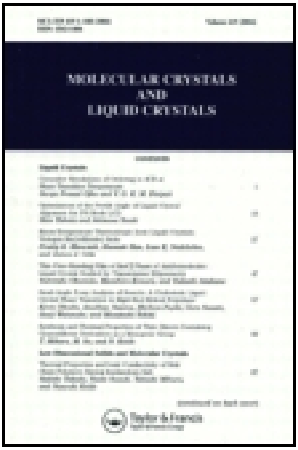

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Assessment of Nematic Guest-Host Systems for Application to Integrated Liquid Crystal Displays

A. C. Lowe [a]
[a] IBM Research Laboratory, San Jose, California, 95193, U.S.A.

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Assessment of Nematic Guest-Host Systems for Application to Integrated Liquid Crystal Displays

A. C. LOWE†
IBM Research Laboratory, San Jose, California 95193 U.S.A.

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An optimized configuration of the nematic guest-host effect is described in which a 90° twist cell is used. In order to assess the suitability of nematic guest-host systems for use in integrated displays in which a significant dc voltage may appear across the liquid crystal, several dye/host systems were tested with up to 1.5V dc superimposed on the normal 5V r.m.s. drive signal. Degradation was monitored by measurement of tilt, clearing point and absorbance. One system tested showed no significant degradation after 9×10^3 hr. Excellent correlation was observed between stability of a dye/host system in a driven display and the reversibility of the reduction of the dye in acetonitrile solution at a platinum electrode.

INTRODUCTION

The design of integrated reflective dot-matrix liquid crystal displays, in which each picture element (pel) is addressed by a low-voltage silicon switch circuit, imposes physical constraints upon the structure of the display and makes stringent demands on materials stability. The opacity of the silicon substrate and the requirement to make an electrical connection, perpendicular to the plane of the substrate, to each pel, preclude use of a rear polarizer. Power supply tolerances and leakage in the addressing circuitry may cause a permanent dc voltage of the order of a few hundred millivolts to appear across the liquid crystal layer. The liquid crystal must be stable to such

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† Present address: IBM United Kingdom Laboratories Ltd., Advanced Display Technology Group, Hursley Park, Winchester, Hampshire, SO21 2JN, England.

fields, exhibit a threshold greater than the bias field, and be capable of operation, in this instance, at voltages less than 5 V r.m.s.

The nematic guest-host effect[1,2] is compatible with the optical and drive voltage requirements. In this communication, we shall describe a display configuration which optimizes the voltage-contrast characteristic, present the results of degradative testing of display cells, and relate the results to the electrochemical properties of dyes and hosts.

EXPERIMENTAL

Materials

The nematic mixtures, components and the dyes used in this study are identified in Tables I and II. Dyes DI, II and III were precipitated, washed and vacuum dried. DIV and V were purified by TLC; IV was precipitated as a waxy solid and V was recrystallized. Both were vacuum dried. All dyes had satisfactory elemental analysis. Commercially available materials were used as received.

For the electrochemical studies, spectroscopic grade acetonitrile (Burdick and Jackson Laboratories Inc.) was further purified by passage through a column of activated alumina (Woelm N, Super I grade). Electrometric grade tetraethylammonium perchlorate (Southwestern Analytical Chemicals Inc.)

TABLE I

Liquid crystalline host materials

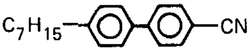
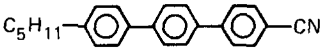
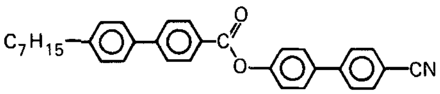
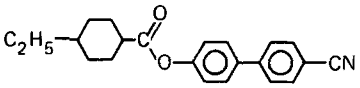
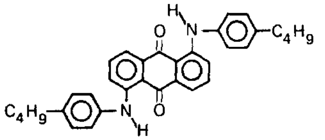
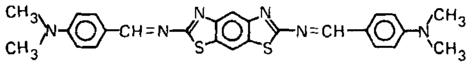
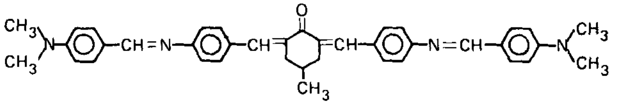
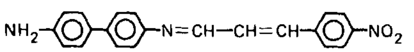
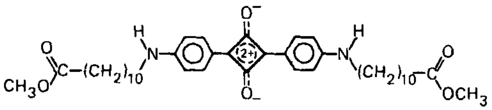
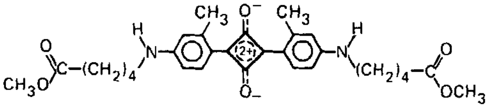
E7	Eutectic Nematic Mixture
E37	Eutectic Nematic Mixture
K21	
T15	
BB21	
CHE	

