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CHROMATIC PROPERTIES OF DYE GUEST-HOST FERROELECTRIC LIQUID CRYSTALS

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Abstract This paper describes the operation of a single polarizer for Dye Guest-Host Ferroelectric Liquid Crystals (DGHFLC). The electrooptical and chromatic properties have been studied for a FLC doped with two dichroic dyes in black and red coloration. The results shows that the increase of dye concentration improves the contrast ratio, color difference ΔE^* and chroma C^*_{uv} of the DGHFLC cell, but decrease lightness L^* Therefore, a distinct difference location is observed on the chromaticity diagram of the coloured and colourless state while voltage is applied. For DGHFLC cell, the color difference ΔE^* and contrast ratio continue to increase with the increase of applied voltage and reach saturation finally, but the threshold voltage almost remain the same as those of the FLC host. The rotational viscosity and response time of the mixture increase with the increase of dye concentration, especially at low temperatures. The response time of the DGHFLC cell also increases due to the increase of rotational viscosity of the FLC host. The increase of rotational viscosity leads to a good memory effect and an excellent bistable state.

INTRODUCTION

The guest-host effect is the first electrooptical effect discovered to be used on liquid crystal displays.[1,2] While all other electrooptical effects depend on the birefrigence of liquid crystals, the guest-host effect make use of the alignment of dichroic dye molecules (guest) by a liquid crystalline matrix (host). The properties have been reviewed for several types of display devices based on the guest-host effect used in nematic system.[3] The concept of ferroelectric liquid crystal (FLC) displays was first demonstrated by Clark and Lagerwall.[4] FLC displays offer potential advantages over the widely used TN and STN displays because of their bistability, memory and fast switching capability.

The use of dichroic dyes in the fabrication of guest-host type displays have been investigated since the 1980's for ferroelectric liquid crystal.[5,6] To compare with the FLC displays devices, dichroic dyes was used to be dissolved in ferroelectric liquid crystal to produce a dye guest-host ferroelectric liquid crystals (DGHFLC) displays mode. There are several advantages which are the possibility to omit a polarizer, without cell thickness constraints, higher brightness, wider view angle and the color switching. The use of DGHFLC device removes many constructional constraints in the FLC birefringence device because the change of light intensity relies on the variation of dye absorption and orientation.

This paper documents a detailed study of single polarizer DGHFLC devices using a ferroelectric liquid crystal host and two dichroic dyes. The electrooptical and colour switching behaviors were focused for DGHFLC devices. The results contain several measurements of device properties, such as phase transition temperature, response time, spontaneous polarization, rotational viscosity, memory effect, color difference and the color positions on the CIE chromaticity coordinates to be discussed in detail.

EXPERIMENTAL

(a) Materials and Sample Fabrication

The host material used in this study was the ferroelectric liquid crystal SCE13 purchased from E.Merck Ltd. The materials properties of SCE13 are summarized in Table 1. The guest materials were two kind of dichroic dyes (S416 produced by Mitsui Toatsu Chemical Co. and a synthesized azo dye). The molecular structure of azo dye is listed in Figure 1. The concentration of the doped dye were 0.5%, 1.0%, 1.5%, 1.8% and 2.0% by weight.

TABLE 1 Physical property of ferroelectric liquid crystal SCE13.

Phase sequence	$K \xrightarrow{<0} SmC^* \xrightarrow{61°C} SmA^* \xrightarrow{86°C} N^* \xrightarrow{103°C} I$
Tilt angle (20 ℃)	29°
Spon. polar. (20 ℃)	+30.6 nC/cm^2
$\Delta\varepsilon$ (7.5kHz, 20 ℃)	-1.5
Δn (589nm, 20 ℃)	0.15

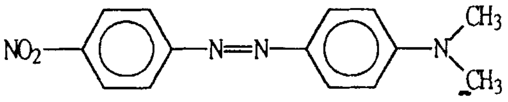

FIGURE 1 Molecular structure of azo dye.

The inner surfaces structure of two ITO-coated glass substrates were coated with Nylon 66 films and rubbed in the antiparallel direction. The cell gap was about 8μm. After the cell was filled with DGHFLC by capillary suction in the isotropic phase, it was cooled slowly (0.5 ℃/min) to the SmC* phase through the N* phase and the SmA* phase. The optical order parameter (S) and dichroic ratio (DR) of the dissolved DGHFLC were determined using plane-polarized light through the follow equations [3,7,8](1),(2):

$$\text{order parameter } S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \qquad (1)$$

$$\text{dichroic ratio } DR = \frac{A_{\parallel}}{A_{\perp}} \qquad (2)$$

where $A_{\parallel}$ is the absorbance of the dye at its maximum absorption wavelength (λ_{max}) when the polarization is parallel to the long axis of the dye, and $A_{\perp}$ is the absorbance at λ_{max} when the polarization is perpendicular to the long axis of the dye. The baseline was determined with cells containing the SCE13 only. Optical absorption spectra were measured at room temperature using a Otsuka MCPD-110A Multi-Channel Photo Detector(MCPD). The dye concentration of test cell for MCPD was 1.0% by weight. The order parameter (S), dichfoic ratio (DR) and absorption wavelengths of dyes in SCE13 are listed in Table 2. The absorption spectra of dyes in SCE13 are shown in Figures 2 and 3.

