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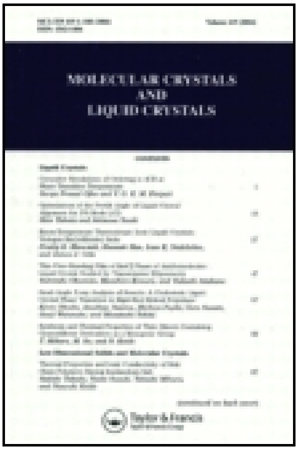

Molecular Crystals and Liquid Crystals

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Guest-Host Interactions in Liquid Crystals

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Guest–Host Interactions in Liquid Crystals

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The liquid crystal display devices using the guest–host interactions do not require that substrates are optically flat, and have wide viewing angle. Therefore, the authors have studied the dichroic dyes used in these display devices. A part of the results obtained was described in another journal.

In this paper, the authors have clarified some dyes available for the guest–host cell. The influence of the thickness of the liquid crystal layer in a cell on color switching and response characteristics have been made clear. If the product of the dye concentration and the cell thickness is kept constant, the variation of the cell thickness will not change the color switching characteristics. The recovery time is proportional to the square of the cell thickness. By adjusting the dye concentration we can make a thin cell with a good color switching characteristic and with the short recovery time.

1 INTRODUCTION

Heilmeier and co-workers[1] reported in 1968 that the orientation of certain host compounds by external electric fields could be used to orient pleochroic dye molecules (guest) and methyl red as a guest dye.

In 1969 they[2] made a report on the data obtained on the guest–host interactions in nematic liquid crystals, in which indophenol blue was used as a guest dye. Recently, Morita and others[3] proposed three types of the pleochroic dyes as guest dyes, and White and Taylor[4] reported a guest–host type cell, in which a mixture of cholesteric and nematic liquid crystals was used. In addition to these, some explanatory remarks have been published.[5–7]

The guest–host type cells with methyl red or indophenol blue used as a guest gave no excellent feature of color switching (coloring ↔ disappearance of color) in our experience. Because of such a poor feature, the guest–host type display devices have become of less interest.

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If the guest–host type cell with an excellent character for color switching can be obtained, it may be full of promise for a color display, because it can be easily made with a wide viewing angle, compared with the other liquid crystal display devices, that is, a DAP cell[8–11] and a TN cell with dichroic filters[12] or birefringent thin films.[13,14] Its good features are as follows.

1) Non-uniformity of the electrode spacing of a liquid crystal layer does not harm uniformity of the displayed color.

2) Viewing angle is very wide.

3) Transmittance is high.

4) Hue and chroma can be controlled by selecting a guest dye.

We reported some dyes having a considerably good characteristics of color switching and fundamental characteristics of guest–host interactions.[15] Since then, we have studied to find good dyes available for guest–host interactions. In this paper, we describe the experimental results obtained.

The characteristics of color switching seem to depend not only on dichroic properties of dyes themselves but on the electrode spacing, the dye concentration and the applied voltage. In this paper, therefore, the authors show excellent dichroic dyes and then describe in detail the effect of the electrode spacing, the dye concentration and the applied voltage on the color display characteristics.

2 EXPERIMENT

The nematic liquid crystal with positive dielectric anisotropy (N_p liquid crystal) was used as a host liquid crystal whose molecules were homogeneously aligned. The N_p liquid crystal was a mixture as described below.

p-methoxybenzylidene-*p*′-*n*-butylaniline (MBBA) 50 wt %

p-ethoxybenzylidene-*p*′-*n*-butylaniline (EBBA) 35 wt %

p-ethoxybenzylidene-*p*′-aminobenzonitrile (EBAB) 15 wt %

The homogeneous alignment was made by using *N*-methyl-3-aminopropyl trimethoxysilane (MAP) treatment[16] and by rubbing. The molecular alignment in such a liquid crystal cell was parallel to the substrate surface by cutting off the applied voltage and perpendicular to the substrate surface by applying the voltage. Therefore, the cell was colored in off-state and color disappeared in on-state.

All the measurements were conducted at room temperature and the applied voltage was a.c. voltage of 50 Hz, with the exception that the response and recovery characteristics were measured by using a square wave voltage of 1 kHz.

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3 RESULTS OBTAINED AND DISCUSSION

3.1 Guest-host interactions of various dyes

Various molecular structures of pleochroic dyes were studied for guest-host interactions. The results obtained can be summarized as follows.

