Cyclic Voltammetric and Phase Transition Studies of Some Liquid Crystalline Materials

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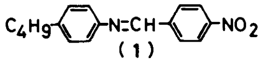
Cyclic voltammograms of some liquid crystalline compounds having electron-donating and -accepting abilities, and the thermal properties of binary mixtures involving these materials have been examined. Electric and thermal properties have been discussed in terms of a charge-transfer interaction in the liquid crystalline phase.

It is known that some binary mixtures display remarkable non-ideal solution behaviour in smectic A–nematic transitions, and sometimes in nematic–isotropic ones.[1,2] The components are known to form 1:1 or more complicated complexes.[3,4] The binary systems can be conventionally classified into two cases, polar–nonpolar systems where one of the components has a polar terminal group such as nitro or cyano, and the other has only an alkyl and/or alkoxy group, and polar–polar systems where one of the components has a relatively polar terminal group such as alkylamino, instead of alkyl or alkoxy. An important difference in these systems is that the latter type frequently show colour. Similar non-ideal solution behaviour in mesophases is known in nonpolar–nonpolar systems,[5] perhaps due to the slight difference in molecular shape of the components. However, the increase or decrease in mesophase stability is not so large in these systems. For the enhanced smectic A phase in the polar–nonpolar systems, Schneider *et al.* postulated the separation of polar molecules from the non-polar components which counteracted the formation of bilayer structures.[6,7] Oh has pointed out the importance of a dipole–induced dipole interaction in mesophases.[8]

On the other hand, Labes *et al.* have reported that in a binary mixture of polar–polar mesogens [4-cyano-4′-pentylbiphenyl and *N*-(4-methoxybenzylidene)-4-butylaniline], the smectic A–nematic transition temperatures display a remarkable enhancement in the middle region of the diagram, and concluded that the charge-transfer (CT) interaction of components of the binary mixture is the origin of the non-ideal solution behaviour.[9] Subsequently, many authors have reported intermolecular CT interactions in mesophases.[10–13] It is believed that CT interactions in smectic A and B phases tend to increase the thermal stability. In binary mixtures where one component is *N*-(4-alkoxybenzylidene)-4-nitroaniline and the other a liquid crystalline material having electron-donating ability, the nematic–isotropic transition temperatures display a remarkable enhancement.[1,2] CT interactions have been also proposed to play a very important role in non-ideal solution behaviour,[14] though some authors have denied the participation of a CT interaction.[15]

CT interactions are essentially oxidation–reduction reactions, and therefore the ionization potentials of liquid crystalline materials should be correlated with non-ideal solution behaviour in so-called polar–polar mixtures.

In this paper, we describe the oxidation and reduction potentials of the liquid crystalline materials (1)—(18) hitherto reported in connection with CT complex formation.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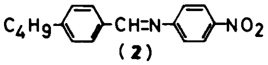
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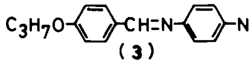
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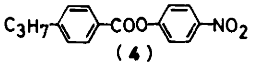
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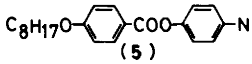
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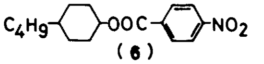
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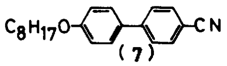
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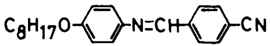
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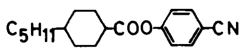
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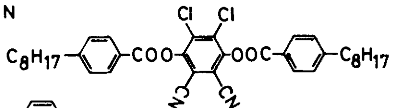
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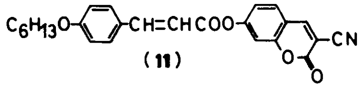
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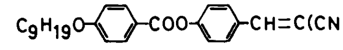
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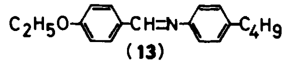
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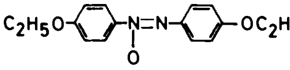
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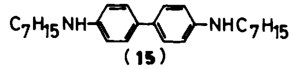
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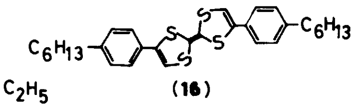
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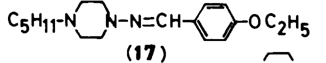
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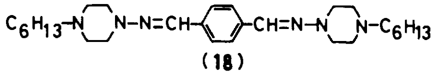
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Experimental