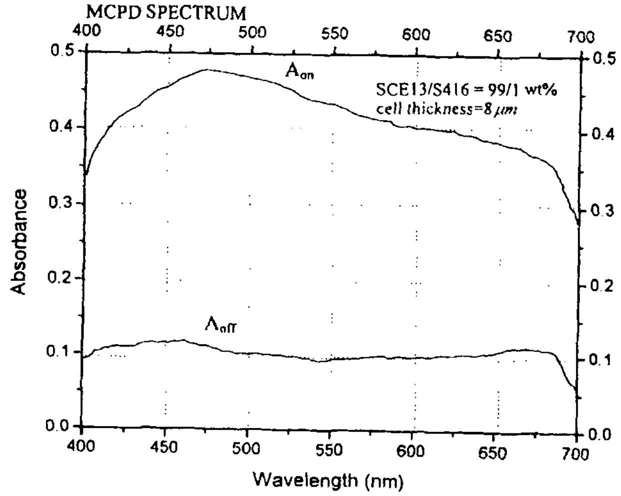

FIGURE 2 The absorption spectra of S416 dye in ferroelectric liquid crystal SCE13 host.

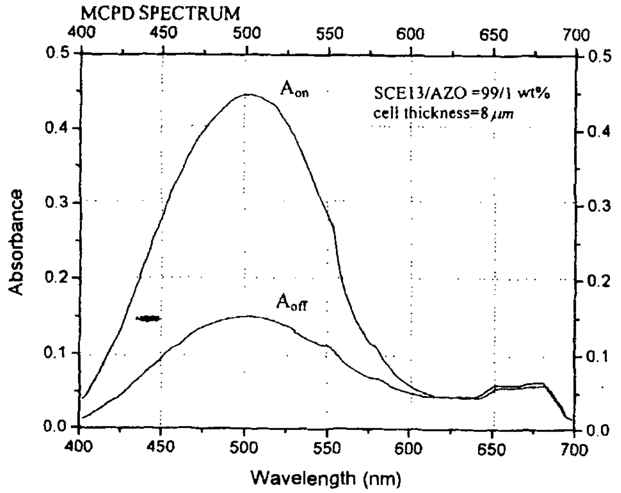

FIGURE 3 The absorption spectra of azo dye in ferroelectric liquid crystal SCE13 host.

TABLE 2 The order parameter,dichroic ratio and absorption wavelength of the DGHFLC.

host	guest	λ_{max}	order parameter (S)	dichroic ratio (DR)	cell gap
SCE13	S416(1.0 %)-black	475nm*	0.5	4	8μm
	azo(1.0 %)-red	500nm	0.4	3	

* Absorption peak is very broad

(b)Measurement of Rotational Viscosity in the DGHFLC

The rotational viscosity in the SmC* phase is an important parameter to understand the dynamic effect of DGHFLC electrooptical switching, memory effect and dye concentration. In this study, optical response method[9] has been employed to determine the rotational viscosity in the SmC* phase associated with the motion of the tilted molecule along the cone of azimuthal angle. Rotational viscosity is calculated using the simple equation(3):

$$\gamma_{\phi} = \frac{Ps \cdot \tau \cdot E}{1.8} \tag{3}$$

where E is electric field strength within the DGHFLC medium, Ps is the spontaneous polarization, τ is the response time and γ_{ϕ} is the rotational viscosity.

Response time was measured using He-Ne laser and a fast response (rise time -10ns) photodiode to obtain the transient optical response (from 10 to 90 percent of maximum transmission under electric field reversal) of the DGHFLC cell under single polarizer. This was performed with square-wave applied voltages(V_{pp}=10V,50Hz). The test cell temperature was controlled to within 1.0 ℃/min by a Mettle FP80 hot stage.

Spontaneous polarization wase measured with the Diament birdge method at V_{pp}=10V (60Hz). The bridge effectively consists of two Sawyer-Tower circuits in parallel. The spontaneous polarization at any given temperature is then determined from the hysteresis loop through the following equation(4):

$$Ps = \frac{C_O(V_{OB})}{2A} \tag{4}$$

where A is the active area of the sample, V_{OB} is the maximum peak to peak voltage of the compensated hysteresis loop and C_O is the value of the fixed capacitor.