1) Long, rod-like molecules of pleochroic dyes give a good characteristic of electronic color switching in the guest-host mixtures. These dues can be found in sensitizing dyes and azo-dyes.

2) If a dye has a strong ionic radical such as a cyanine dye shown in Figure 1, color is irreversibly changed because of electro-chemical reaction in dyes. Therefore, guest dyes must be non-ionic. This condition can be satisfied in some kinds of azo-dyes and, merocyanine, styryl and oxonole sensitizing dyes.

3) Familiar sensitizing dyes with considerably long molecules tend to fade with the lapse of time. Especially, dyes having a methine group with carbon atoms of six or above on the central chain fade easily.

4) In guest-host cells, molecular structures of a guest dye and a host nematic liquid crystal should be selected in order to obtain good solubility of a guest dye in a host liquid crystal.

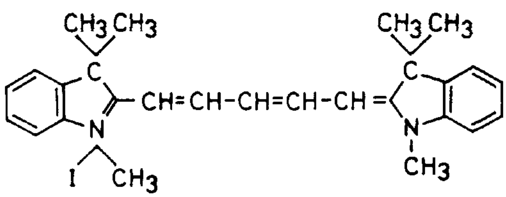

FIGURE 1 An example of a dye with a strong ionic radical.

Table I shows guest dyes with good electronic color switching characters. The table also shows their molecular structures, the added quantity for the electrode spacing of 25 μm, the wavelength at the maximum absorbance and the characteristic color. The cell with lower dye concentration gives light coloration and the cell with higher one gives imperfect discoloration under the applied voltage. Then there is an optimum concentration of each guest dye, and the added amount of dye in Table I shows the optimum value.

The color can be also displayed by using a mixture of dyes. This method is effectively available for the color which it is difficult to display by using a single dye or tends to fade because of the long molecular chain. Table II shows some examples of mixtures of two dyes.

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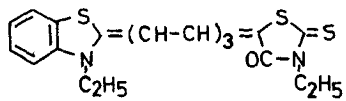
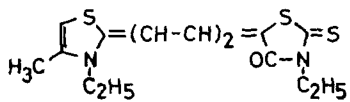
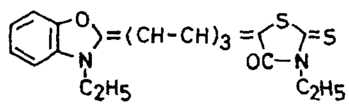
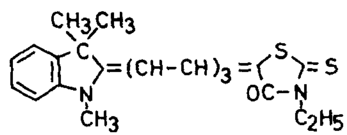
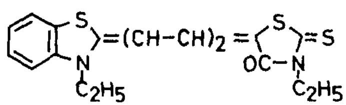
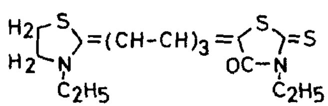
TABLE I

Dyes available for electronic color switching

Dye	Molecular structure	Added quantity of dye	Maximum absorption wavelength	Displayed color
NK1575[a]		0.1 wt%	640 nm	Bluish-green
NK1313[a]		0.1 wt%	632 nm	Bluish-green
NK2233[a]		0.1 wt%	624 nm	Greenish-blue
NK2288[a]		0.1 wt%	612 nm	Blue
NK1321[a]		0.1 wt%	610 nm	Blue
NK2232[a]		0.1 wt%	603 nm	Blue

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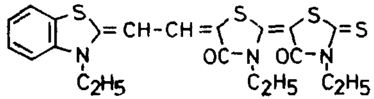
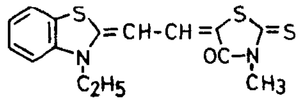
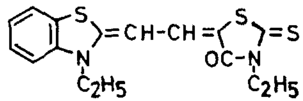
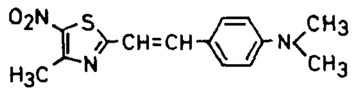
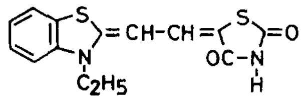
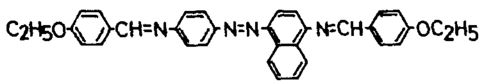
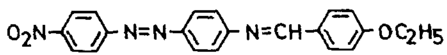
NK2097[a]		0.1 wt %	580 nm	Violet
NK2026[a]		0.1 wt %	530 nm	Reddish-violet
NK1247[a]		0.1 wt %	530 nm	Red
NK2019[a]		0.2 wt %	510 nm	Red
NK1896[a]		0.1 wt %	475 nm	Yellowish-orange
ENAEB[b]		0.2 wt %	—	Yellowish-orange
ENAB[b]		0.2 wt %	—	Yellow

[a] Nihon Kanko Shikiso Lab., Inc.
[b] Synthesized in our laboratory.