TABLE II

Dye	Dyes	λ max in E37 (nm)
D37*		552
DI		457
DII		425
DIII		<420
DIV		668
DV		650

was used as supporting electrolyte and was dried at 110°C overnight before use. Solutions were deoxygenated with either argon or nitrogen.

Test cells

1.5 mm thick substrates with a flatness tolerance of 1 in 10^4 were used. Electrodes were of diode-sputtered indium tin oxide (ITO) on Corning 7059 (supplied by Varian Inc.) or on soda-lime glass substrates (supplied by Saunders-Roe Developments Ltd.), or of aluminium, or aluminium which had been barrier anodized to produce a surface oxide layer approximately 55 nm in thickness, on 7059 substrates. Standard test cells, with overlapping 1 cm diameter electrodes, were used. Alignment was accomplished by oblique evaporation of SiO_2. Cells were assembled using epoxy-coated Mylar spacers (Ablestik types I and II, supplied by Ablefilm Laboratories Inc.). The fabrication of test cells and details of the alignment technique have previously been described.[3] In studies in which the effect of dc bias on tilt was investigated, a second electrode was provided on one substrate.

Cells were from 6 to 15 μm in thickness, the thickness being determined ±5% from a capacitance measurement on the empty cell. Cells were filled above the clearing point by evacuation through one fill hole and admission of liquid crystal through a second, diagonally opposite the first, followed by slow cooling. The fill holes were not sealed. Tilt was measured by the magneto-capacitive null method[4–6] using a Boonton Model 75C bridge at 5 kHz and an 11 kG magnet.

Optical measurements

Voltage-contrast characteristics were measured in transmission, at normal incidence, using collimated white light from a tungsten-halogen source. Optical density measurements were made on a Cary 17 spectrophotometer using an attachment similar to that described by Heilmeier, Castellano and Zanoni, fitted with a single polarizer.[2] Rotation of the polarizer in such an attachment causes intensity modulation in the absence of a test cell because of partial polarization of light incident from the monochromator. This leads to errors in order parameters calculated from maximum and minimum absorbance measurements. Consequently, changes in absorbance at a fixed polarizer setting, not order parameter, are reported.

Degradative testing

Cells were maintained at 50°C under one of the following conditions; zero field, and 5 V r.m.s., 500 Hz square wave biased at zero, 1 or 1.5 V dc. Initially, cells were contained in a vacuum oven at 0.9 atm in desiccating conditions. Towards the end of the test, an oven containing no desiccant and operated at atmospheric pressure was used. Clearing points were measured with a Mettler FP5 hot stage. The measured transitions were erroneously high because of the substrate thickness of 1.5 mm, but since the same heating rate (2°C/min) was used throughout, the changes in clearing point reported here require no correction.

Electrochemical measurements

Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using platinum working and counter electrodes and a PAR173/175 potentiostat/programmer. The working electrode was cleaned by abrading with 50 nm alumina powder before each use. For experimental convenience, an anodized silver wire was used as reference electrode. Its potential was measured against SCE/NaCl (sat), in the working solution, at the completion of each reported voltammogram. Results are reported vs SCE/NaCl (sat). Solutions were 0.001 M or less in the material under investigation and 0.1 M in TEAP.

RESULTS AND DISCUSSION

Voltage-contrast characteristics

A conventional nematic guest-host display[1,2] uses a nematic of positive dielectric anisotropy, a dye with a longitudinal transition moment, and parallel or low-tilt alignment with no twist (Figure 1a). The display is illuminated with light polarized parallel to the dye transition moment. When the cell is turned on, residual layers near the cell walls (A and B), which result from competition between surface forces and the applied field, exhibit 10% residual absorption at fields nearly six times the threshold (Figure 2, curve a).

