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Phase behaviour of binary mixtures of 4-substituted phenyl 4'-*n*-alkoxybenzoates

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Phase behaviour of binary mixtures of 4-substituted phenyl 4′-*n*-alkoxybenzoates

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Five homologous series **I**a–e, of the title compounds have been prepared and investigated for their mesophase behaviour in binary mixtures. Each series differs from the other by a substituent X, which changes between CH_3O, CH_3, Cl, CN, and NO_2. The number of carbons in the terminal alkoxy group, within a homologous series, varies between 6, 8, 14, and 16. All possible binary combinations, made from any two components bearing an alkoxy group of the same chain length but two different substituents X, were prepared and similarly characterized for their phase behaviour. Transition temperatures of the mixtures were measured by differential scanning calorimetry and identified by polarizing optical microscopy. Phase diagrams were constructed for the various binary systems and discussed in terms of electronic effects.

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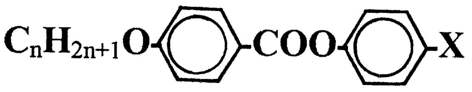
1. Introduction

An enormous number of liquid crystal (LC) materials have by now been prepared and although many are very similar; each has its own specific combination of structural moieties, which confer a certain phase morphology and particular values of melting points and transition temperatures. Furthermore, the combination of structural moieties determine the physical properties of materials, very important when they are being considered for specific applications. Accordingly, much care is required in the design and synthesis of LC materials in order to generate the desired properties and the necessary general physical characteristics. The generation of LC phases is limited to materials of specific molecular structures.

The ester (−COO−) group is one of the most commonly used linking units in LCs because it is relatively stable, easily synthesized, and can provide useful LC materials with low melting points. It is a planar linking group with a degree of polarizability due to the π-electrons associated with the carbonyl group; but the ester group is not a completely conjugative unit, hence it is versatile and capable of being used in a wide range of different molecular and electronic situations. Furthermore, the ester linkage is a polar group that can aid lamellar packing and generate smectic phases, especially when the terminal chains are sufficiently long. On the other hand, extension of the terminal *n*-alkoxy chain substituent gives rise to a gradient in the LC transition temperatures [1, 2]. In the lower homologues of a series, a nematic phase appears, and when the terminal chain length increases, there is a tendency for a smectic phase to appear.

The goal of the present study is to prepare five groups of compounds of type **I**, where X varies from the electron-donating CH_3O and CH_3 groups to the electron-withdrawing NO_2 and CN groups, passing through the Cl substituent which possesses opposing mesomeric and inductive effects, while the terminal alkoxy group changes between *n*-hexyloxy and *n*-hexadecyloxy.

The study aims to investigate the effect of terminal chain length as well as polarity of the substituent X on the mesophase behaviour of their binary mixtures. Such a variation in the molecular electronic properties could be a probe to investigate factors bearing on the phase transitions. The literature [2–7] contains some isolated data of these esters, but there has been no systematic study of the thermal behaviour of their binary mixtures



I*n*a–e

I6, $n = 6$; **I**8, $n = 8$; **I**14, $n = 14$; **I**16, $n = 16$
a, $X = CH_3O$; b, $X = CH_3$; c, $X = Cl$; d, $X = CN$; e, $X = NO_2$

In these series of esters, mutual conjugation between the oxygen atom of the alkoxy group and the ester carbonyl group plays an important role in persistence of the mesomorphic phase. Thus, the alkoxy group, situated in *para*-position to the ester carbonyl group, will promote the polarity of the ester (C=O) group and, consequently, the intermolecular force of attraction.