TABLE II

Displayed color by a mixture of dyes

Dye	Added quantity	Displayed color
NK1321 ENAB	0.1 wt% 0.2 wt%	Bluish-green
NK1321 ENAEB	0.1 wt% 0.25 wt%	Green
NK1321 NK2026	0.05 wt% 0.08 wt%	Violet
NK2026 NK2019	0.1 wt% 0.2 wt%	Red
NK2019 ENAEB	0.1 wt% 0.3 wt%	Orange

3.2 The influence of the electrode spacing on the electronic color switching

For an example, the dye NK2233 was used as a guest dye in the measurements in this section. The quantity of the guest due to be added is usually 0.1 wt%. Figure 2 shows that the influence of the electrode spacing depends on the wavelength of transmittance of the guest-host cell, where the incident light is the linearly polarized light with its electric vector parallel to the molecular orientation of off state. In the figure, the solid lines stand for the transmittance with no applied field and the broken lines that with the applied field of 20 V, 50 Hz.

Figure 3 shows the voltage dependence of transmittance at the maximum absorption wavelength (624 nm).

The transmittance T of the incident light in a material dispersed in a non-absorbing solvent can be expressed by using Lambert–Beer's law as follows.

$$T = 10^{-kcd} \tag{1}$$

where k is the absorption coefficient, c the concentration of the material to be measured and d the thickness of the material layer. Now, assuming that the same relation holds in a guest–host cell, transmittances $T_{\parallel}$ and $T_{\perp}$ of the incident linear polarized lights, whose electric vectors are parallel with and perpendicular to the molecular orientation with no applied field, as shown in Figure 4, are given as follows.

$$T_{\parallel} = 10^{-k_{\parallel}cd} \tag{2}$$

$$T_{\perp} = 10^{-k_{\perp}cd} \tag{3}$$

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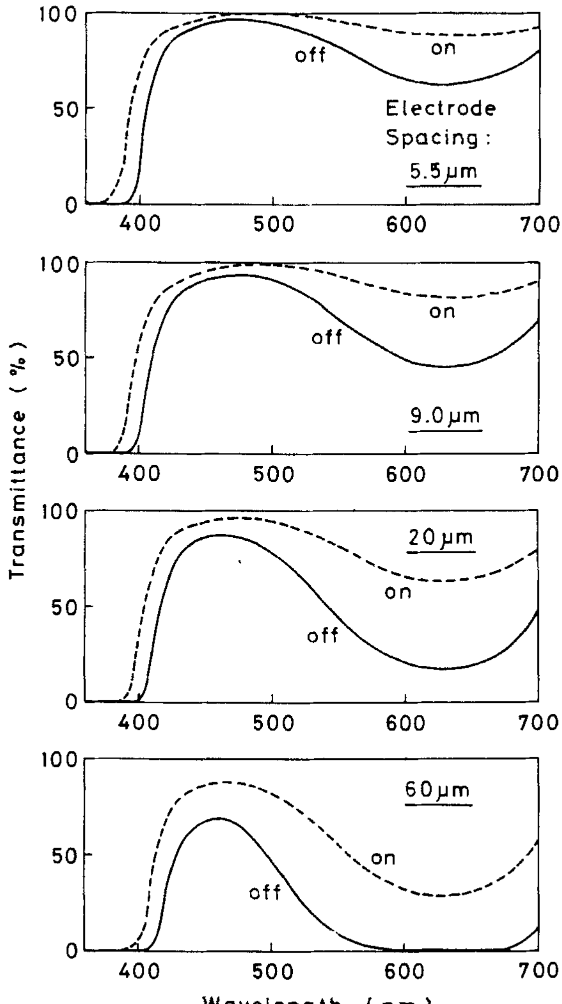

FIGURE 2 The effect of the electrode spacing to wavelength dependences of transmittance (NK2233: 0.1 wt%).