(C)Measurment of Bistability and Contrast Ratio in the DGHFLC

Bistability (i.e. memory effect) was measured with a sequence of bipolar pulse ±40V applied to the DGHFLC cell and simultaneous transmission through the cell under operated single polarizer. Cells were placed in normal layers along with the polarizer in order to linearize the optical single. The light source is He-Ne laser.

Constrast ratio were measured using a photomultiplier attached to a polarizing microscope. Constrasts were defined as the intensity ratio of the transmitted light in bright and dark states.

(D)Measurement Transion Temperature and Molecular Relaxation in the DGHFLC

Transition temperature (SmA*→SmC*) of DGHFLC cell was used for the measurement of the dielectric method. The dielectric constant was measured out using impedance analyer (HP 4192A). The measurement field was 1 V_{pp} and no bias field was applied. The frequency was 500Hz. The temperature controlled by Mettle FP80 decreased at the rate of 0.5 ℃/min.

This study will show the low frequency molecular relaxation characteristic at SmC* phase through dielectric constant measurement. The measurement field was 1 V_{pp} (30Hz) and 0.1 to 5 bias voltage was applied at room temperature.

(E)Measurment of Colour in the DGHFLC

The color switching characteristics of the single and non-polarizer DGHFLC cells were measured using polarizing micro-spectrometer (ORC Ltd.) at room temperature under applied ±5 DC voltage. Input experment parameters of the polarizing micro-spectrometer include standard light source D65, colorimetric observer (2° observer) and spectra interval $\Delta\lambda$ =5nm. Color properties of the DGHFLC cells were studied by means of CIE x,y chromaticity diagram and CIE 1976 (L*,u*,v*) colour space. The results consist of the measurement of color properties, such as CIE 1976 (L*,u*,v*) color difference ΔE^*_{uv},chroma C^*_{uv}, hue-angle h^*_{uv}, lightness L* and chromaticity x,y value through the follow equations [10](5),(6),(7):

$$h^*_{uv} = \arctan\left(u^*/v^*\right) \tag{5}$$

$$C^*_{uv} = \left(u^{*2} + v^{*2}\right)^{1/2} \tag{6}$$

$$\Delta E^*_{uv} = \left[\left(\Delta L^*\right)^2 + \left(\Delta u^*\right)^2 + \left(\Delta v^*\right)^2\right]^{1/2} \tag{7}$$

RESULTS AND DISCUSSION

(A) Rotational Viscosity (γ_φ)

The rotational viscosity of the DGHFLC mixture increases with an increase of S416 dye concentration in the SCE13 host. A significant increase is observed in rotoational viscoity of the mixture, especially at low temperatures. Figure 4 shows the relationship between γ_φ and temperatures. The rotational viscosity of SCE13 was rised through the inclusion of the S416 dye concentration from 0.12 to 0.4 kg/ms at 30^0.

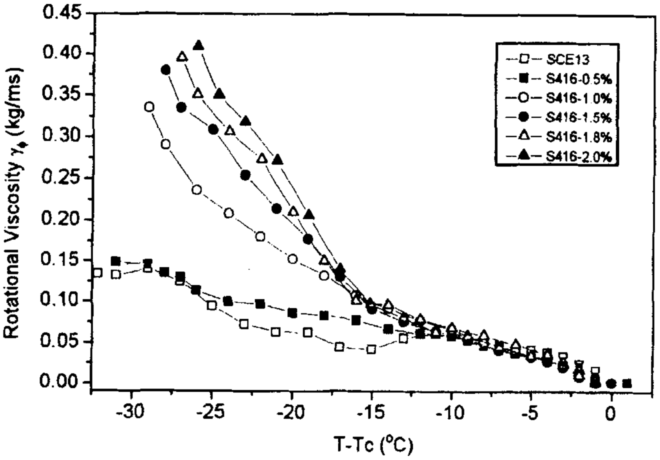

FIGURE 4 Relationship between temperature and rotational viscosity of DGHFLC at different S416-dye concentration.

(B) Bistability

The intensity of the light transmitted through the cell was measured under the application of bipolar pulses. The bistable (i.e.memory) states, which appear after a votage pulse is turned off, was studied. The optical response of the cell is shown in Figure 5. A better memory effect was obtained in the 1.5% and 1.8% dye concentration of DGHFLC cell than FLC host cell. In other words, no relaxation phenomenon of the transmittance was observed under the apparent cone angle between the two color position in the memory condition. Other dyc concentration of DGHFLC and pure FLC cell show relaxation phenomenon, specially for pure FLC cell which has maximun relaxation speed. This is because the relaxation speed of the memory state depends on not only rotational viscosity but also the anchoring condition of the substrates. The increase of dye concentration will increase the rotational viscosity of the cell and its response time, but a very good memory effect can be obtained.