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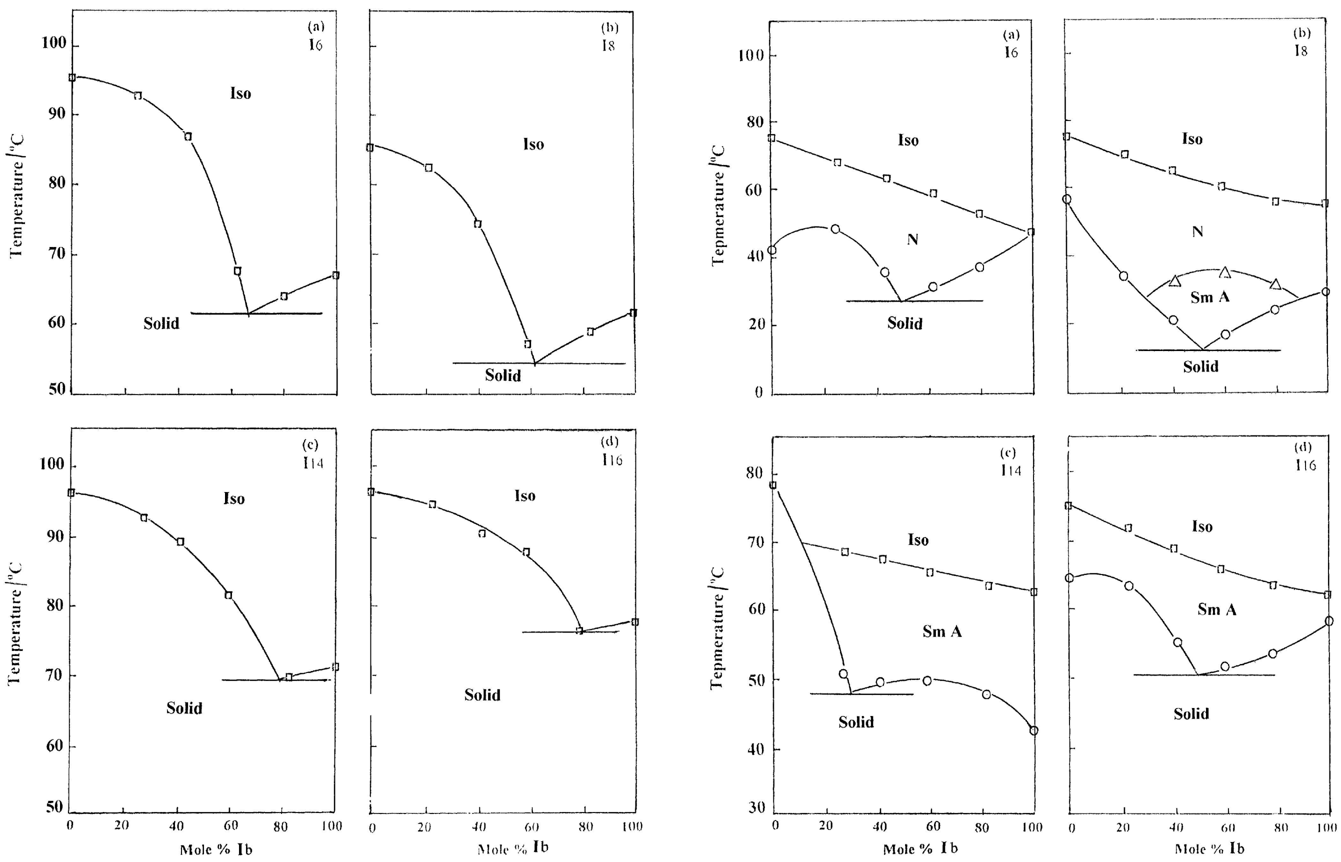
Table. Transition temperatures (°C) for compounds 4-$C_nH_{2n+1}O$–C_6H_4–COO–C_6H_4–X-4. Values beween parentheses are those determined by the extrapolation method.

Compound	n	X	$T_{C\text{-}A}$	$T_{C\text{-}N}$	$T_{C\text{-}I}$	$T_{A\text{-}N}$	$T_{A\text{-}I}$	$T_{N\text{-}I}$
I6a	6	CH_3O	—	—	95.0	—	—	(71.2)
I6b	6	CH_3	—	—	66.7	—	—	(50.0)
I6c	6	Cl	—	—	89.9	—	—	(53.0)
I6d	6	CN	—	72.0		—	—	82.2
I6e	6	NO_2	—	—	68.0	—	—	(58.5)
I8a	8	CH_3O	—	—	85.0	—	—	(76.2)
I8b	8	CH_3	—	—	61.8	—	—	(55.2)
I8c	8	Cl	—	—	79.4	—	(65.0)	—
I8d	8	CN	—	78.0	—	—	—	84.1
I8e	8	NO_2	53.1	—	—	62.6	—	69.2
I14a	14	CH_3O	—	—	96.3	—	(75.0)	—
I14b	14	CH_3	—	—	71.1	—	(53.0)	—
I14c	14	Cl	—	—	79.8	—	(71.0)	—
I14d	14	CN	78.0	—	—	—	94.8	—
I14e	14	NO_2	74.6	—	—	—	87.9	—
I16a	16	CH_3O	—	—	96.1	—	(80.0)	—
I16b	16	CH_3	—	—	77.7	—	(54.5)	—
I16c	16	Cl	—	—	84.7	—	(71.0)	—
I16d	16	CN	85.9	—	—	—	96.9	—
I16e	16	NO_2	79.4	—	—	—	88.7	—



(*a*) (*b*)

Figure 1. (*a*) Phase diagrams, on heating, for the binary systems **I**a/**I**b: alkoxy chain length (a) $n = 6$, (b) $n = 8$, (c) $n = 14$, and (d) $n = 16$. (*b*) Phase diagrams, on cooling, for the binary systems **I**a/**I**b: alkoxy chain length (a) $n = 6$, (b) $n = 8$, (c) $n = 14$, and (d) $n = 16$.

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These esters were chosen because in a single series (**I**6–**I**16) the difference between its members lies in the electronic nature of the terminal substituent *X*, while the difference between corresponding homologues of the four series is the length *n* of the alkoxy group.

2. Experimental

Chemicals were purchased from the following companies: Aldrich, Wisconsin, USA; E. Merck, Darmstadt, Germany; and Fluka, Buchs, Switzerland. The preparation of materials **I**6a–e–**I**16a–e was carried out by the method described in a previous paper [8].