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where $k_{\parallel}$ and $k_{\perp}$ are the absorption coefficients whose electric vectors are parallel with and perpendicular to the molecular orientation. From Eqs. (2) and (3), we have

$$\log T_{\parallel} = -k_{\parallel} cd \tag{4}$$

$$\log T_{\perp} = -k_{\perp} cd \tag{5}$$

The relationships between log $T_{\parallel}$ and log $T_{\perp}$, and the concentration c or

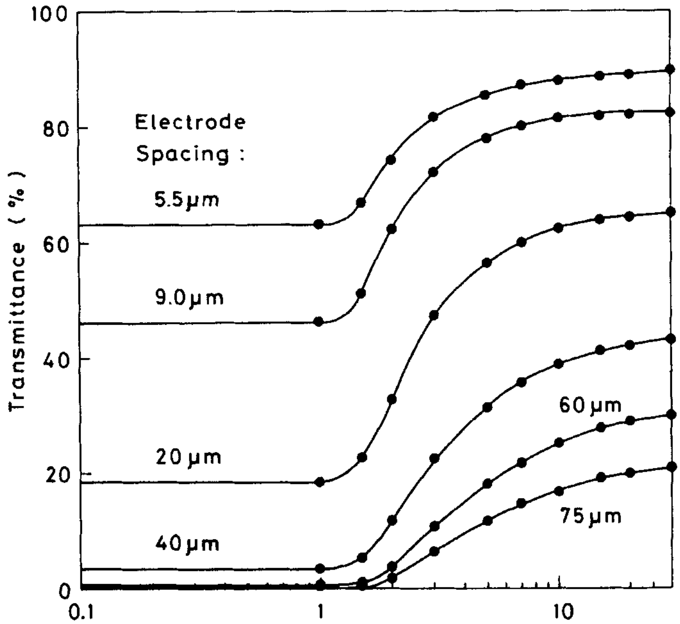

FIGURE 3 The effect of the electrode spacing to the voltage dependence of transmittance (Wavelength: 624 nm).

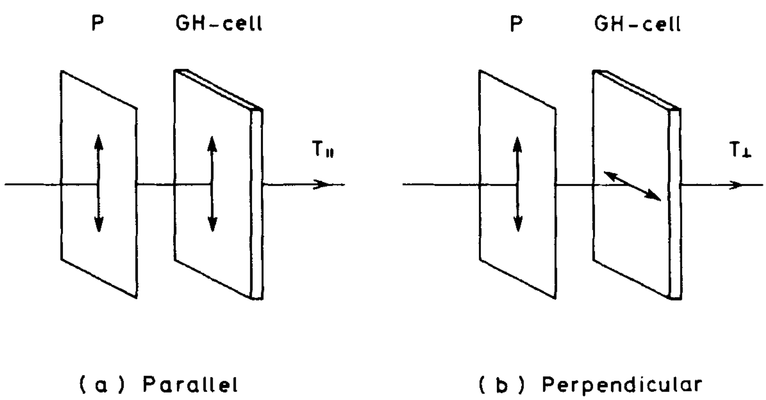

FIGURE 4 The direction of the electric vector of the polarized light transmitted through the polarizer (P) and the direction of the orientation of molecules in the guest-host type cell (GH-cell).

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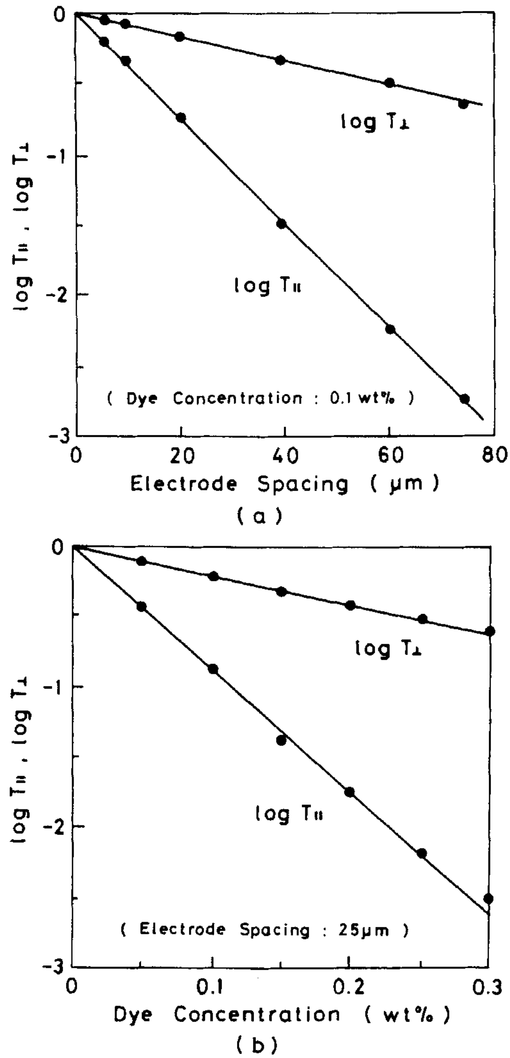