Materials.—The Schiff's bases (1)—(3) were prepared by the condensation of the corresponding aldehydes and amines.[16] The ester compounds (4)—(6) and (9) and their homologues were prepared by the reaction of the corresponding acid chlorides and phenols. Compounds (7) and (8) were purchased from Merck. The preparation of compound (11) has been described earlier.[17] Compound (12) was prepared by the reaction of 2,3-dichloro-5,6-dicyanohydroquinone and 4-octylbenzoyl chloride. Compound (13) and azoxyphenetole (14) were purchased from Tokyo Kasei. The diaminodiphenyl derivative (15) were prepared by the method of Demus *et al.*[18] The tetrathiofulvalene (TTF) derivative (16) was prepared by the method of Babean *et al.*[19] The preparations of piperazine compounds (17) and (18) have been reported in a previous paper.[20] The purity of the materials was confirmed by elementary analysis.

Method.—The cyclic voltammograms were measured by using a Hokutodenshi model HA-501 poteniogalvanostat and a Hokutodenshi model HB-104 function generator. The voltammograms were directly recorded with a chart recorder. The cell contained platinum electrodes (1 cm^2) separated by 1 cm,

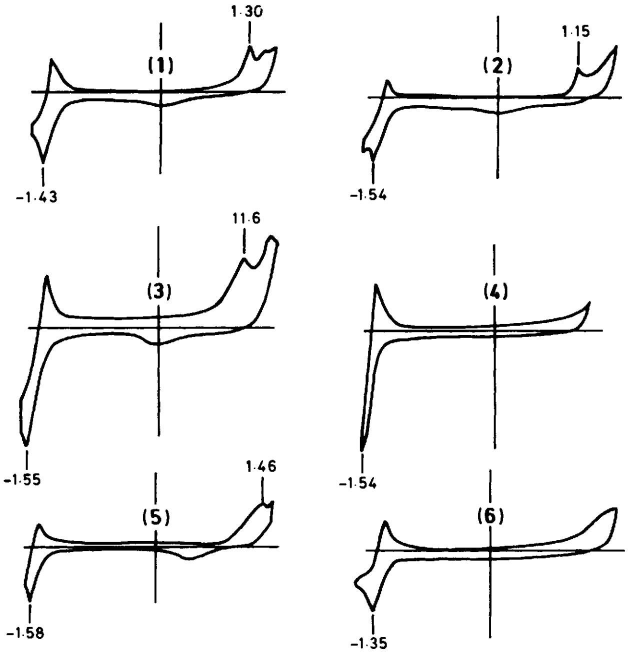


Figure 1. Cyclic voltammograms. The horizontal axes are values relative to Ag–Ag$^+$ in acetonitrile. The measurements were carried out in dichloromethane solutions containing the sample (0.001M) and tetrabutylammonium perchlorate (0.1M) at 25 °C, with a sweep rate of 100 mV s^{-1}. The vertical and horizontal axes represent current (arbitrary unit) and voltage, respectively