By incorporating a 90° twist into the cell (Figure 1b) the absorbance of the off state remains substantially the same as for the untwisted case. On application of a field, once sufficient tilt is induced in the central region of the cell that the polarization rotational property of the nematic layer is lost, the number of dye molecules oriented with their transition moments in the plane of the incident electric vector and the transmission axis is substantially reduced (region A′ only). This results in a steeper voltage-contrast characteristic (Figure 2, curve b) which remains significantly less steep than that of a twisted nematic display of similar thickness (Figure 2, curve c). However, the voltage-contrast characteristic of twisted guest-host cells (designated twisted nematic plus dye (TND)) is adequate for use with drive voltages of the order of 5 V.

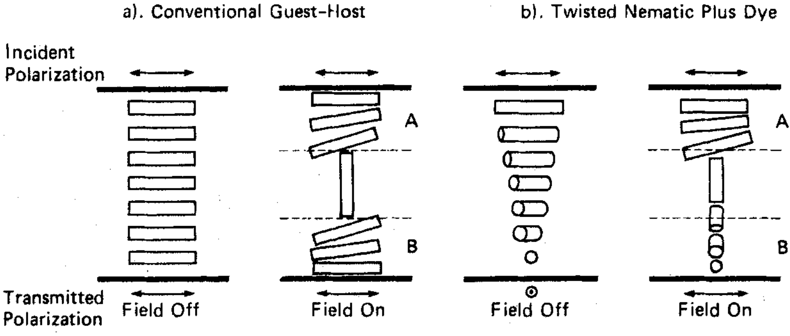


FIGURE 1 Schematic representation of a) conventional guest-host and b) TND displays.

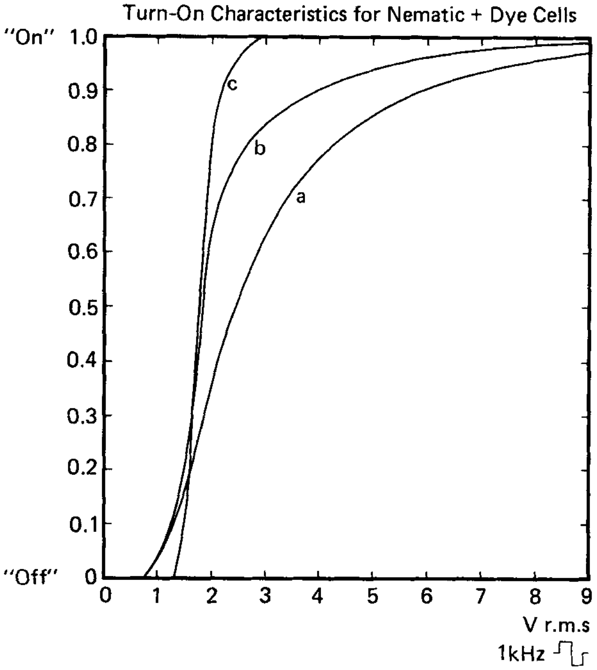


FIGURE 2 Normalized voltage contrast characteristics for a) conventional guest-host, b) TND and c) TN displays. The data for curve c are reproduced with permission from BDH Chemicals Ltd.

Degradation studies

The criteria for stability in dynamic scattering systems have been described by Gosse and Gosse,[7] and although the dc fields discussed in this study are at least half an order of magnitude lower than those associated with dynamic scattering displays, similar criteria apply. They state that the current carrying species must be reversibly oxidized and reduced at the display electrodes, and be chemically unreactive in the liquid crystal medium. It is not clear why complete reversibility (which infers only that the kinetics of the electrode reactions are fast compared to the rate of supply of reactant to the electrode) is required, but the electrode reactions should be sufficiently reversible to sustain the faradaic current through the cell without polarization into the regime of deleterious reactions. In addition, the flow- and adsorption-induced degradation mechanisms described by Sussman[8] for twisted nematic displays will apply to TND displays. Adsorption-induced tilt changes will cause severe contrast loss, but the formation of reverse twist domains is expected to be less deleterious for TND than for TN displays because of the former uses only a single polarizer.