Calorimetric investigations were made using a Polymer Laboratories differential scanning calorimeter, PL-DSC (England), with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultra-pure metals, a value of 28.45 J g^{-1} being used for the enthalpy of fusion of indium. The typical heating rate was 10 K min^{-1}, and the sample mass was 2–3 mg. Transition temperatures were identified with a standard polarizing optical microscope (C. Zeiss, Germany), attached to a FB 52 hot-stage equipped with a FB 80 central processor (Mettler, Switzerland).

For the phase diagrams, binary mixtures of any two components, in each series (**I**6–**I**16), covering the whole range of composition, were prepared by melting the appropriate amounts of each component, stirring to give an intimate blend, and then cooling while stirring in air to room temperature. The transition temperatures, obtained for the prepared blends, as measured by both techniques, agreed within 2–3°C. In the phase diagrams, constructed by plotting the transition temperatures versus mixture composition, the symbol '□' denotes solid–isotropic or mesophase–isotropic transitions, '○' solid–mesophase transitions, and '△' smectic–nematic transitions.

3. Results and discussion

Transition temperatures, as measured by DSC and identified by polarizing optical microscopy, for all the compounds investigated, are summarized in the table. In the table the subscripts, C, A, N, and I denote solid, smectic A, nematic, and isotropic, respectively. As shown in this table, the methoxy (**I**a) and methyl (**I**b) derivatives in the first two series (**I**6 and **I**8) possess only a monotropic nematic phase, while the higher homologue:

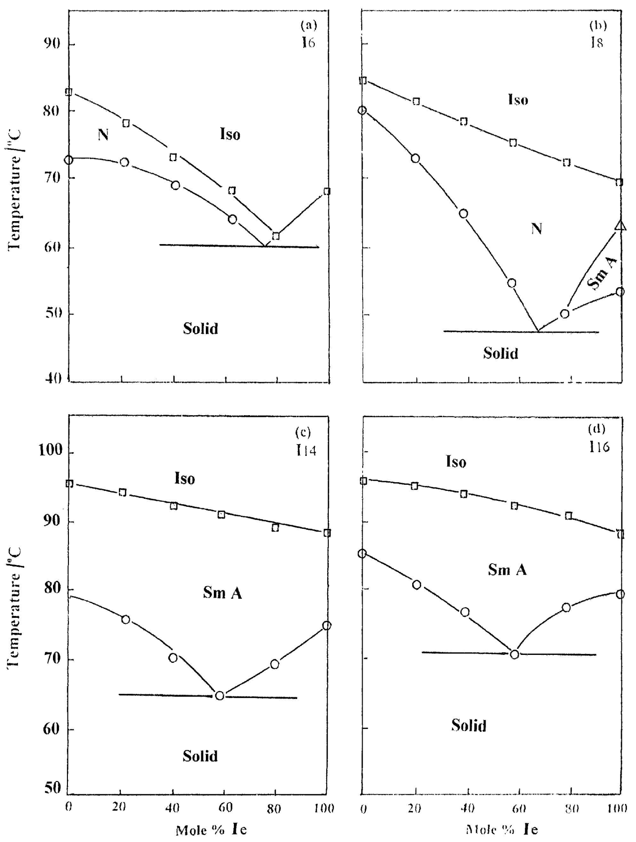

Figure 2. Phase diagrams for the binary systems **I**d/**I**e: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

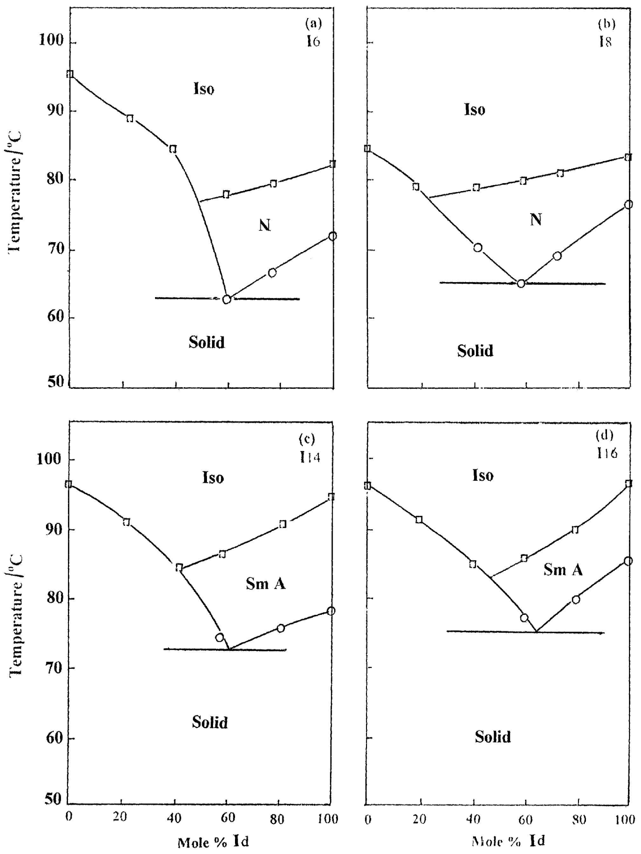

Figure 3. Phase diagrams for the binary systems **I**a/**I**d: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