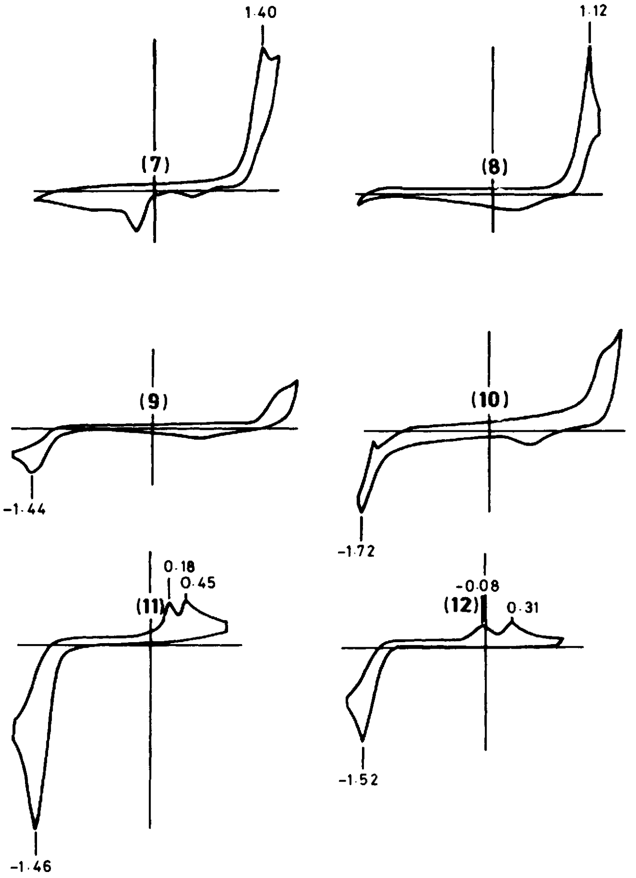


Figure 2. Cyclic voltammograms. Experimental conditions as in the caption to Figure 1

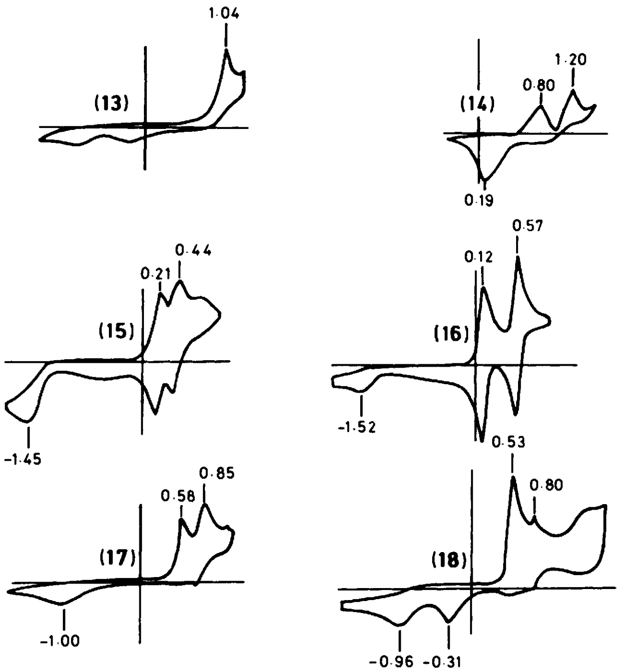


Figure 3. Cyclic voltammograms. Experimental conditions as in the caption to Figure 1

where silver–silver nitrate (0.01M) was used as reference electrode. The experimental conditions are described in Figure 1. The transition temperatures were determined by using a Nikon model POH polarising microscope fitted with a Mettler FP 52 heating stage and an FP 5 control unit.

Results and Discussion

Under our conditions, the oxidation and reduction potentials for tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and tetrathiofulvalene (TTF) are as follows:

	Reduction (V)	Oxidation (V)
TCNE	−0.24 and −1.44	−0.10 and −0.96
DDQ	−0.67	−0.55
TTF	0.08 and 0.37	−0.11 and −0.18

These are the most popular electron acceptors and donor for an electron donor–acceptor complex (EDA).

Cyclic voltammograms for liquid crystalline materials with a nitro or a cyano group are illustrated in Figures 1 and 2. Most voltammograms show remarkable irreversible processes. The azomethine compounds (**1**)—(**3**) with a nitro group show both oxidation and reduction peaks. The reduction peaks in the negative region correspond to the reduction of the nitro group. Oxidation peaks in the positive region, on the other hand, correspond to the oxidations of the nitrogen in the azomethine linkage, and an oxygen in the alkoxy chain. The reduction potential decreases by the order of (**3**) > (**2**) > (**1**). The reduction potential for compound (**1**) is lower by 0.11 V than (**2**), indicating that the nitrogen atom at the 4-position of the nitrobenzene slightly decreases the electron-withdrawing ability of the nitro group.