FIGURE 5 The relations between log $T_{\parallel}$ or log $T_{\perp}$ and the electrode spacing or the dye concentration (dye: NK2233).

the electrode spacings in the cell were measured as shown in Figure 5. In Figure 5(b), the concentration c was expressed in wt% for the experimental convenience. These figures verify the relations (4) and (5).

Nextly denoting the transmittance by $T'_{\parallel}$ when a voltage is applied to the cell as shown in Figure 4(a), we can rewrite Eq. (4) as follows.

$$\log T'_{\parallel} = -k'_{\parallel} cd \tag{6}$$

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where $k'_{\parallel}$ gives an apparent absorption coefficient. It is generally known that the molecular orientation can be schematically expressed as shown in Figure 6. Therefore, for convenience sake, this cell can be supposed to consist of the surface layers with parallel orientation and the bulk with perpendicular orientation. The thickness of the surface layer is expressed by $d_s/2$. As the long axis of the molecules intersects the electric vector of the incident light in the perpendicular orientation, the absorption coefficient is expressed by $k_{\perp}$. In parallel orientation of the surface layer the absorption coefficient is given by $k_{\parallel}$.

Then, $k'_{\parallel}$ in Eq. (6) means the average absorption coefficient over the cell thickness, which is given as follows:

$$k'_{\parallel} = \frac{k_{\perp}(d - d_s) + k_{\parallel} d_s}{d} \tag{7}$$

where d_s depends upon the applied voltage and the cell thickness d.

Now, Figure 7 shows the relationship between log $T'_{\parallel}$ and the cell thickness for various parameters of the applied voltage. In this figure log $T'_{\parallel}$ is directly proportional to the cell thickness. Figure 8 shows the cell thickness dependence of d_s given by substituting experimental results in Figures 5 and 7 in Eq. (7). When the applied voltage is a parameter, d_s is directly proportional to d, and then the ratio d_s/d is independent of d. In Figure 9, the ratio d_s/d (the slope of the straight lines in Figure 8) is plotted as a function of the applied voltage. The ratio d_s/d is less than 4% at the voltage above

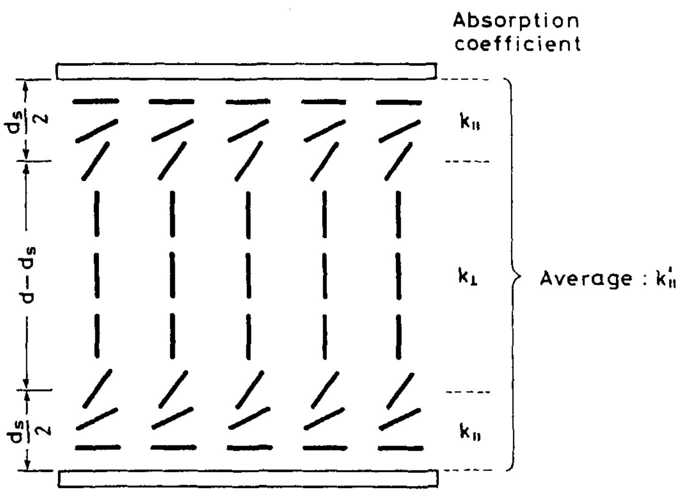

FIGURE 6 Molecular orientation under the applied voltage: $d_s/2$ is the effective thickness of the surface layer.