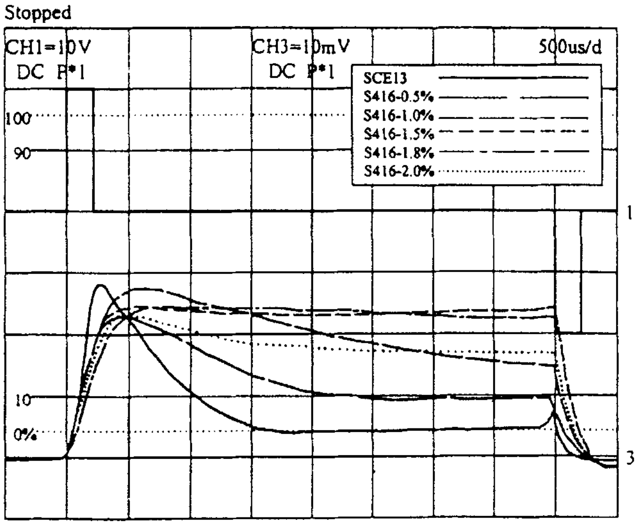

FIGURE 5 Change of memory effect of FLC and DGHFLC cells under crossed polarizers and single polarizer when a voltage pulse with width of 250 μs is applied.

(C) Phase Transition Temperature

For conventional ferroelectric liquid crystals under the transition temperature between SmA or SmA* and SmC* phases, T_c, dielectric constant rapidly increases with the decrease of temperature in the beginning, then reaches a maximum value at few degrees below T_c. In this paper, phase transition temperature was measured with dielectric method. The SmA*$\rightarrow$ SmC* transition temperature (T_c) of the DGHFLC is basically controled by the T_c of the SCE13 host. It should be noted that the addition of S416 dye concentration slightly decreases the T_c of the DGHFLC (about 1°~6°) as shown in Figure 6 and Table 3. This effect could possbily explained as the increase of dye concentration causes the flexibility change of the end chain of the ferroelectric liquid crystal molecules. In the meantime, the different solute (dye) concentration might cause the different ability of the dye molecules to detroy the SCE13. On the other hand, two peaks were observed under SmC* phase in SCE13 and its DGHFLC mixtrues at 500Hz through the observation of temperature and dielectric constant relationship. The SCE13 and DGHFLC show an anomalous behavior of dielectric constant dropping around 35° although both remain wide temperature range. The dielectric constant increases as the decrease of the temperatrue below the SmA*$\rightarrow$ SmC* phase transition (T_c). After it reaches a maximum value, it starts to decrease and drop to a minmum value at T_L below which the dielectric constant increases again. The T_L of the mixtures remarkably shifts to higher temperature with an increase of dye concentration in the host. This results clearly indicate that the contribution of the Goldstone mode to the dielectric constant is suppressed at T_L. However, this anomalous dielectric behavior was vanished at low frequencies (100Hz and 200Hz) as shown in Figure 7. The explanation of this effect is unclear presently.

(D) Molecular Relaxation

The rotational viscosity γ_φ is the most important coefficient mainly to determine the molecular reorientation of the director. The relationship has been studied between the low frequency dielectric constant and D.C biasing elctric field. The results obtained from this method are

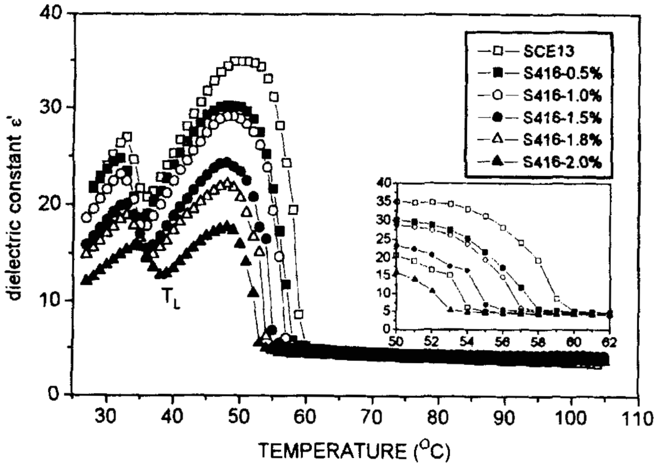

FIGURE 6 Relationship between temperature and dielectric constant for the DGHFLC measured at 500Hz under different S416-dye concentration.