Stable systems

The stable system chosen was E7 or E37 host and D37 dye which is one of a series of 1,5 dianilino anthraquinone dyes which has been shown to be stable under ac conditions for periods of more than 2×10^3 hr.[9] Cells have been tested at bias voltages of 1 V for more than 9×10^3 hr and at 1.5 V for more than 4.5×10^3 hr. Resistance and capacitance measurements at 5 kHz (the lowest operating frequency of the bridge) showed no significant variation, indicating no gross compositional changes of the guest-host system. Whilst cells were tested in a dry environment, T_{NI} remained constant ±1°. Between 3×10^3 and 4×10^3 hr before the end of the test, cells were transferred to a convection oven situated in a laboratory of ambient relative humidity from 40 to 55%. From this time, an upward trend in T_{NI} was observed in all cells. The data are shown in Figure 3. Al or Al/Al_2O_3 electrodes are much less efficient in transferring charge to and from the electrolyte than ITO electrodes, and would be expected to inhibit electrochemical degradation. No significant differences were observed between ITO//Al and ITO//

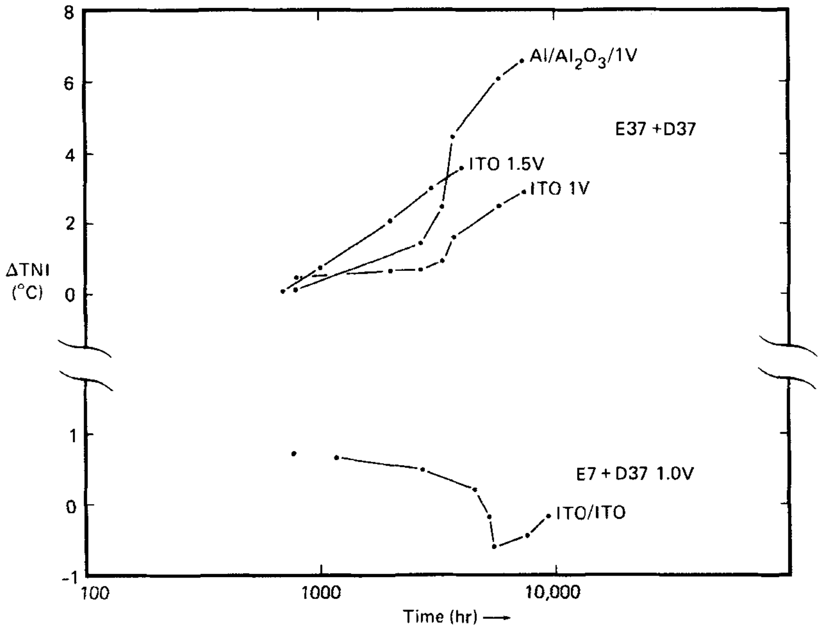


FIGURE 3 Variation of clearing point with time for TND test cells.

Al/Al_2O_3 cells, whether polarized positive or negative. The data are combined and also shown in Figure 3 from which it is apparent that these cells exhibited a significantly more rapid increase in T_{NI} than did ITO//ITO cells subjected to the same drive voltage. The reasons for the increase in T_{NI} and for the differences between different electrodes are not known. It is possible that absorption of atmospheric water vapor may be the cause (the trend is not reversed by heating cells to 80°C under vacuum for 100 hr) but it is noteworthy that the trend was not associated with the incidence of visual defects, nor with changes in absorbance or, by inference, tilt. The influence of small bias fields on tilt was investigated by applying fields between the two overlapping electrodes (connected in common) and a third electrode, adjacent to one of the common electrodes. The test conditions were 5 V r.m.s. biased