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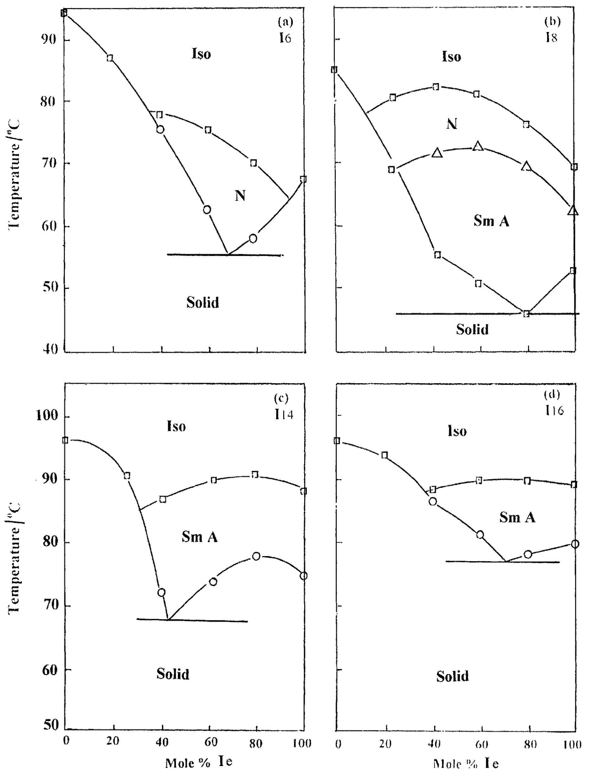

Figure 4. Phase diagrams for the binary systems **Ia**/**Ie**: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

(**I**14a,b and **I**16a,b) exhibit only monotropic smectic A phases. As for the chloro derivatives, the lowest homologue (**I**6c) is shown to be non-mesomorphic whereas the higher homologues (**I**8c–**I**16c) exhibit monotropic smectic A phases. In the case of the electron-withdrawing cyano-substituted derivatives, the lower two homologues (**I**6d and **I**8d) show only an enantiotropic nematic phase, whereas the two higher homologues (**I**14d and **I**16d) possess enantiotropic smectic A phase. The first nitro-substituted homologue (**I**6e) exhibits a monotropic nematic as the only mesophase; occurrence of the smectic A phase starts from the second homologue (**I**8e) alongside the nematic phase which disappears at the expense of the smectic A in the last two homologues (**I**14e and **I**16e).

The mesophase–isotropic transition temperatures, i.e. the clearing temperatures T_c, determined on heating for non-mesomorphic compounds or monotropic phases, were estimated from their binary phase diagrams with one of the enantiotropes, **Id** or **Ie**, by the extrapolation method of Bogojawlensky and Winogradow [9]. The visible portions of the mesophase–isotropic transition lines were extrapolated to give results that are supported by the concordant values obtained from two different systems. Average values are included in parentheses in the table.

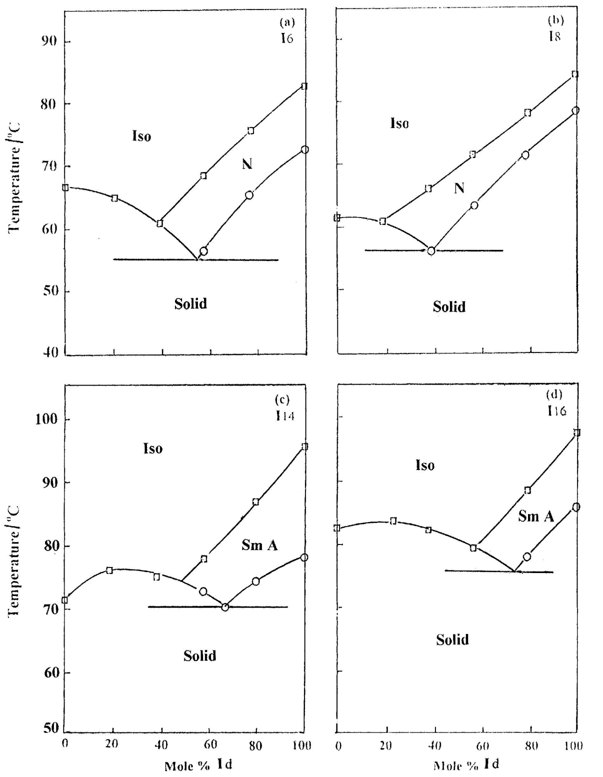

Figure 5. Phase diagrams for the binary systems **Ib**/**Id**: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