TABLE 3 Phase transition temperature and maximum dielectric constant of all investigated DGHFLC cells.

host	guest	T_C	ε'_{max}
	S416-dye weight%	(SmA*→SmC* phase)	
SEC13	0.0 %	60 ℃	34.8 (50 ℃)
	0.5 %	58 ℃	30.3 (48 ℃)
	1.0 %	57 ℃	29.2 (48 ℃)
	1.5 %	56 ℃	24.3 (48 ℃)
	1.8 %	55 ℃	22.1 (48 ℃)
	2.0 %	53 ℃	17.6 (48 ℃)

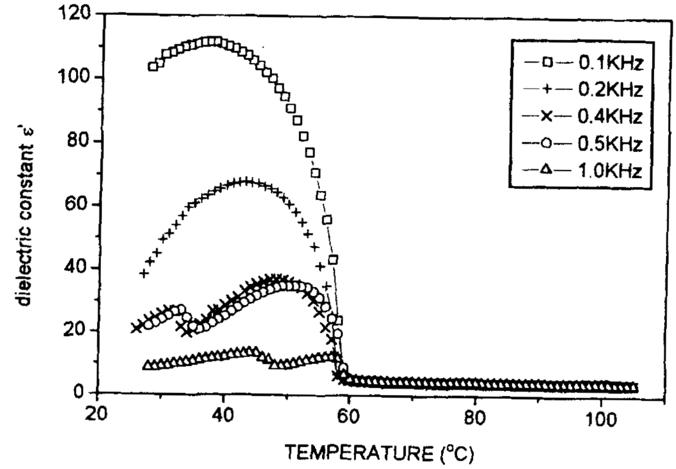

FIGURE 7 Relationship between temperature and dielectric constant for the SCE13 host measured at different frequency.

valuable to understand the molecular orientation and relaxation processes of the DGHFLC at the SmC* phase. It should be noted that the dielectric constant of the DGHFLC decreases with the increase of dye concentration in the host at room temperature when a D.C. biasing electric field is applied, as shown in Figure 8. The electric field at the maximum of dielectric constant remarkably shifts to higher D.C. biasing when dye concentration increases. At that field, the dielectric constant is larger than that measured at 0.01 D.C. voltage, especially at dye concentration of 2.0%. This can be explained by means of rotational viscosity and normal molecular mechanisms (Goldstone mode and the Soft mode). The increase of rotational viscosity causes the twist, splay and random deformation at layer structure of DGHFLC molecules. Therefore, DGHFLC cell has lower dielectric constant than pure host cell when D.C. bias voltage is not applied. The increase of D.C biasing strongly reduces dieletric constant after the cell reaches maximum dielectric constant. When the voltage is above 3V, the bistable effect is totally quenched (i.e. the Goldstone mode disappears), only the soft mode left.

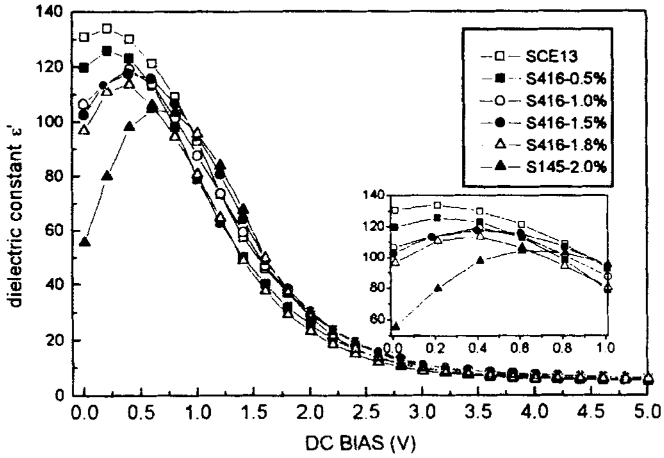

FIGURE 8 Relationship between voltage and dielectric constant for the DGHFLC cells measured at 30Hz under different S416-dye concentration.

(E) Contrsat Ratio and Transmission

Figures 9 and 10 show the relationship between the constrast ratio and transmission of DGHFLC cell and the dye concentration. The constrast ratio and transmission were measured using polarizing-microscope under single polarizer and crossed polarizer. From Figure10 the increase of dye concentration causes the increase of contrast ratio and slightly decrease of colourless and coloured state transmission. This means that a small increase in dye concentration (0.5%~2%) can improve contrast ratio without a heavy loss in transmission. Although, the DGHFLC contrast ratio value is not perfect, this can be improved through color difference. Figure 9 shows the contrast ratio and transmission decreases with the increase of dye concetration under crossed polarizer. Therefore, a DGHFLC cell cannot obtain a better visual effect under the crossed polarizer mode.

(F) Colour

The chromatic property of DGHFLC cell was measured by the polarizing micro-spectrometer. The chromatic diagram of Figures 11 and 12 shows that azo dye-DGHFLG cells lowers the cell's lightness and rises its chroma close to red with the increase of the dye concentration under the function of non-polarizer and single polarizer. When reversal electric field is applied to the cells,