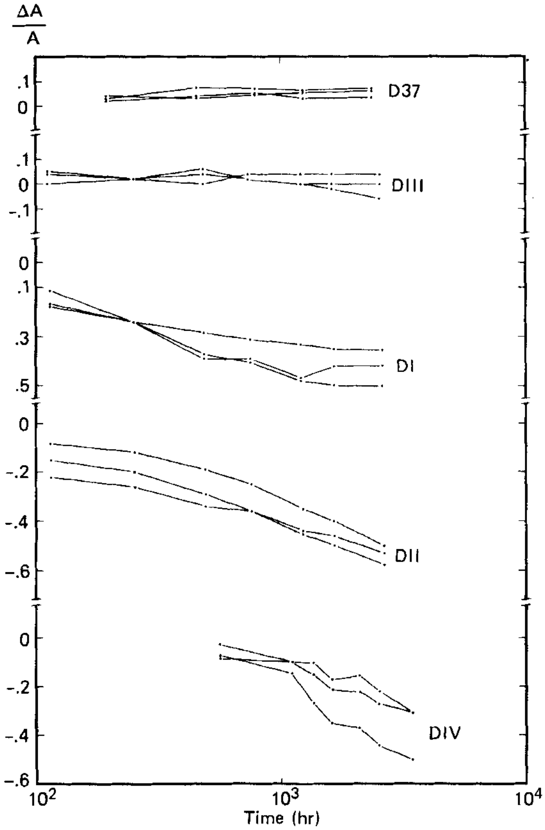


FIGURE 4 Relative change in maximum absorbance with time for TND cells. Curves are identified from the top at the right-hand end. D37, no field, ac only, ac + 5 V dc; DIII, ac only, ac + 1 V dc, ac + 1.5 V dc; DI, ac only, ac + 1 V dc, ac + 1.5 V dc; DII, ac + 1.5 V ac, ac only, ac + 1 V dc; DIV, ac + 1.5 V dc, ac only, ac + 1 V dc.

at 1.5 V with the common electrodes polarized positive or negative, 5 V r.m.s. only, and no field. Cells filled with E37 only and with an E37/D37 mixture were tested for 2×10^3 hr. Tilt measurements, made at intervals, between the two overlapping electrodes, indicated no changes in tilt ($\pm 0.5°$) in any of the cells, demonstrating that, under the conditions of the test, no significant polarity-dependent adsorption of impurity ions occured.

Absorbance measurements (Figure 4, upper curve) showed a slight increase in absorbance with time under all test conditions. This trend may be associated with the increase in T_{NI} of $3 \pm 0.3°C$ for the nine cells tested.

It is relevant to comment at this point on the dc faradaic charge passed through a TND cell over a period of one year (8.8×10^3 hr). The limiting current through a 6.5 μm ITO/ITO cell filled with E37/D37 is about 2.7 nA (3.5 nA/cm^2). In one year, this corresponds to a charge of approximately 0.1 C. The dye contained in a test cell filled with a 2.5% solution by weight of D37 will be electrolyzed by 3×10^{-3}C, assuming a one-electron process. Thus, the charge passed in one year is sufficient to electrolyze the dye in the cell approximately 30 times over. No visual degradation has been observed of the cells reported here.[†]

In summary, the results indicate that the E7/D37 and E37/D37 guest-host systems appear to be sufficiently stable for application to integrated TND displays in which a significant dc bias appears across the liquid crystal.

Comparison of dyes

Solutions of DI, II, III and IV in E37 were tested at 5 V r.m.s. biased at zero, 1 and 1.5 V dc. The relative changes in maximum absorbance are plotted against time in Figure 4. If changes in absorbance are due to destruction of dye and not to shifts in λ_{max} or changes in order parameter, $\Delta A/A$ represents the fractional change in dye concentration on a scale 0 to 1. Within experimental error, DIII is seen to be stable under all drive conditions. The other dyes show significant degradation under all drive conditions. T_{NI} showed an upward trend in all cases. The increases for DII and DIV were 30% less than for DIII and D37 and may be interpreted as a relative decrease in T_{NI}. Deterioration of DI, II and IV was associated with the formation of many reverse twist loops and, in the case of DI, the appearance of discolored areas on the electrodes. Cells filled with E37/DV showed similar deterioration over a period of 4×10^3 hr.

[†] Degradation was observed in cells in which the epoxy seals had been cured for less than 30% of the recommended time. In these cases, loss of alignment emanated from the seal and, on reaching the electrodes, often showed the worst degradation in positions similar to those indicated by Sussman.[8] In addition, loss of alignment, which was associated with a large increase in tilt, was always worse on the positive electrode.

In order to examine the possible reasons for the observed differences in stability, the electrochemical redox behavior of the dyes already described, together with a representative sample of components of the eutectic nematic hosts, were investigated.

Voltammetric peak potentials for all the compounds examined are given in Table III. Representative cyclic voltammograms are shown in Figures 5 (cathodic) and 6 (anodic). Figure 5 also contains data for oxygenated and deoxygenated blank solutions.

