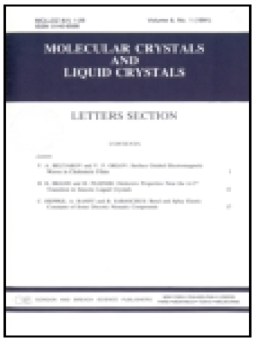

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The Electro-Optical Properties of Twisted Nematic Liquid Crystals Modified by N-Alcohols

JUN-WEI CHEN, CHAO-RAN WANG, TSU-RUEY CHOU,
WEI-TING CHEN, AND CHIH-YU CHAO*

Department of Physics, National Taiwan University, Taipei, Taiwan, R.O.C.

We present a simple and efficient way to improve the performance of the twisted nematic liquid crystal (LC) system by doping a small amount of n-alcohols. The LCs modified by n-hexanol demonstrates the optimum electro-optical properties of lower driving voltage and shorter response time. Our measurements indicate that the n-alcohols can be treated as surfactants to modify LCs for lowering zenithal anchoring energy relative to undoped LCs. Without the drawbacks of precipitation and aggregation that the nanoparticles could have, the method of doping n-alcohol liquids provides a more stable and reliable choice to apply in the various LC display systems.

Keywords: Liquid Crystals; Surfactant; Doping.

1. Introduction

The nematic liquid crystals (LCs) are the most common type of anisotropic fluid with the electrically controllable property. Based on the specific feature, nematic LCs have been developed to a mature technology providing a wide range of applications including various electro-optical devices such as LC displays (LCDs) [1–4], switchable grating [5] and phase modulator etc [6]. Nowadays, LCDs are still a major monitor with different size full of our life from television to mobile phone. In order to obtain better electro-optical performance of LCDs, it is always an important issue to shorten the response time and decrease the driving voltage for the aim of fast switching and energy-saving. For this purpose, in recent years, nanoparticles have been used as dopants in LC systems to improve their electro-optical properties [7–11]. For instance, the conductive carbon nanotubes (CNTs) were found to successfully decrease the driving voltage of twisted nematic (TN) LCs by lowering the ion effect. But, because of the conductive property of CNTs, the CNTs doped LCs were not able to maintain enough voltage-holding ratio (VHR) across the LC cells [12]. In LCDs, the low VHR condition may lead to a poor contrast and the phenomenon of image sticking, which degrades the performance of LCDs [13]. Since maintaining high VHR is such an important work, our team developed an alternative way that replaces the conductive CNTs with insulating nanoparticles such as diamond powders, ZnO, TiO_2, and Si_3N_4 for doping into LCs [14,15]. −t has been demonstrated that these insulating nanoparticles used as dopant can efficiently decrease the driving voltage and still maintain a high VHR level. Although

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[*] Address correspondence to C. Y. Chao, Department of Physics, National Taiwan University, Taipei 10617, Taiwan, R.O.C. E-mail: cychao@phys.ntu.edu.tw

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the method of doping insulating nanoparticles into LCs obtains a huge success in improving the quality of LCDs, however, these nanoparticles might precipitate or aggregate after a long time use without suitable treatments such as surface modifications. To overcome the struggle, we propose a much simpler way to avoid the drawbacks of using nanoparticles and can successfully obtain comparable results.

In this paper, functional liquids, different kinds of n-alcohols were used to dope into the LC host for modification as surfactants. And the LCs modified by the n-alcohols demonstrate fantastic electro-optical properties in the ways of decreasing driving voltage and shortening response time. Besides, from the results of time-evolved transmittance, it shows that the ability of voltage holding would not be obviously influenced after the doping of the n-alcohol liquids. Moreover, according to the calculation results from the measurements of LC parameters, our data conclude that the doped n-alcohols can be treated as surfactants to efficiently lower the zenithal anchoring energy between the alignment layer and LCs. Essentially, the n-alcohol liquids doping method provides a more reliable choice than the use of nanoparticles doping. The surfactant n-alcohols are possibly used in different LC systems that open a simple and efficient way to enhance the performance of LC electro-optical devices for the display applications.