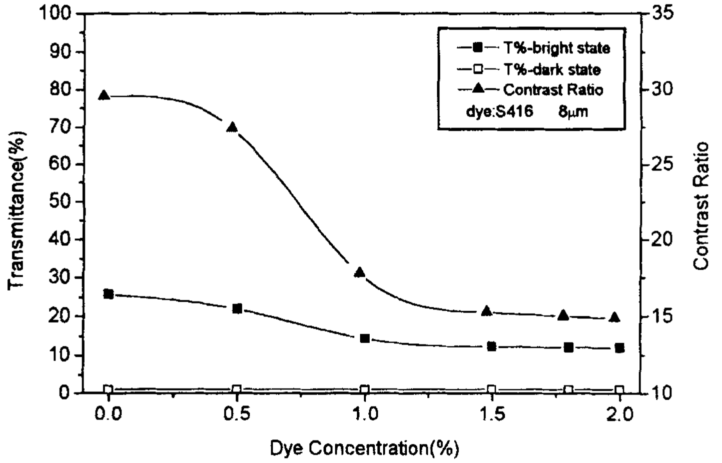

FIGURE 9 Relationship between S416-dye concentration and transmittance and contrast ratio of DGHFLC cells under crossed polarizers.

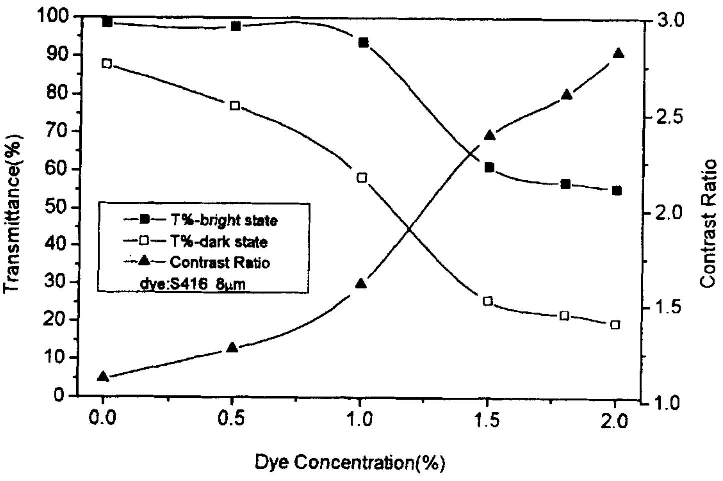

FIGURE 10 Relationship between S416-dye concentration and transmittance and contrast ratio of DGHFLC cells under single polarizer.

the color differential and chorma value between coloured state and colourless state increase with the increase of the dye concentration. Meanwhile, the hue angle is lower and u* axis is closer which could be plotted it under the colour coordinates diagram as shown in Figures 13,14 and it data in Table 4,5. In the relationship diagram of color difference and voltage of Figure 15, it is found that saturated voltage rises a little but threshold voltage almost does not change because the rotational viscosity of DGHFLC was much more than that of ferroelectric liquid crystals. On the other hand, the use of the DGHFLC cell made of black dye S416 to measure chromatic property causes the hue of the cell not black but close to yellowish brown and a very low chroma because the cell gap was very thin and in a transmitted mode, as shown in Figure 16. Basically, light at any wavelengths could be absorbed. It will be a perfect B/W FLCD under the reflected mode.

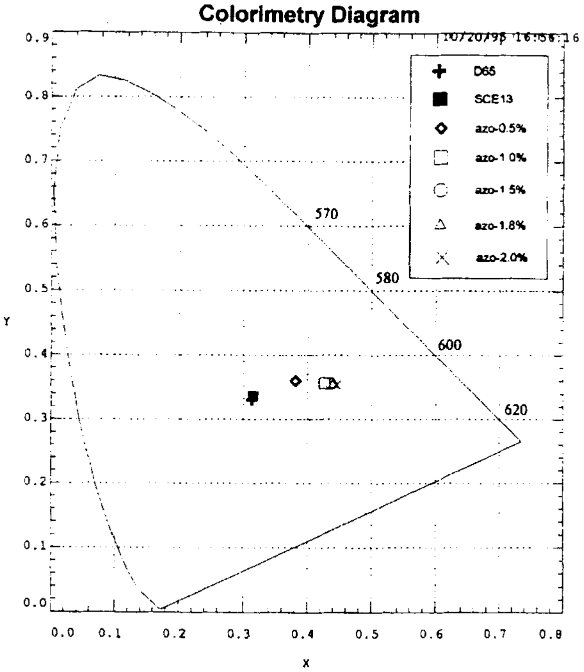

FIGURE 11 Chromaticity diagram for different azo-dye concentration of DGHFLC cells under non-polarizer.