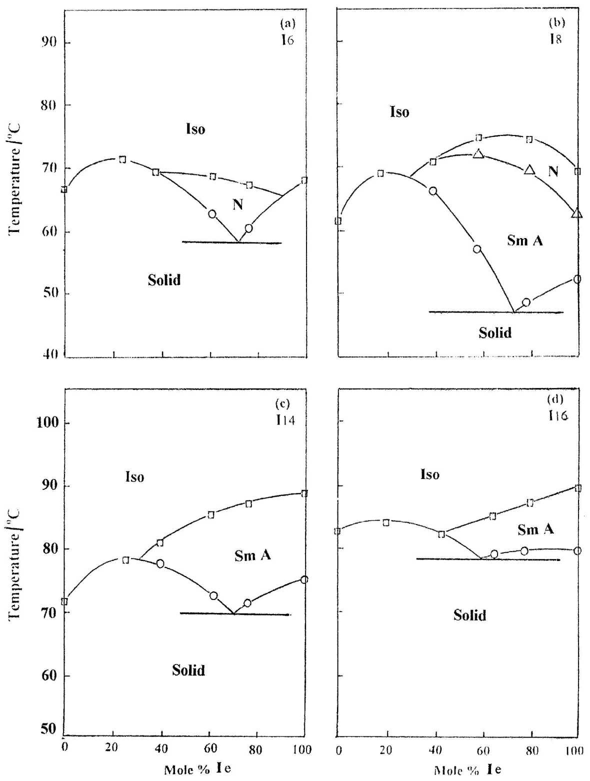

Figure 6. Phase diagrams for the binary systems **Ib**/**Ie**: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

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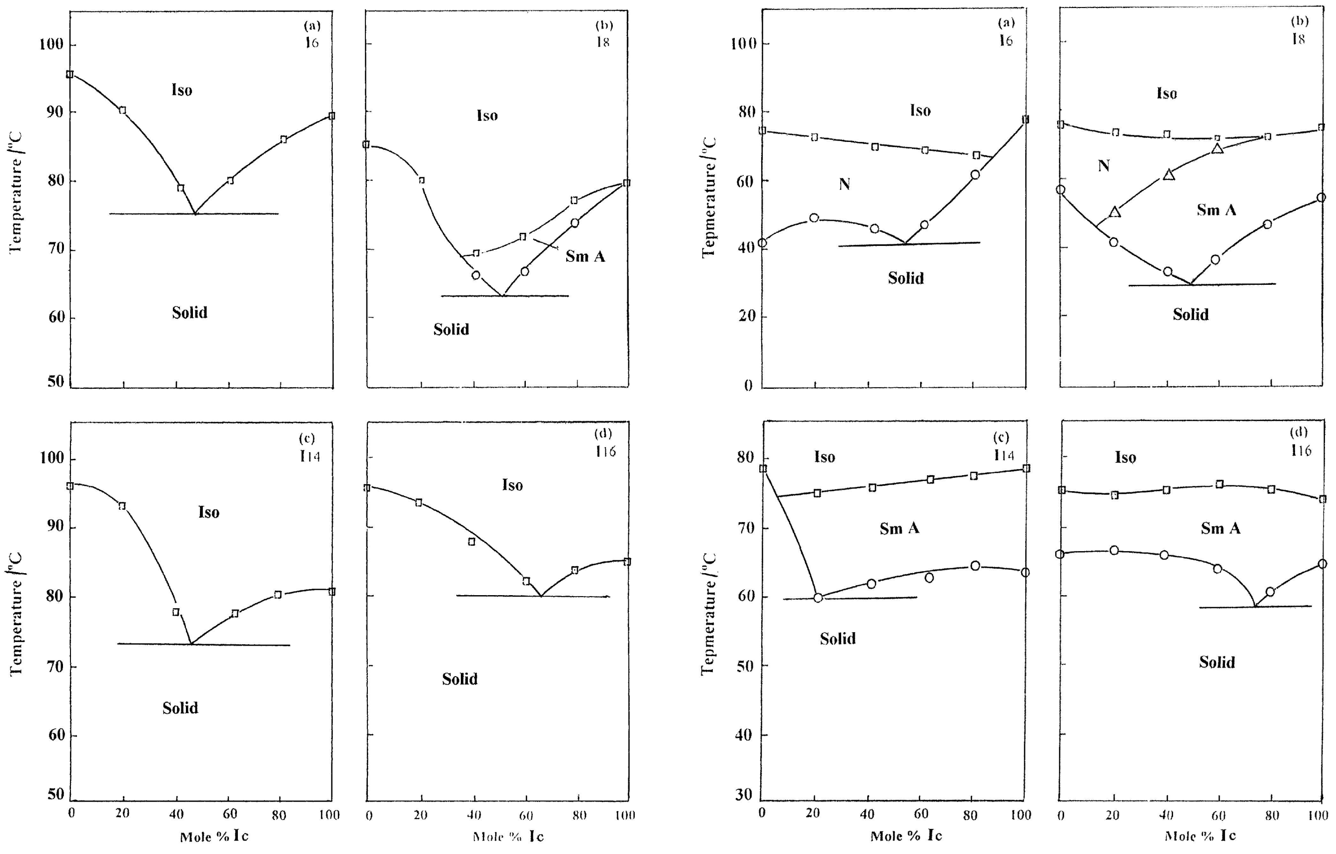
3.1. *Binary mixtures of electron-donating substituted derivatives*

The four phase diagrams of binary systems made from the methoxy (**Ia**) and methyl (**Ib**) substituted analogues in the four series, **I6**–**I16**, are represented collectively in figure 1 (*a*). Since both components in each binary system show their mesophases only monotropically, their binary phase diagrams show no mesomorphic range, on heating, throughout the whole composition range. Conversely, the corresponding phase diagrams, constructed on cooling (figure 1 (*b*)) show a mesomorphic range dependent on the alkoxy chain length. Thus, the first binary system, **I6a**/**I6b**, figure 1 *b*(a), possesses only a monotropic nematic phase, throughout almost the whole composition range. In the second system, **I8a**/**I8b**, figure 1 *b*(b), an injected smectic A mesophase was observed within the composition range 30–90 mol % of **I8b**, in addition to the monotropic nematic phase which covers the whole composition range.