Compounds (**4**)—(**6**) have an ester group instead of the azomethine linkage. The reduction potentials are fundamentally similar to those of azomethine compounds (**1**)—(**3**). The

Compound	Reduction potential (V)	Compound	Oxidation potential (V)
(1)	−1.43	**(13)**	1.04
(2)	−1.54	**(14)**	0.80, 1.20
(3)	−1.55	**(15)**	0.21, 0.44
(4)	−1.54	**(16)**	0.12, 0.57
(5)	−1.58	**(17)**	0.58, 0.85
(6)	−1.35	**(18)**	0.53, 0.80
(7)			
(8)			
(9)	−1.44		
(10)	−1.72		
(11)	−1.46		
(12)	−1.52		

For experimental conditions see Figure 1.

difference in the reduction potential for compounds (**4**) and (**5**) is only 0.04 V, indicating that the electron-withdrawing ability of the nitro group is almost irrespective of the electronic nature of the substituent at the terminal position. A similar trend is observed in the oxidation potential of compounds (**2**) and (**3**).

For cyano compounds (**7**) and (**8**), any reduction of the cyano group could not be observed in the range between 0 and −1.6 V. This fact indicates that the electron-accepting ability of the cyano group is lower than the nitro group. For compounds (**7**) and (**8**), the oxidations occur at 1.40 and 1.12 V, respectively. The peak at 1.12 V corresponding to the oxidation of nitrogen in the azomethine linkage is slightly lower than that of the nitro compound (**1**), probably due to a weak electron-withdrawing effect of the cyano group.

Compound (**10**), incorporating the partial structure of DDQ, is non-mesogenic, perhaps because of the large molecular breadth. The reduction potential is −1.72 V which is very high compared with that of DDQ. However, the value appears to be lower than those of cyano compounds (**7**) and (**8**).

The cyanocoumarin and dicyanoethenyl compounds (**11**) and (**12**) have relatively low reduction potentials, which are comparable with those of nitro compounds (**1**)—(**3**). A characteristic in compound (**11**) is that the peak area for the oxidation corresponding to the reduction at −1.46 V is quite small. Instead, the diagram shows two-step oxidation at 0.18 and 0.45 V. This fact indicates that the reduced form of (**11**) is unstable and changes to an unknown substance(s) which is reduced at the respective voltages. Thereby, the 'unknown' compound(s) produces very strong fluorescence, which disappears at 0.45 V. A similar reaction is observed for compound (**12**), for which the oxidation potentials are −0.08 and 0.31 V.

The cyclic voltammograms for so-called 'electron donors' are shown in Figure 3. EBBA (**13**) shows an oxidation peak at 1.04 V, which corresponds to the oxidation of nitrogen in the azomethine linkage. An interesting fact is that the oxidation potential for compound (**13**) is almost comparable with those of compounds (**2**), (**3**), and (**8**), which have been considered to be electron acceptors. Azoxyphenetole (**14**) shows two oxidation peaks at 0.80 and 1.20 V, in which the former would arise from the oxidation of the azoxy group. The diaminobiphenyl derivative (**15**) shows a two-step oxidation at 0.21 and 0.44 V. The TTF compound (**16**) also shows a two-step oxidation at 0.12 and 0.57 V, which are the lowest values in the present compounds. The piperazine compounds (**17**) and (**18**) also have low oxidation potentials. In these cases, the reductions corresponding to the oxidations at 0.58, 0.85, 0.53, and 0.80 V are quite small, and the reductions occur in the negative region. A similar trend is observed in the cyclic voltammogram for compound (**15**). For compound (**14**) the reduction corresponding to oxidations at 0.80 and 1.20 V occurs at 0.19 V. The results are summarized in the Table.