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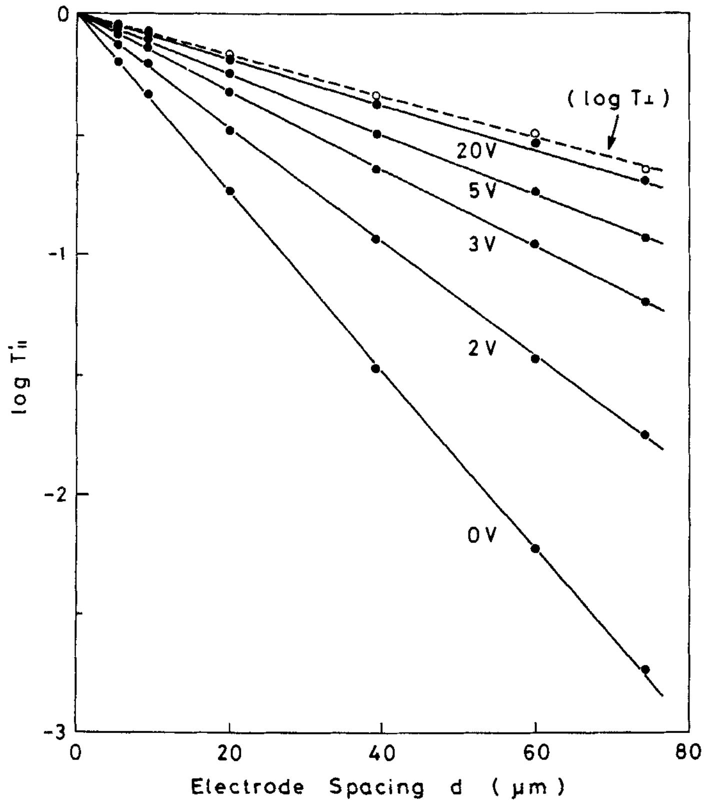

FIGURE 7 The effect of the applied voltage to the electrode spacing dependence of log $T'_{\parallel}$ (dye: NK2233, 0.1 wt %).

15 volts, and then the surface layers can be neglected. As such a voltage is applied to the cell, the influence of the surface layers to the color switching characteristics can be neglected.

From these results, we can conclude that in a thinner cell we can obtain the optimum color switching characteristics if the cell is provided that the product of the cell thickness and the dye concentration shown in Table I (for example, 25 μm $\times$ 0.1 wt % = 2.5 for NK2233) is kept constant, then we can realize the cell with much faster response time.

3.3 The effect of the electrode spacing on the recovery characteristics

By using the guest-host cell containing the dye NK2233 of 0.1 wt %, the rise time t_{rise} and the recovery time t_{rec} were measured. Figure 10 and Figure 11

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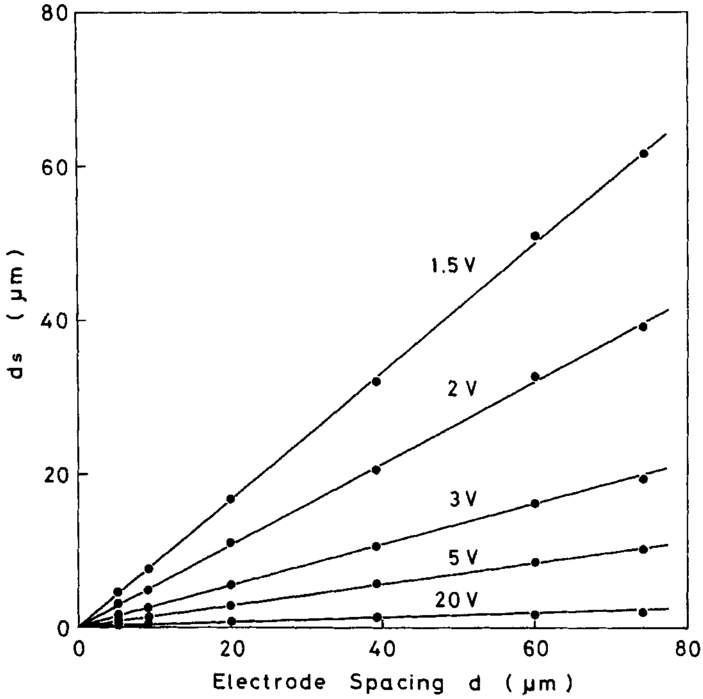

FIGURE 8 The effect of the applied voltage to the electrode spacing dependence of d_s.