2. Experimental Details

In our experiment, a nematic LC mixture of the ZCE-5099LA (Chisso) and the n-alcohols such as n-ethanol, n-butanol, n-hexanol and n-octanol were employed. And the 4.2 μm thickness ITO (indium tin oxide) glass cells with mutually perpendicular rubbed polyimide as alignment layers were prepared. To realize the effect of n-alcohols doping in the nematic LCs, a small amount of n-alcohols were added into LC ZCE-5099LA. Then these materials were uniformly mixed by gently stirring in glass bottles for 1 h. In our experiments, we deal with these alcohols in a very careful way. These materials were uniformly mixed by gently stirring in glass bottles for 1 h. We stir these materials in a very slow speed and the glass bottles were sealed for avoiding alcohols leaking. Subsequently, the LC ZCE-5099LA mixed with different concentrations of n-alcohols (modified LCs) were injected into the cells by capillary action. After these materials were injected into cells, these cells were sealed with UV gel immediately. To further understand the electro-optical properties of modified LCs, the transmittances of the cells under various applied voltage were measured. The voltage-transmittance curves were measured by an electro-optical measuring system consisting of a He-Ne (632.8 nm) laser, a pair of polarizers, sample cell mounted in rotatable

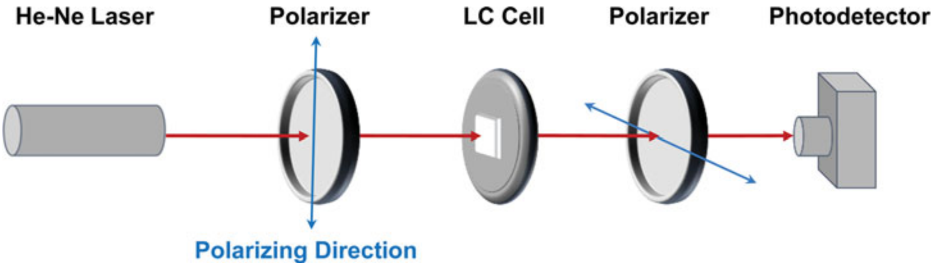

Figure 1. The illustration shows the setup of the electro-optical measurement system. The LC cell is placed between a pair of polarizers with mutually perpendicular polarizing directions for the operation of a normally white TN mode.

holder and the photodetector, as shown in Fig. 1. At the beginning, the polarizers were tuned to be perpendicular with each other to make sure the transmittance minimum. Then the sample cell with modified LCs was placed between the crossed polarizers and tuned to make the transmittance reach maximum by setting the rubbing directing to be parallel or perpendicular with the polarization of polarizers. And the sample cell was driven by an AC field (1 kHz, square wave) supplied by the function generator SRS DS360 which was controlled by a computer with LabView programming. Then the transmittances under applied voltage were recorded through the photodetector. The voltage required for reaching 90% and 10% transmittance relative to the initial light intensity was defined as driving voltage V_{90} and V_{10}, respectively. The contrast ratio (CR) was obtained by calculating the maximum light transmission over the minimum transmission in the electric field off and on (5 V) states, respectively. And so on, the polarized optical microscope (POM) observations of sample cells in bright and dark states were conducted using Olympus BX51. The response time was calculated by the sum of rise time τ_{on} and decay time τ_{off}. The switching times of the τ_{on} and τ_{off} were recorded for varying the transmittances 100-10% and 0-90% in the electric field (5 V) on and off, respectively. In addition, to confirm the ion problem would not occur by doping n-alcohols in LCs, the time-evolved transmittances were measured in 3 DC volts. For verifying the influence of n-alcohols in anchoring energy W_θ, the modified LCs were injected into the 15 μm thickness ITO glass cells with anti-parallel alignment layers. Then the dielectric anisotropy $\Delta\varepsilon$ and elastic constants K were found out by the measurements through Instec ALCT instrument. And the saturation voltages V_{s} were examined by the measurement of the phase retardation.

3. Results and Discussion

The results of voltage-transmittance curves of the pure LC ZCE-5099LA and those doped with different n-alcohols at 5 wt% in concentration are shown in Figure 2(a). It can be seen that the pure LC ZCE-5099LA needs higher driving voltage to switch from bright to dark state. Relatively, for the modified LCs doped with 5 wt% n-alcohols, the driving voltages required for switching are all below to that of the undoped LC. Among these dopant liquids, the n-hexanol provides the most remarkable effect for decreasing the driving voltage of the LC ZCE-5099LA. These results demonstrate that the n-alcohols, especially the n-hexanol, may influence the basic electro-optical parameters of the LC ZCE-5099LA. For further understanding the properties of the n-alcohols doped LC, these modified LCs are injected into the cell with anti-parallel alignment layers. Then the dielectric anisotropy $\Delta\varepsilon$ and elastic constants K were obtained by the measurements through the use of Instec ALCT instrument. The saturation voltages V_{s} were found by the measurement of the phase retardation. Combined with the dielectric anisotropy $\Delta\varepsilon$, elastic constants K and saturation voltages V_{s}, the zenithal anchoring energy W_θ can be calculated from the equation as the saturation voltage is large [16]:

$$W_\theta = \frac{V_s\sqrt{\varepsilon_0 \Delta\varepsilon K}}{d}, \tag{1}$$

where d is the cell gap of the LC cells and ε_0 is the vacuum permittivity, and these parameters of the doped LCs were listed in table 1. From Table 1, the results show that the dielectric anisotropy $\Delta\varepsilon$, elastic constants K and saturation voltages V_{s} would be influenced by the doping of 5 wt% of n-alcohols. In addition, the zenithal anchoring energy W_θ is obviously decreased relative to the pure LC. Figure 2(b) and 2(c) show the relationship between

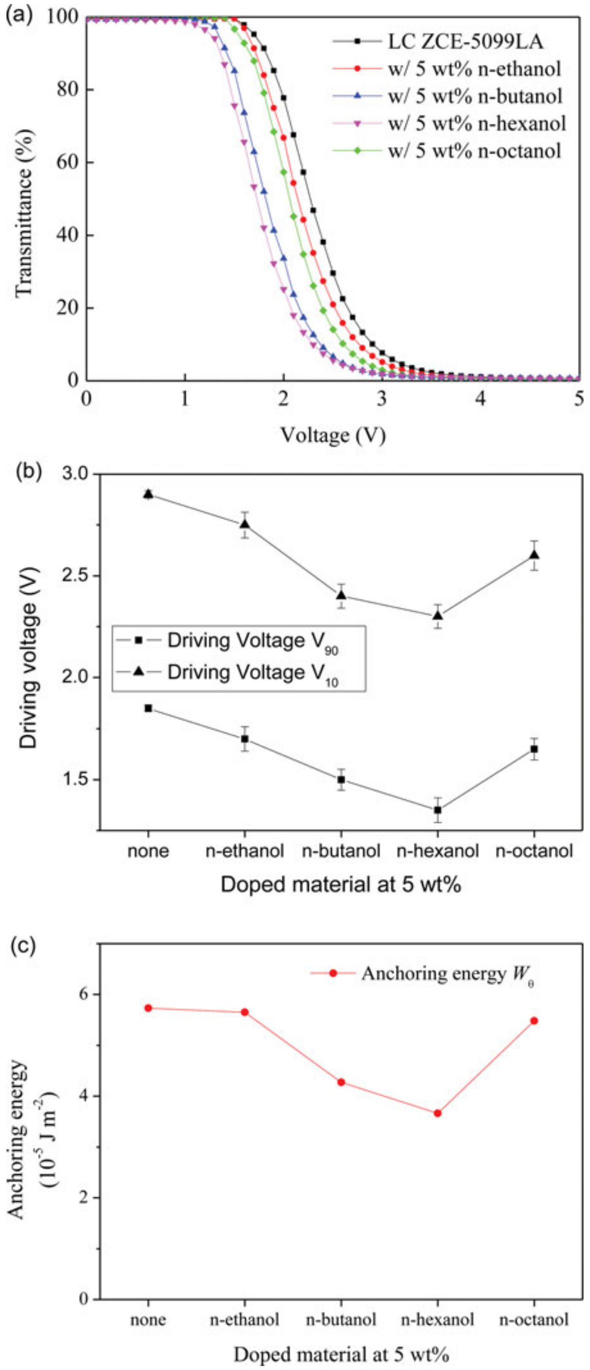

Figure 2. (a) The transmittance-voltage curves of LC ZCE-5099LA with 5 wt% n-alcohols in the 4.2 μm thick TN LC cells. The transmittances were normalized by the initial light intensity. (b) The driving voltage V_{90}, V_{10} of the LC ZCE-5099LA modified by n-alcohols at 5 wt%. (c) The anchoring energy W_θ of the LC ZCE-5099LA modified by n-alcohols at 5 wt%

Table 1. The properties of LC ZCE-5099LA doped with n-alcohol at 5 wt% in concentration