The appearance of the smectic A mesophase in this system may be attributed to the supercooling effect, where its eutectic melting point is below 20°C. This smectic A phase increases to cover about 90% of the composition range in the third system, **I14a**/**I14b**, figure 1 *b*(c), and the whole composition range in the last system, **I16a**/**I16b**, figure 1 *b*(d). It can also be seen from figure 1 (*b*) that the eutectic melting point decreases at first, from the first to the second system, where the smectic A phase starts to appear, and increases again in the last two systems, where the smectic A mesophase predominates.

3.2. *Binary mixtures of electron-withdrawing substituted derivatives*

Corresponding phase diagrams of binary systems made from the cyano (**Id**) and nitro (**Ie**) substituted analogues, in the four **I6**–**I16** series, are illustrated in figure 2. As can be seen from figure 2 (*a*), which represents the system **I6d**/**I6e**, an enantiotropic nematic phase is the only mesophase observed up to a composition of 80 mol % of **I6e**. This may be attributed to the fact that the nitro derivative **I6e** shows its nematic phase only monotropically, while the cyano analogue, **I6d**, shows it enantiotropically. In the second binary system, **I8d**/**I8e**,



(*a*) (*b*)

Figure 7. (*a*) Phase diagrams on heating, for the binary systems **Ia**/**Ic**: alkoxy chain length (a) $n=6$, (b) $n=8$, (c) $n=14$, and (d) $n=16$. (*b*) Phase diagrams, on cooling, for the binary systems **Ia**/**Ic**: alkoxy chain length (a) $n=6$, (b) $n=8$, (c) $n=14$, and (d) $n=16$.

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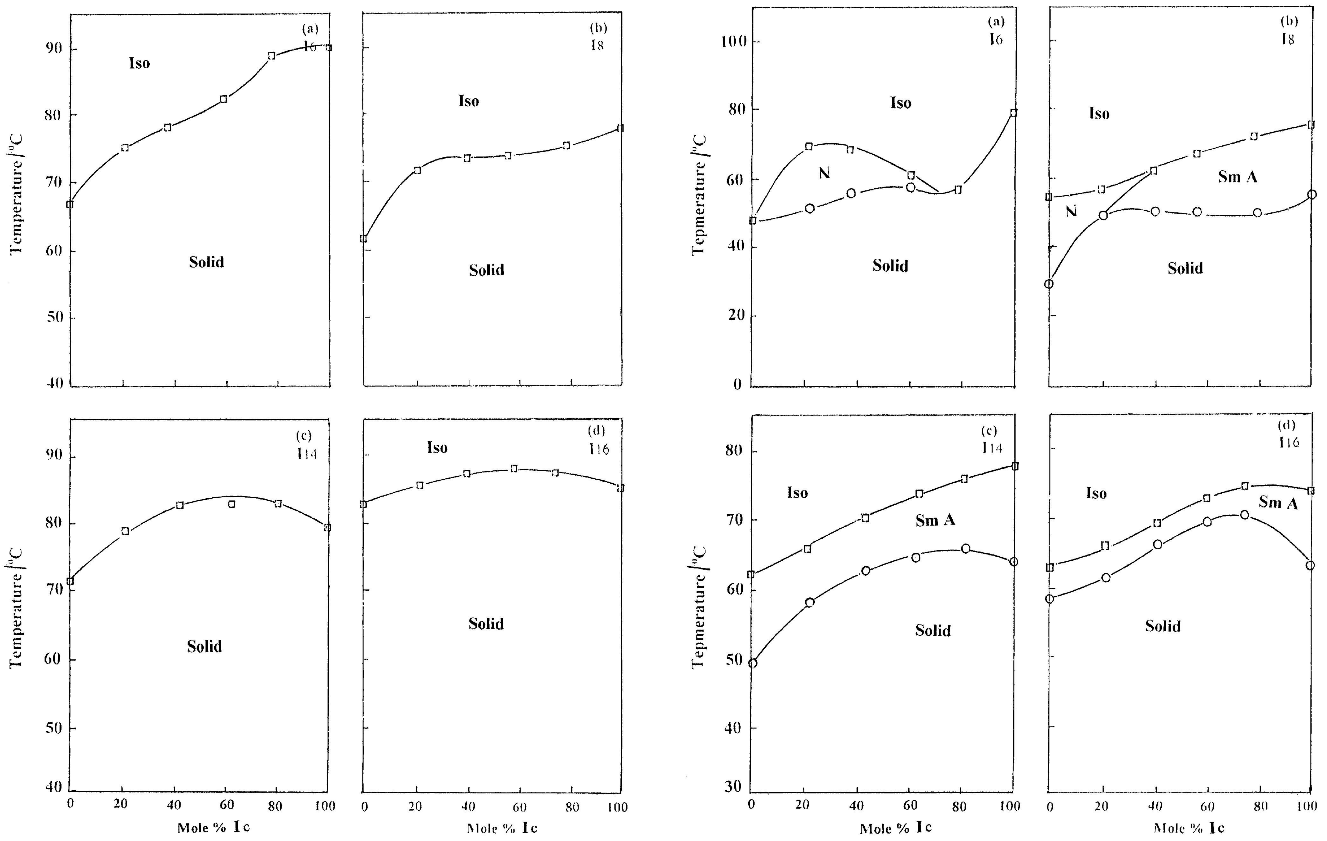
figure 2(*b*), the smectic A mesophase of the nitro analogue is totally destroyed by the addition of about 20 mol % of the cyano analogue, so that the nematic phase becomes the only mesophase in mixtures containing more than 20 mol % of **I**8d. In the higher two systems, **I**14d/**I**14e and **I**16d/**I**16e, figure 2(*c*, *d*), the smectic A is the only mesophase observed and covers the whole range of composition.