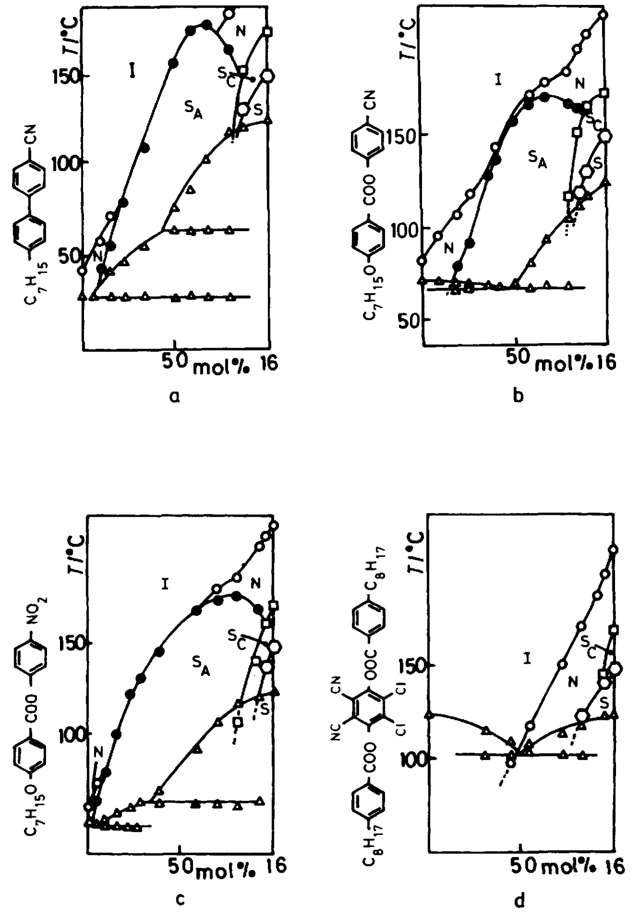


Figure 4. Isobaric diagrams. ○, Nematic–isotropic; ●, smectic A–nematic (isotropic); □ and ⬡, smectic–smectic; and △, crystal–smectic transitions

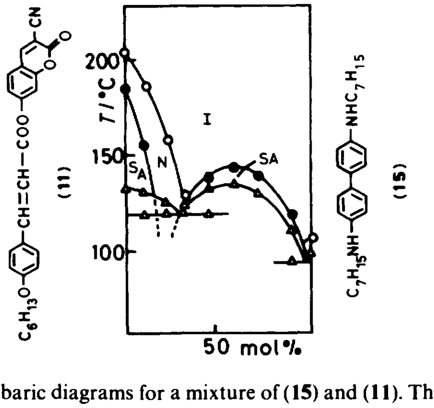
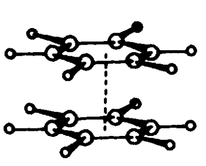


Figure 5. Isobaric diagrams for a mixture of (**15**) and (**11**). The notation is in the caption to Figure 4

Phase Diagrams.—Some phase diagrams of binary mixtures in which the TTF derivative (**16**) were used as an 'electron-donating' mesogen were examined, and the results are shown in Figure 4. In Figures 4a—c, the remarkably enhanced smectic A phases are recognized around the middle regions of the diagrams.



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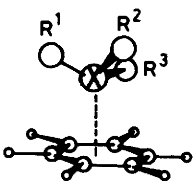

X=N,O,S,·····

(V)

An interesting phase diagram of a binary mixture is shown in Figure 5. In the isobaric diagram, the nematic–isotropic transition temperatures show a remarkable depression in the middle region. The mixture is dark brown when the components were mixed in air, and pale yellow when mixed under vacuum. The mixture has high conductivity.[21]

A charge-transfer interaction is essentially oxidation–reduction reaction (1) as successfully demonstrated by Mulliken.[22]

$$\underset{\textbf{(I)}}{A + D} \rightleftharpoons \underset{\textbf{(II)}}{A{:}D} \rightleftharpoons (A^-\|D^+ \rightleftharpoons \underset{\textbf{(III)}}{A^-} + D^+) \longrightarrow \text{Products} \quad (1)$$

Species **(III)** is a strongly associated complex, frequently an ionic species such as a contact, solvent-separated ion-pair or a free ion. These complexes sometimes form covalent bonds, giving products. The occurrence of an equilibrium between **(I)** and **(II)** is very important, since the population of the ionic species is usually not large even in relatively strong donor–acceptor systems. In general, the formation of weakly and strongly associated complexes **(II)** and **(III)**, respectively, is easily detected by absorption and n.m.r. spectroscopy