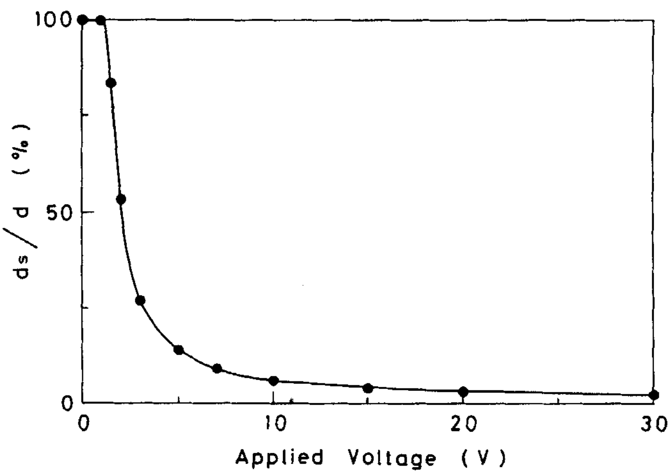

FIGURE 9 The voltage dependence of d_s/d.

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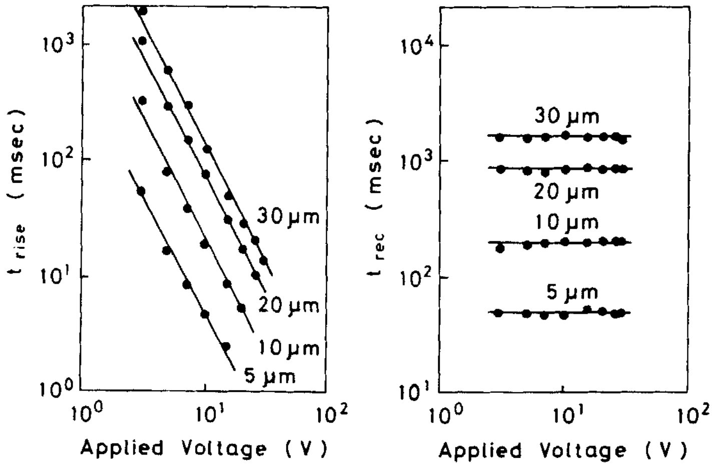
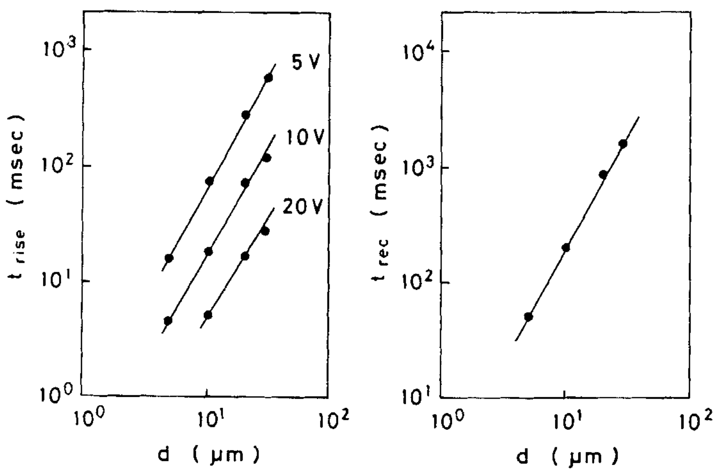


(a) Rise character (b) Recovery character

FIGURE 10 The voltage dependence of the rise time t_{rise} and the recovery time t_{rec}.



(a) Rise character (b) Recovery character

FIGURE 11 The relations between the electrode spacing d and the rise time t_{rise} and the recovery time t_{rec}.

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show the results obtained when the electrode spacing and the applied voltage were parameters, respectively. The rise time and the recovery time are defined as being 90% change in transmittance at the wavelength of maximum absorption. From these results we can find the following relations.

$$t_{\text{rise}} \propto (d/V)^2 \tag{8}$$

$$t_{\text{rec}} \propto d^2 \tag{9}$$

4 CONCLUSION

Several types of dyes available for guest–host cells were found and the effects of the electrode spacing and the concentration of a dye to electronic color switching characters were made clear. As a result, the thin guest–host cell is available to electronic color switching by increasing the dye concentration adequately and then we can fabricate a cell with short recovery time.

Acknowledgements

We would like to express our hearty thanks to Nihonkanko Shikiso Lab., Inc. for cooperation at dye synthesis and also to Dr. H. Watanabe and to the members of our laboratory for valuable discussion.

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