Material Type	$\Delta\varepsilon$	K (pN)	V_s (V)	W_θ (10^{-5} J/m^2)
ZCE-5099LA	5.50	6.16	15.8	5.73
w/ 5 wt% n-enthaol	5.29	5.93	16.2	5.65
w/ 5 wt% n-butyaol	5.18	4.43	14.3	4.27
w/ 5 wt% n-hexanol	4.36	3.89	14.2	3.66
w/ 5 wt% n-octanol	4.96	5.54	16.8	5.48

driving voltage V_{90}, V_{10}, and the anchoring energy W_θ of the LC ZCE-5099LA modified by n-alcohols at 5 wt%. It can be seen that the driving voltage V_{90} and V_{10} would decrease as the anchoring energy W_θ reduced. Especially, the utility of n-hexanol can efficiently reduce the zenithal anchoring energy about half relative to the condition of pure LC ZCE-5099LA. It is believed that the reduction of the zenithal anchoring energy is the main reason that induces the decrement of driving voltage [16,17].

Resulting from the largest decrease of driving voltage caused by doping n-hexanol, the effect of various concentration of n-hexanol doping in the LC is further investigated. The LC ZCE-5099LA with 0, 1, 3, 5, and 7 wt% of n-hexanol were injected into the cells. The voltage-transmittance curves of the LC ZCE-5099LA doped with n-hexanol at 0, 1, 3, 5, and 7 wt% in concentration are shown in Figure 3(a). And the experiment results of driving voltage V_{90}, V_{10}, and contrast ratio (CR) are shown in Table 2. It can be observed that the driving voltage decreases more as the concentration of n-hexanol increases. Relative to the pure LC, the LC with 5 wt% of n-hexanol demonstrates the best results with the driving voltage V_{90} & V_{10} decreased from 1.85 V to 1.35 V and 2.90 V to 2.30 V (about 27% and 21% decrements), respectively. And the contrast ratio is enhanced from 197 to 240. However, as the doped concentration of n-hexanol reaches 7 wt%, different trend of data i.e. the higher driving voltage and lower contrast ratio are obtained. To explain the phenomenon, the zenithal anchoring energies of different concentrations of n-hexnaol doping into LC ZCE-5099LA were obtained by the eq. (1) through the measurements described previously (shown in Table 2). And Fig. 3(b) and 3(c) show the relationship between driving voltage V_{90}, V_{10}, and the anchoring energy W_θ of the LC ZCE-5099LA modified by n-hexanol at 0,

Table 2. The electro-optical properties of LC ZCE-5099LA with 0, 1, 3, 5 wt% of n-hexanol doping

Material Type	V_{90} (V)	V_{10} (V)	τ_{on} (ms)	τ_{off} (ms)	CR	W_θ (10^{-5} J/m^2)
ZCE-5099LA	1.85	2.90	2.80	15.52	197	5.73
w/ 1 wt% n-hexanol	1.75	2.80	2.62	15.64	220	5.40
w/ 3 wt% n-hexanol	1.60	2.70	2.53	15.71	236	4.59
w/ 5 wt% n-hexanol	1.35	2.30	2.25	15.90	240	3.66
w/ 7 wt% n-hexanol	1.55	2.35	2.20	16.18	140	2.02