A dipole–induced dipole interaction is also classified as a weak CT process. The interaction is proportional to the dipole moment of one molecule and the polarisability of the other and inversely proportional to the distance (d^{-6}) of the interacting molecules, and such interaction is known to be very stereospecific.[22] For example, a polar group such as carbonyl, azomethine, nitro, and cyano is well solvated by aromatic compounds.[23,24] Here, we neglect the dipole–induced dipole interaction, since this interaction would be present in binary mixtures not only of 'charge transfer' systems but also so-called 'polar–nonpolar' ones. Oh has pointed out the importance of the dipole–induced dipole interactions in binary systems,[8] while de Jeu *et al.* have considered that the dipole–induced dipole interaction is a minor influence on mesomorphic phenomena.[25] However, we consider that the dipole–induced dipole interaction must be greater in so-called 'charge transfer' systems than in 'polar–nonpolar' ones, since the acceptor mesogens used in the CT systems are usually more polar than the nonpolar mesogens used in the 'polar–nonpolar' systems. The CT interaction is essentially an interaction of participating orbitals, of which there are two types. One is a π–π interaction and the other is *n*–π. The interactions would facilitate two types of molecular arrangements **(IV)** and **(V)**.[22]

Models **(IV)** and **(V)** correspond to the π—π and *n*—π types, respectively. For model **(V)**, such an interaction will decrease the orientational ordering in mesophases, decreasing the mesophase stabilities. On the other hand, the CT interaction in model **(IV)** appears to facilitate a layer arrangement of molecules, a general requisite of smectic stabilities, as noted by Waclavek *et al.*[3] Simultaneously, the CT interaction in model **(IV)** would generate a dipole perpendicular to the long molecular axis, which may be favourable for thermal stability of the disordered phase such as nematic and smectic A phases.[13] Thus, many authors have considered that the CT interaction results in an increase in smectic stabilities, especially in the smectic A phase.

In this paper, we examined the oxidation–reduction potentials for som liquid crystalline materials. We suppose that for a related series of the compounds, variations in ionization potential are much greater than those in the solvation energy of the materials in dichloromethane, and the oxidation and reduction potentials can be used as a criterion of electron-donating and -accepting abilities.

Most of the present compounds show remarkable irreversible processess, as shown in Figure 1—3. The reaction on a surface of the electrode are given by equations (2) and (3). The

$$A + e \rightleftharpoons A^- \rightleftharpoons [A_n]^- + \sigma\text{-bonded products (or decomposed)} \quad (2)$$

$$D \rightleftharpoons D^+ + e \rightleftharpoons [D_n]^+ + \sigma\text{-bonded products (or decomposed)} \quad (3)$$

side reactions are of importance for compounds **(11)**, **(12)**, **(15)**, **(17)**, and **(18)**, though we don't have any information about the products. In 'polar–nonpolar' and '–polar' systems, the polar mesogens **(1)**—**(8)** and the related compounds incorporating a cyano or a nitro group have been used as an electron acceptor. However, the reduction potentials are very high compared with those of DDQ and TCNQ. For nitro compounds **(1)**—**(6)**, the oxidation potentials of the nitrobenzene core is *ca.* −1.4 to −1.5 V which is almost independent of the substituent at the *para* position, and **(6)** has the lowest value. On the other hand, the reduction potentials for **(7)** and **(8)** are quite high, while the related compounds have been used as electron acceptors in binary systems displaying a remarkable enhanced smectic A phase.[8–10,26–29] As is evident from Figures 2 and 3, the oxidation potentials for **(7)** and **(8)** and also **(1)**—**(3)** are almost comparable with those for **(13)** and **(14)**, indicating that the so-called 'acceptor' mesogens **(1)**—**(3)**, **(7)** and **(8)** have similar electron-donating ability to those of electron donors **(13)** and **(14)**.