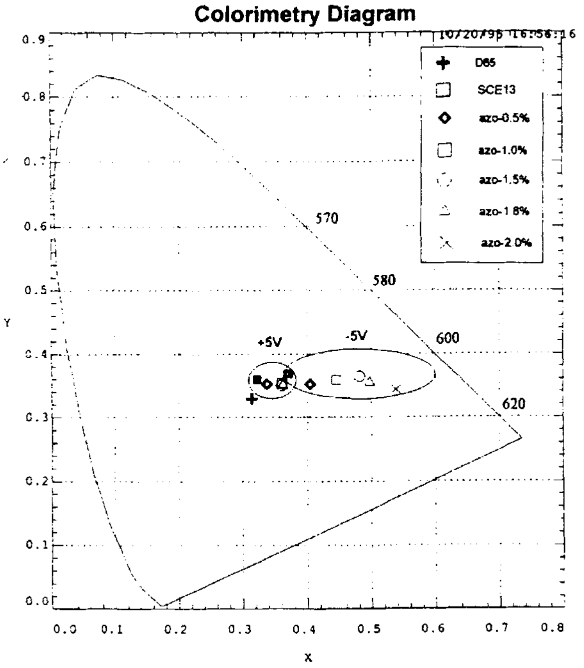

FIGURE 12 Chromaticity diagram for different azo-dye concentration of DGHFLC cells measured at ±5V under single polarizer.

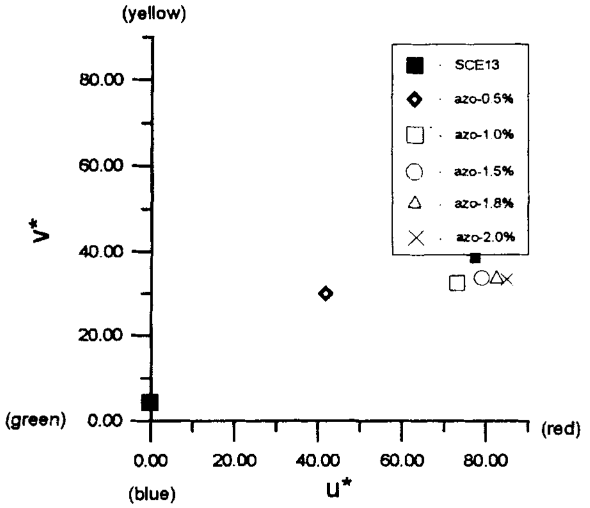

FIGURE 13 1976 CIELUV colour coordinates for different azo-dye concentraton of the DGHFLC cells under non-polarizer.

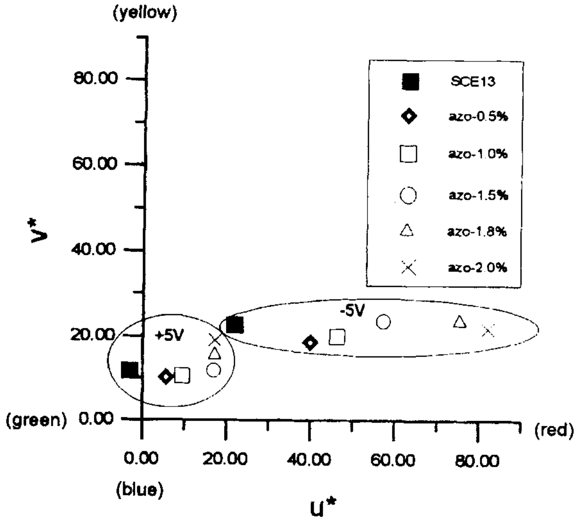

FIGURE 14 1976 CIELUV colour coordinated for different azo-dye concentration of the DGHFLC cells measured at ± 5V single polarizer.

TABLE 4 1976 CIELUV colour space data for different azo-dye concentration of the DGHFLC cells under non-polarizer.

	Y	x	y	L*	u*	v*	C*uv	h*uv	ΔE*
D65	–	0.313	0.329	–	–	–	–	–	–
SCE13	99.97	0.315	0.335	100	−0.33	4.32	4.333	94.37	–
azo,wt%=0.5	77.47	0.382	0.359	90.84	41.57	29.95	51.23	35.77	49.96
azo,wt%=1.0	59.05	0.428	0.356	81.59	73	32.62	79.96	24.07	80.73
azo,wt%=1.5	56.55	0.438	0.356	80.19	78.83	33.86	85.79	23.24	86.78
azo,wt%=1.8	54.01	0.442	0.355	78.00	82.35	33.52	88.91	22.15	90.40
azo,wt%=2.0	53.05	0.447	0.354	78.17	84.76	33.38	91.10	21.50	92.52