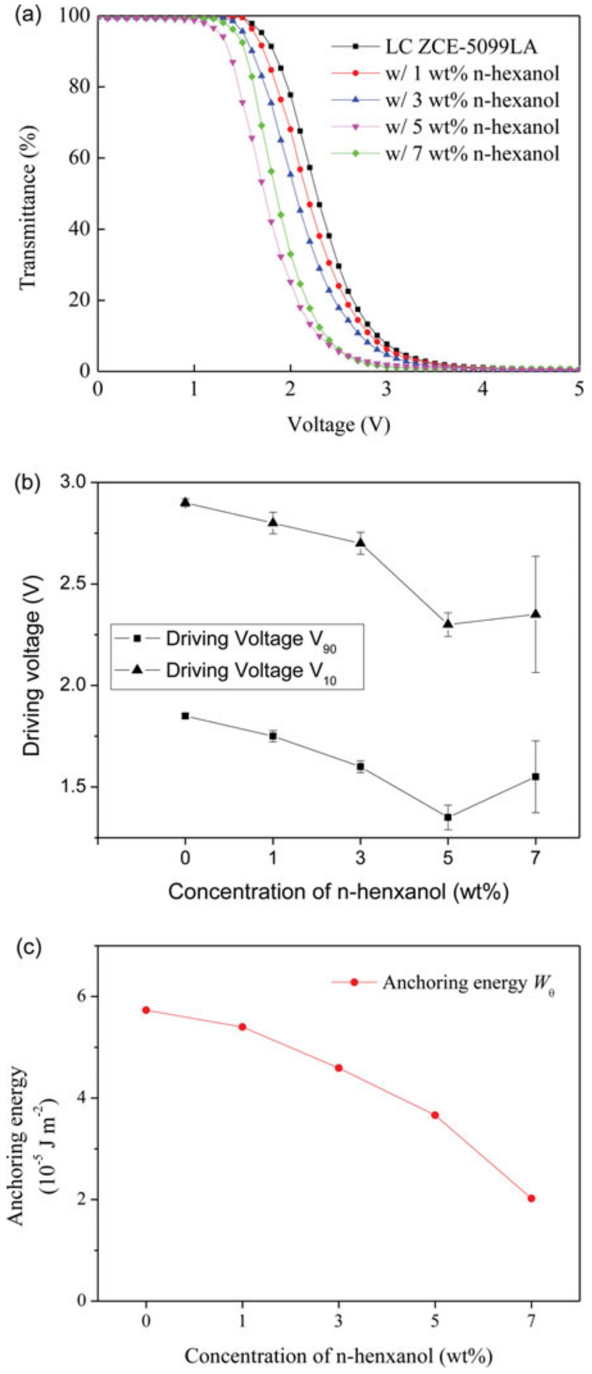

Figure 3. (a) The transmittance-voltage curves of LC ZCE-5099LA doped with 0, 1, 3 and 5 wt% of n-hexanol in the 4.2 μm thick TN LC cells. (b) The driving voltage V_{90}, V_{10} of the LC ZCE-5099LA modified by n-hexanol at 0, 1, 3, 5, and 7 wt%. (c) The anchoring energy W_θ of the LC ZCE-5099LA modified by n-hexanol at 0, 1, 3, 5, and 7 wt%.

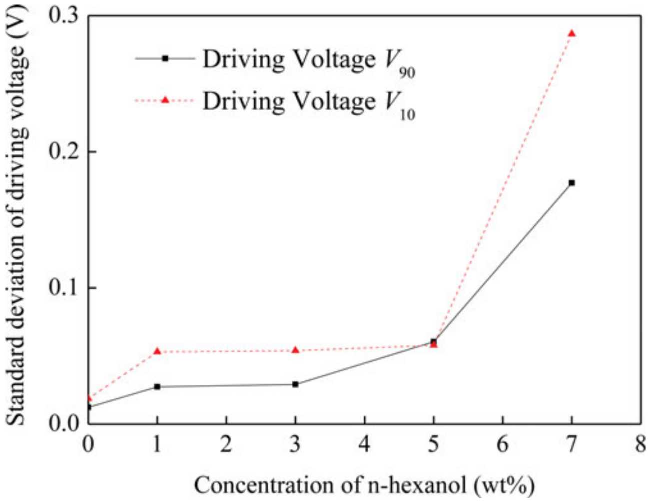

Figure 4. The standard deviations of measured driving voltage V_{90} & V_{10} of LC ZCE-5099LA doped with different concentrations of n-hexanol.

1, 3, 5, and 7 wt%. It can be seen that the anchoring energy W_θ reduces as the concentration of n-hexanol increases. The anchoring energy W_θ attains minimum as the 7 wt% of n-hexanol is doped into LCs. For the concentration of n-hexanol doping below 7 wt%, we find that the driving voltages V_{90} and V_{10} keep decreasing while the anchoring energy W_θ is reduced. Based on the success of 5 wt% of n-hexanol doped into the LC, we also expect that LCs doped with higher concentration of 7 wt% n-hexanol should obtain better performance. However, the data show that the adding of higher concentration of n-hexanol in the LCs did not cause better results. We considered that as the higher concentration (>5%) of alcohols were used, the anchoring energy are largely reduced so that the order parameters decrease, which leads a poor electro-optical performance. Fig. 4 shows the standard deviation of measured driving voltage V_{90} and V_{10} with different concentrations of n-hexanol in LCs. The result demonstrates a low standard deviation of driving voltage V_{90} and V_{10} as the n-hexanol concentrations of lower than 5 wt% were doped into the LCs. It indicates that the modified LCs exhibit stable electro-optical properties in the range of doped n-hexanol concentration lower than 5 wt%. But the standard deviations of driving voltage V_{90} and V_{10} dramatically increased as the concentration of n-hexanol with 7 wt% was added to the LCs. It is believed that the alignment of LC molecules would be influenced by over low anchoring energy caused by high doping concentration of n-hexanol surfactant (> 5 wt%), and that leads to the poor electro-optical performance.