3.3. *Binary mixtures of electron-donating and electron-withdrawing substituted derivatives*

Four possible binary systems can be prepared from the methoxy (**I**a) or methyl (**I**b) analogues, as the first component, and the cyano (**I**d) or nitro (**I**e) substituted derivatives, as the second component, from each of the four series **I**6–**I**16. The various phase diagrams for the systems **I**a/**I**d, **I**a/**I**e, **I**b/**I**d, and **I**b/**I**e, possessing alkoxy groups with increasing chain length, are illustrated, respectively, in figures 3–6. Figure 3 (for the **I**a/**I**d systems) shows that T_c linearly varies with composition. In the lower systems (**I**6a/**I**6d and **I**8a/**I**8d) only the nematic phase is observed, while in the higher systems (**I**14a/**I**14d and **I**16a/**I**16d) smectic A becomes the only mesophase. Increasing the alkoxy chain length is accompanied by an increase in the eutectic melting point; these are 63, 65, 73, and 76°C, respectively.

Regarding the methoxy/nitro substituted binary systems, figure 4, the T_c–composition dependences are somewhat curved, indicating stronger molecular interaction between the electron-rich methoxy derivatives and the electron-deficient nitro-substituted analogues. The nematic phase, which is not observed on heating in either **I**6a or **I**6c, appears within the composition range 30–90 mol % of **I**6e. This is again due to the strong supercooling which results in a eutectic melting point of ≈55°C. The eutectic melting point decreases in the second system (**I**8a/**I**8e) and increases again to 68 and 77°C respectively, in the last two systems.

The methyl-substituted derivatives (**I**b) gave phase diagrams, with the cyano (figure 5) and nitro (figure 6) substituted analogues, which are quite similar to those obtained with the methoxy-substituted (**I**a) analogues



(*a*) (*b*)

Figure 8. (*a*) Phase diagrams, on heating, for the binary systems **I**b/**I**c: alkoxy chain length (a) $n=6$, (b) $n=8$, (c) $n=14$, and (d) $n=16$. (*b*) Phase diagrams, on cooling, for the binary systems **I**b/**I**c: alkoxy chain length (a) $n=6$, (b) $n=8$, (c) $n=14$, and (d) $n=16$.

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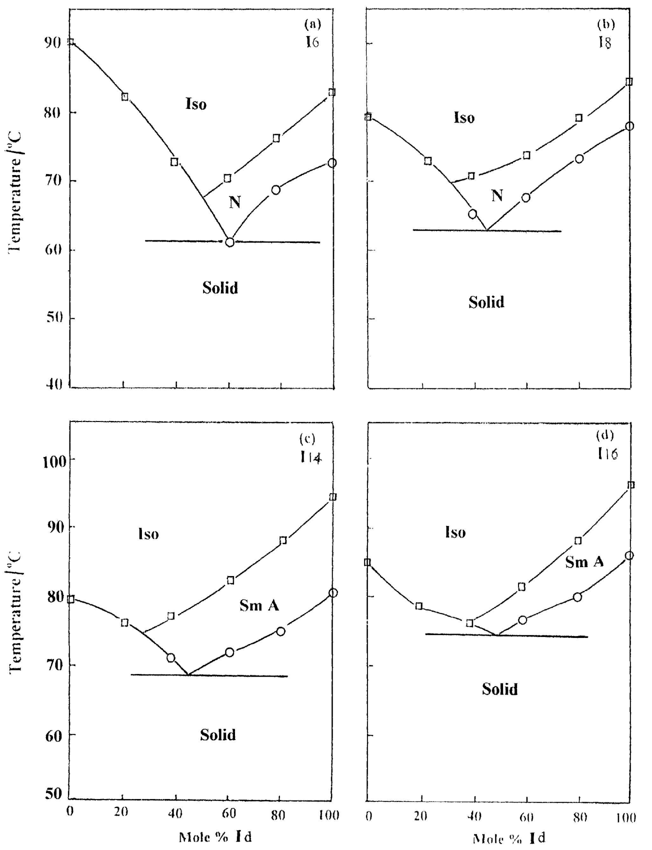

Figure 9. Phase diagrams for the binary systems **Ic**/**Id**: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

(figures 3 and 4). In the former system (**Ib**/**Id**) the eutectic point increases from 55 to 56, 70, and 76°C, with increasing alkoxy chain length, while in the latter systems (**Ib**/**Ie**), it first decreases from 58 to 48°C and then increases to 70 and 78°C.