From Table III, it is seen that all the host components are rather stable both to oxidation and reduction with potential differences between the first oxidation and first reduction peaks from 3.93 to 4.35 V. All electrode reactions of these materials were irreversible. By comparison, the dyes, whether stable or not, were more easily oxidized and reduced than the host.

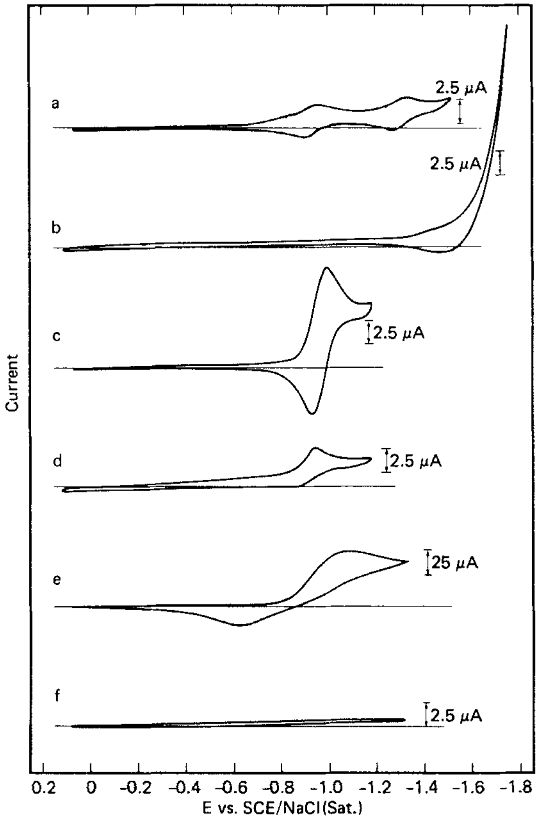


FIGURE 5 Cyclic voltammograms of dyes in solution in acetonitrile/0.1 M TEAP. Potentials reported vs SCE/NaCl (sat). Sweep rate 10 mV/s. a) D37, b) DII, c) DIII, d) DIV, e) blank solution, oxygenated, f) blank solution after deoxygenation.

TABLE III

Cyclic voltammetric peak potentials vs SCE/NaCl (sat)

Material	2nd Cathodic* Peak (V)	1st Cathodic Peak (V)	1st Anodic Peak (V)	2nd Anodic* Peak (V)	1st Anodic-1st Cathodic Potential Difference (V)
K21		-2.16	2.01		4.17
T15		-2.20	1.73		3.93
BB21		-2.26	1.98		4.24
CHE		-2.30	2.05		4.35
D37	-1.34	-0.96	1.20		2.16
DI		-0.94	1.50+		2.44
DII		-1.43	0.85		2.28
DIII	-1.33	-1.00	0.61		1.61
DIV		-0.96	0.58	1.01	1.54
DV		-0.83	0.69	1.05	1.52
O_2		-1.08			

*These values are reported only when resolvable, somewhat reversible peaks are observed.

+No resolvable oxidation peaks are observed for this dye. Significant anodic current is passed above the potential quoted.

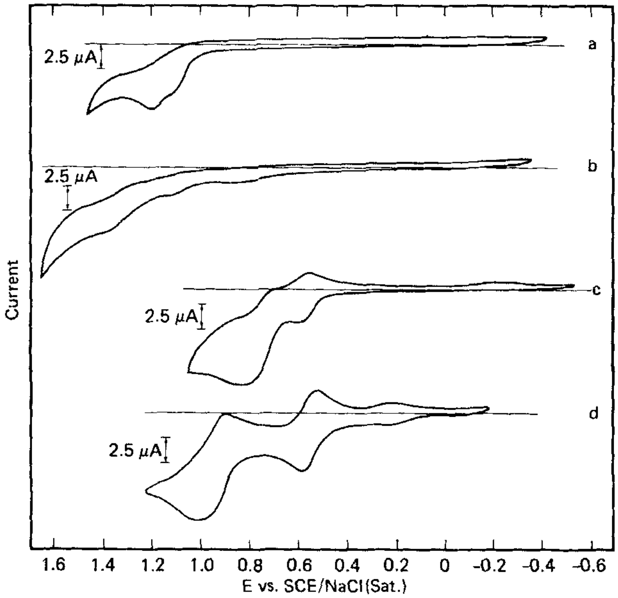


FIGURE 6 Cyclic voltammograms of dyes in solution in acetonitrile/0.1 M TEAP. Potentials reported vs SCE/NaCl (sat). Sweep rate 10 mV/s. a) D37, b) DII, c) DIII, d) DIV.