The rise time τ_{on} and decay time τ_{off} of the LC doped with n-hexanol at the various concentrations were measured by using 5 V as bias voltage and shown in table 2. It can be seen that as the concentration of n-hexanol increases, the rise time would decrease and the decay time would increase. This property is consistent with the result of decrement of the anchoring energy. For the optimum case of 5 wt% of n-hexanol doped into LCs, the rise time τ_{on} is shortened from 2.80 to 2.25 ms (about 20% decrement) relative to the undoped condition. And the response time for the modified LCs is slightly shorter than the undoped case. Fig. 5 shows the POM images of the dark states and bright states of the cell with pure LCs and modified LCs by 5 wt% n-hexanol. It can be seen that the resulting contrast ratios of the cell with pure LCs and 5 wt% modified LCs were not obviously influenced by this

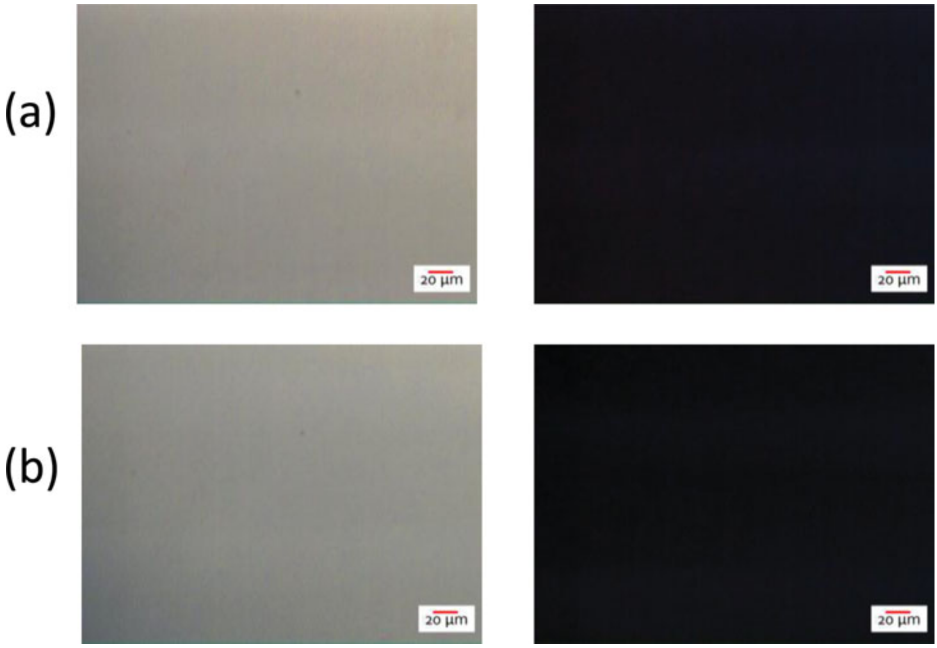

Figure 5. The POM pictures of (a) pure LC ZCE-5099LA and (b) LC ZCE-5099LC doped with 5 wt% n-hexnaol in the TN LC cell at bright and dark states, respectively.

doping work. In our experiments, we found the viscosity would reduce as the alcohols were mixed with LC. And the results are consistent with the influence of decrement of anchoring energy. From these experiment results, it implies that the n-hexanol can be treated as a kind of surfactant to effectively reduce the anchoring energy between the alignment layer and LC molecules, and thus induces smaller driving voltages, shorter rise times and longer decay times in LCs [16–18].