3.4. *Binary mixtures of chlorine-substituted and electron-donating substituted derivatives*

Two systems, namely **Ia**/**Ic** and **Ib**/**Ic**, were investigated and are illustrated in figures 7 (*a*) and 8 (*a*), respectively. Since all the components of these binary systems show their mesophases monotropically, the binary phase diagrams were also constructed on cooling and are illustrated in figures 7 (*b*) and 8 (*b*), respectively. In spite of the fact that both the methoxy and methyl groups are electron-donating, the binary phase behaviour of their substituted derivatives with the chloro analogues was different. That is, the methoxy derivatives gave eutectic solid behaviour while the methyl derivatives gave mixed melting points with the chloro that varied gradually with composition, indicating the formation of an ideal solid solution. Furthermore, in the system **I**6b/**I**6c, enhanced T_c values were observed, resulting in the formation of a nematic phase up to a composition of about 70 mol % of **I**6c. In the next higher system, **I**8b/**I**8c, in addition to the observed smectic A phase, the nematic phase of **I**8b disappears on addition of less than 40 mol % of **I**8e. In the higher two systems, **I**14 and **I**16, small smectic A ranges are observed throughout the whole composition range.

Returning to figure 7, i.e. for the systems **Ia**/**Ic**, in the lowest system the nematic is observed as the only mesophase, whereas smectic A starts to appear in the second system and becomes the only phase in the last two systems (see figure 7 (*b*)). The induced smectic A phase observed in the second system (figure 7 (*a*)) is again attributed to the low eutectic melting point. The eutectic melting points first decrease from 75 to 64°C then increase to 73 and 80°C in the last two systems, respectively.

3.5. *Binary mixtures of chlorine-substituted and electron-withdrawing substituted derivatives*

Figures 9 and 10 represent the binary phase diagrams for systems comprising the chloro-substituted derivatives as one component and the cyano- or nitro-substituted analogues as the second one, respectively. As can be seen

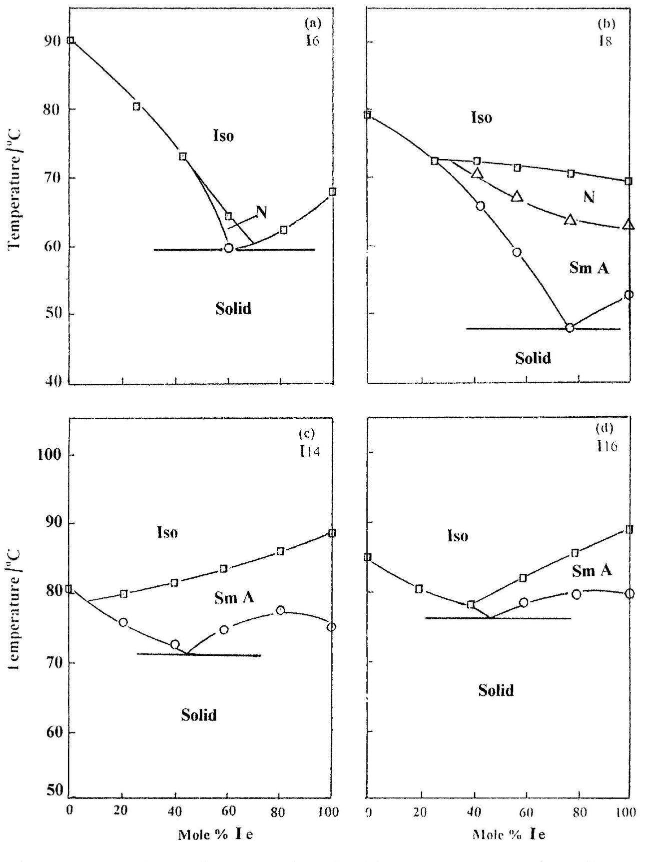

Figure 10. Phase diagrams for the binary systems **Ic**/**Ie**: alkoxy chain length (*a*) $n = 6$, (*b*) $n = 8$, (*c*) $n = 14$, and (*d*) $n = 16$.

from figure 9, the mesophase stability (T_C) of the cyano-substituted component decreases gradually on addition of the chloro analogue. The lower two systems exhibit nematic mesophases, while the other two systems possess the smectic A phase. Their eutectic melting points increase with increasing alkoxy chain length, from 61 to 63, 68, and 74°C. Because of the monotropic nature of the mesophases in the lowest chloro (**I**6c) and nitro (**I**6e) analogues, the binary phase diagrams (figure 10) show a small nematic range around the eutectic composition. In the second higher system (**I**8c/**I**8e) both nematic and smectic A phases were observed for mixtures containing more than 20 mol % of **I**8e. The last two systems gave phase diagrams similar to the chloro-/cyano-substituted mixed systems. The eutectic melting point first decreases from 60 to 48°C and then increases to 72 and 77°C for the last two systems, respectively.

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