The criteria for electrochemical reversibility are that the potential difference (ΔE) between the forward and reverse current peaks is $59/n$ mV at 25°C and is independent of sweep rate.[10] n is the number of electrons involved in the reaction. $n = 1$ for the reversible reactions described here, and has not been identified for the others. A reaction is regarded as reversible if $\Delta E \sim 59$ mV and changes by no more than 2–3 mV for scan rates of 10 and 100 mV/s.

Thus, DIII shows one reversible reduction peak and D37 two. DIV and V are reversibly oxidized but show significant but unresolved shoulders at less anodic potentials. DIII shows three oxidation peaks, too close to be resolved, but it can be seen that the first step is somewhat reversible. All other electrode reations, both anodic and cathodic, are irreversible.

Comparing dye stability in TND test cells with electrochemical properties, we find that:

Stable dyes show reversible cathodic behavior.

Unstable dyes show irreversible cathodic behavior.

These observations are consistent with the mechanism proposed by

Lacroix and Tobazeon,[11] and demonstrated in dynamic scattering displays containing redox dopants by Lim, Margerum and Graube,[12] of a unipolar charge injection by reduction of dye, followed by migration of the resultant radical anion to the opposite electrode where it is oxidized back to the neutral species. The data are not consistent with the double-injection process described by Voïnov and Dunnett.[13] The further conditions which must be satisfied for stability is that the radial anion generated by reduction of the dye be stable in the guest-host medium. Such an investigation requires the application of e.g., ESR spectroscopy,[7] and is beyond the scope of this study.

The similar rates of degradation of unstable dyes, whatever the dc bias, can be understood by considering that the faradaic current flowing in a 6.5 μm TND cell driven with a 5 V 500 Hz square wave is of the order of 10 nA. This corresponds to an IR drop of the order of 1 V. Thus, the cell will be polarized sufficiently for electrolysis to occur even when driven with a pure ac wave form. An increase in applied voltage above that necessary for electrolysis to occur is largely offset by the IR drop, and relatively little additional polarisation of the electrodes results. Such an effect is seen in Figure 1 of Ref. 7. In the same work, the reduction of alkylcyanobiphenyl and phenyl benzoate liquid crystal in the liquid crystal medium is reported to be reversible. This explains why cells filled with host alone do not degrade. It is not clear why the electrochemical behavior of dyes in acetonitrile solution does correlate with display stability whilst that of hosts does not. Possibly the irreversibility of the host reduction is influenced by the proximity of the reduction potential of the solvent, which is present to such excess that the cathodic currents attributable to host and solvent are of similar magnitude.

Finally, the influence of dissolved oxygen must be considered. O_2 reduction is seen to be irreversible and to occur near the reduction potentials of the dyes, so O_2 reduction must occur in the test cells, which are exposed to the atmosphere, and would be expected to cause degradation. Unless the electrochemical reduction of O_2 becomes reversible in the liquid crystal medium, this observation cannot be explained. It is clear that some caution must be exercised when correlating electrochemical behavior in acetonitrile with stability in displays. Nevertheless, the technique shows promise for the rapid evaluation of dyes.†

CONCLUSION

A nematic guest-host display has been described in which the incorporation of a 90° twist results in an improved voltage-contrast characteristic.

† Preliminary data indicate that the correlation between stability and reversible cathodic behavior holds for the BDH dyes D43 and D52, which are stable, and D3, which is not.

The suitability of conventional liquid crystal components for integrated liquid crystal displays in which the LC is subjected to bias fields of the order of a few hundred millivolts has been investigated. The systems E7/D37 and E37/D37 have proved stable under conditions of temperature and bias fields more severe than those likely to be encountered in normal display use for periods of the order of 9 × 10^3 hr. Although increases in the clearing point were observed, no visual defects were noted.

Finally, electrochemical studies indicate that stable dyes undergo reversible electrochemical reduction, and from these and other preliminary studies, it appears that electrochemical screening may be of use in evaluating the stability of dyes for display use.

Acknowledgement

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