For understanding whether the doping of n-alcohols would induce the drawback of ion effect, the time-evolved transmittances were measured in this work. Fig. 6 shows the results of pure ZCE-5099LA and modified LC doped with 5 wt% n-hexanol in 3 DC volts. As the time went by, the transmittance of modified LC would decrease just about 6% after 4 min. This result implies that the doping of 5 wt% n-hexanol would not result in the increment of ion concentration or influence the maintenance of VHR. To examine the generality of the surfactant effects, the n-hexanol was also doped into another LC material E7 with the concentration of 0, 1, 3, and 5 wt%. The voltage-transmittance measurement results of the doped LC E7 are shown in Figure 7. The results exhibit the same phenomenon that the driving voltage can be decreased by doping of n-hexanol in the LC E7. As the concentration of n-hexanol doping increases, more decrement in the driving voltage is observed. The appearance of the peak comes from the fact that the E7 is not perfectly suitable for the 4.2 um TN LC cell. But it can be seen that the n-hexanol also works as a surfactant in the LC E7. Therefore, through the experiment, it is realized that the n-hexanol can be used in the TN LC systems and plays the role of surfactant to reduce the anchoring energy for improving the electro-optical performance of LCDs.

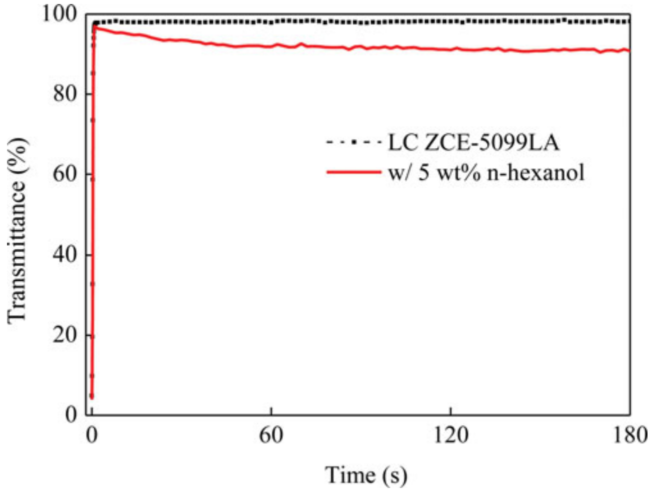

Figure 6. The time-evolved transmittance curves of pure LC ZCE-5099LA and modified LC by 5 wt% n-hexanol in 3 DC volts.

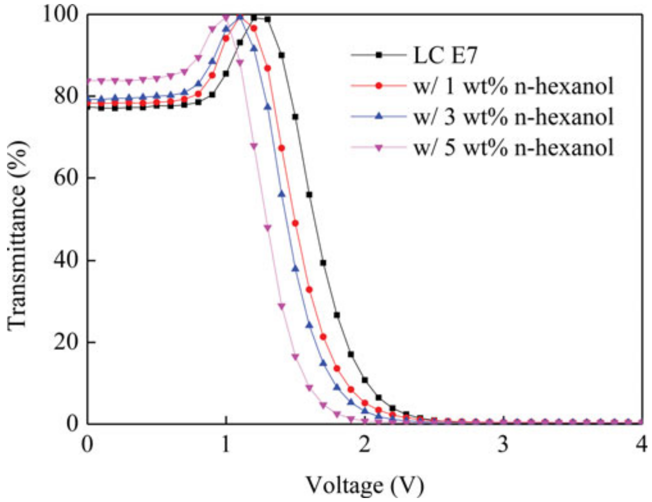

Figure 7. The transmittance-voltage curves of LC E7 with 0, 1, 3 and 5 wt% of n-hexanol doping in the 4.2 μm thick TN LC cells.

4. Conclusions

In conclusion, we present a simple and efficient way to improve the performance of the TN LC system by modifying the LC with a small amount of n-alcohols as surfactants to reduce the zenithal anchoring energy between the alignment layer and LCs. The LCs modified by the n-alcohol surfactants demonstrate lower driving voltage and shorter rise time. In the case of LC doped with 5 wt% n-hexanol, the driving voltage decreases about 27 and 21% in V_{90} and V_{10}, and the rise time τ_{on} can be shortened about 20% relative to the undoped LC host. Besides, the contrast ratios of the modified LCs are also better than the undoped case. The modified LCs exhibit high stability in electro-optical properties as the doped concentration of n-hexanol is lower than 5 wt%, which indicates that the orientation of LC molecules would not be influenced by the liquid doping method. And the result of time-evolved transmittance further shows that the ability of voltage holding is still maintained after the doping of n-hexanol liquid. Besides, the generality of the n-alcohol surfactant effects is demonstrated through the experiments with two kinds of LC host materials. To sum up, without the drawbacks that doping solid nanoparticles could have, the simple n-alcohol liquid doping method provides a more promising opportunity for applications in various LC display systems.

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