Compounds **(13)** and **(14)** and the related compounds have frequently been used as an electron donor in 'polar–polar' systems.[3,9,11] However, the oxidation potentials are not so low compared with those of alkoxyphenyl ester compounds [for example, the oxidation potentials of 1,4-bis-(4-octyloxybenzoyloxy)benzene is 1.50 V[21]] which are used in 'polar–nonpolar' systems.[6,8,27–29]

Let us consider a binary mixture consisting of an electron donor such as **(13)** and an acceptor such as compounds **(1)**—**(3)**, **(7)**, or **(8)**. Here, three kinds of CT interactions have to be taken into consideration. The first is an intermolecular CT interaction between acceptor molecules themselves. The second is an intermolecular CT interaction between the donor and acceptor molecules. The third is an intramolecular CT interaction of the acceptor molecule itself. This last mechanism should be independent of the concentration, and of the enhanced mesophases. The first mechanism must facilitate formation of the anti-parallel dimers. Although the formation of anti-parallel dimers in polar mesogens **(1)**—**(11)** has been confirmed by *X*-ray measurements, a dipole–dipole interaction perpendicular to the long molecular axis has been supposed to be the origin, but not a CT interaction.[30] The second and third mechanisms must operate competitively, since the oxidation potentials for both components are close. Supposing that the second mechanism plays the most important role in displaying the remarkable enhancement of the mesophases, one would expect that a binary mixture of **(11)** or **(12)** as an electron acceptor and compounds **(15)**—**(18)** as an electron donor shows very large enhancement of the mesophases. With this assumption, we examined the thermal properties of some binary mixtures, as shown in Figure 4. Certainly, these mixtures show some colouration. We could not find any apparent difference in the enhanced smectic A phases, while the reduction potentials for the acceptor mesogens are different. For example, a binary mixture of compounds (**10**) and (**16**) shows no induced smectic phase, while the reduction potential is lower than that of cyanobiphenyl (**7**) and cyanophenyl ester (**8**).

Compounds (**11**), (**12**), and (**15**)—(**18**) have relatively low oxidation or reduction potentials. An interesting fact is shown by the cyclic voltammograms for compounds (**11**), (**12**), (**15**), (**17**), and (**18**) in Figures 2 and 3. These compounds show remarkable irreversible oxidation—reduction processes, indicating that the reduced (or oxidized) forms formed by the electrode reaction are unstable, and change to intractable substances.

Demus *et al.* have reported that binary mixtures involving (**15**) or (**12**) show remarkably enhanced smectic A phases due to strong CT interaction.[12,13] From the present results, we can assume that these components have relatively strong CT interactions. However, we are interested in the non-ideal solution behaviour of the nematic–isotropic transition temperatures. Nematic–isotropic transition temperatures display the upward convexed features, but not an upward concave one.[12,13] We examined the thermal properties of a similar binary mixture as shown in Figure 5. In Figure 5, the nematic–isotropic transition temperatures show a remarkable depression in the middle region of the diagram, in addition to the enhanced smectic A phase. Furthermore, the enhancement of the smectic A phase is lower than those in Figures 4a—c. Another characteristic in Figure 5 is that both nematic and smectic A phases have broad two-phase regions. Similar phase behaviour can be observed in binary mixtures of (**15**)—(**18**) and (**11**) and (**12**).[21] These results are apparently opposite to the general trend observed in EDA systems. The depression in the nematic stability may be related to the fact that a strong CT interaction tends to facilitate parallel packing of molecules,[3,22] while the molecules in disordered phases such as nematic and smectic A phases tend to form a herringbone-like packing.[31,32]

In this paper, the oxidation and reduction potentials of some liquid crystals are compared with their thermal properties. However, we did not find a good correlation. As mentioned above, the CT interaction is essentially an interaction between participating π and n orbitals, and bulky molecules like liquid crystalline materials do not favour this interaction. A long alkyl chain in liquid crystals is especially unfavourable for this interaction, since it will increase the molecular breadth, and prevent approach of the participating orbitals. Furthermore, we can assume that the CT interaction is more effective in ordered phases such as S_B and S_E and also a solid phase, rather than disordered phases such as S_A and nematic.

Recent work has suggested that the longitudinal dipoles of polar liquid crystals play an important role in determining the molecular arrangement in disordered phases such as nematic, S_A, and S_C.[30] From these facts, dipole–dipole interactions between polar molecules[7] and dipole–induced dipole interactions between polar and non-polar molecules[8] might play an important role in enhancing smectic stability not only in 'polar–nonpolar' systems but also in 'polar–polar' ones.

We conclusively assume that the CT interaction is a minor factor in enhanced mesomorphic phenomena, and the role of the dipoles of very polar molecules must be taken into consideration.

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