		Y	x	y	L*	u*	v*	C*uv	h*uv	ΔE*
D65		–	0.313	0.329	–	–	–	–	–	–
SCE13	+5V	21.84	0.322	0.360	54.05	3.16	11.72	12.18	105.04	27.6
	−5V	33.45	0.372	0.366	64.75	21.77	22.56	31.35	46.02	
azo	+5V	20.69	0.337	0.352	56.09	5.57	10.22	11.64	61.41	35.42
wt%=0.5	−5V	23.80	0.405	0.352	52.80	39.84	18.57	43.96	24.99	
azo	+5V	20.92	0.361	0.354	53.05	9.35	10.56	14.10	48.48	39.11
wt%=1.0	−5V	13.82	0.446	0.358	44.13	46.25	19.96	50.37	23.34	
azo	+5V	20.41	0.360	0.350	52.49	16.87	11.87	20.63	35.13	43.14
wt%=1.5	−5V	12.69	0.482	0.364	42.46	57.14	23.64	61.84	22.48	
azo	+5V	20.37	0.362	0.35	53.40	17.10	15.5	23.08	42.19	60.25
wt%=1.8	−5V	12.03	0.498	0.354	40.20	75.34	23.47	78.91	17.30	
azo	+5V	24.44	0.369	0.368	56.73	17.12	19.11	25.66	48.14	67.25
wt%=2.0	−5V	10.83	0.539	0.343	39.45	82.05	21.84	84.91	14.91	

TABLE 5 1976 CIELUV colour space data for different azo-dye concentration of the DGHFLC cells measured at ± 5V under single polarizer.

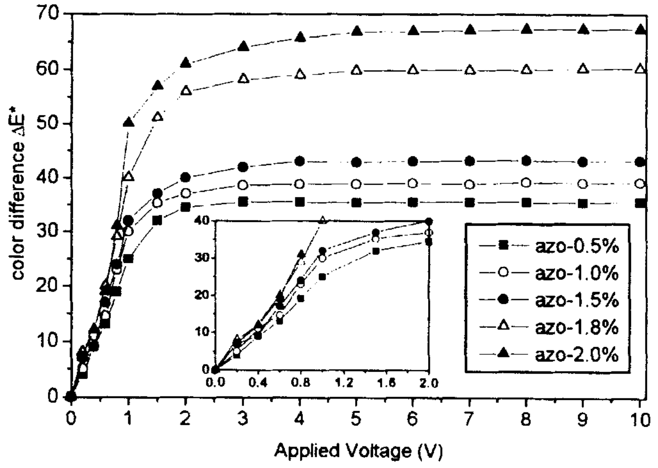

FIGURE 15 1976 CIELUV color different versus applied voltage under different azo-dye concentration.

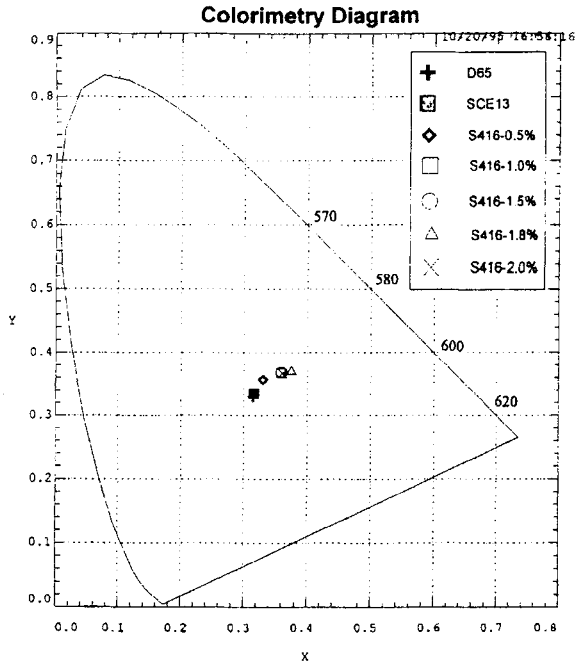

FIGURE 16 Chromaticity diagram for different S416-dye concentration of DGHFLC cells under non-polarizer.

CONCLUSION

The study results show that the addition of dye increases the rotational viscosity of the whole DGHFLC mixed system and lower response time. On the other hand, it rises the bistability and memory effect of DGHFLC much more than those of ferroelectric liquid crystals.

For the measurement of dielectric property, it is discovered that the internal viscous force of DGHFLC molecule increase with the increase of dye's concertration, causing diecetric constant decreases progressively and relaxation frequency moves toward low frequency. At the same time, the arrangements of molecules between layers are inconsistent due to the increase of the rotational viscosity. It therefore restrains the rising of D.C bias voltage required by Goldstone mode effect. Besides, it is discovered that ferroelectric phase transition temperature tends to go down to lower temperature after the addition of dye during the experiment. The results could be attributed to the phase equilibrium of two mixed compounds the dye and liquid crystal which induces a little change of liquid crystal phase transition temperature.

In the measurement evaluation of chromatic of DGHFLC cell, it is concluded that the increase of the dye concentration relatively decrease lightness and increase chroma. Meanwhile, the hue of the cell closely matched with the color of the dye's greatest absoption wavelength. When reversal electric field is applied to the cell, it is discovered that the color differential value between coloured state and colourless state would rise with the increase of dye concentration. In this way, visual effect could be more clear. The primary design goal of Guest-Host Liquid Crystal Display is achieved becuase the use of single plaorizer for DGHFLC cell increases the whole lightness.

Acknowledgements

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