Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures IX. Multi-mixtures of a monotrope and enantiotropes

Magdi M. Naoum[a]; Refaat I. Nessim[a]; Tayseer Y. Labeeb[a]
[a] Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt,

Online publication date: 06 August 2010

To cite this Article Naoum, Magdi M. , Nessim, Refaat I. and Labeeb, Tayseer Y.(2000) 'Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures IX. Multi-mixtures of a monotrope and enantiotropes', Liquid Crystals, 27: 7, 889 — 895
To link to this Article: DOI: 10.1080/02678290050043824
URL: http://dx.doi.org/10.1080/02678290050043824

LIQUID CRYSTALS, 2000, VOL. 27, NO. 7, 889–895

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures IX. Multi-mixtures of a monotrope and enantiotropes

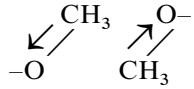
MAGDI M. NAOUM*, REFAAT I. NESSIM and TAYSEER Y. LABEEB
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

(*Received 1 May 1999; in final form 9 October 1999; accepted 27 December 1999*)

Transition temperatures of the ternary and quaternary mixtures, prepared from the enantiotropic cyano and nitro derivatives of the two series, 4-hexadecyloxyphenyl 4-substituted benzoates (**Ia**,**b**) and 4-substituted phenyl-4′-hexadecyloxy benzoates (**IIa**,**b**) with the monotropic methoxy derivative (**IIc**), have been determined by DSC and identified with polarized light microscopy. The equation deduced to calculate the eutectic composition of a multicomponent system from values determined for their individual binary systems, was found to be fairly applicable to our non-ideal systems. Conversely, values of clearing temperatures (T_c), calculated from the polarizability anisotropy ($\Delta\alpha_X$) of the individual C_{Ar}–X bonds, are often less than those measured, indicating complex formation between the methoxy and nitro derivatives.

1. Introduction

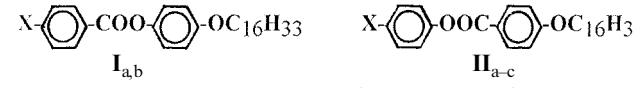
In the two series, 4-hexadecyloxyphenyl 4-substituted benzoates, **I**, and 4-substituted phenyl 4-hexadecyloxy benzoates, **II**, the cyano and nitro derivatives in both series are enantiotropic, i.e. they show their mesophases both on heating and on cooling. On the other hand, the cyano and nitro substituents, having comparable electronic properties, interact similarly with the mesogenic portion of the molecule, and hence their binary mixtures show ideal solution behaviour [1]. In such molecules, bimolecular smectic structures [2, 3] are believed to be formed as a result of molecular complexing, either in the pure state or in their binary [1], ternary [4], or quaternary [5] mixtures. Conversely, in the monotropic methoxy derivative (**IIc**) which shows its mesophase only on cooling, molecular interactions arising from the dipolar characteristics of this compound as well as from the lateral interactions between the terminal methoxy dipolar groups of neighbouring molecules, can force these molecules to a linear association with end-to-end orientation of the mesophase.



Any mesophase system in which a bimolecular smectic is mixed with one which perturbs their molecular complexing would result in non-ideal behaviour [6]. Furthermore, it was found by van der Veen [7] that the clearing temperature, T_c, is in general related to the anisotropy of polarizability of the C_{Ar}–X bond.

The first objectives in this work were (i) to investigate the effect of admixing the linearly associated molecules of **IIc**, on the mesophase behaviour of the six binary and four ternary mixtures prepared from the bimolecular smectic molecules (**Ia**,**b** and **IIa**,**b**), and (ii) to test the applicability of the method previously adopted [3, 4] to characterize the eutectic mixtures of their ternary and quaternary systems, making use of the eutectic compositions of the individual binary mixtures.

The second aspect of this study was to examine the applicability of the van der Veen relation [7], extended later [5] to cover binary, ternary, and quaternary mixtures of the electronically similar molecules (**Ia**,**b** and **IIa**,**b**), to the above-mentioned monotrope/enantiotropes mixed systems.



I$_{a,b}$ **II**$_{a–c}$

a $X = CN$, **b** $X = NO_2$, **c** $X = CH_3O$

2. Experimental

The preparation and characterization of compounds **Ia**,**b** and **IIa–c** have been described in a previous paper [8]. Calorimetric investigations were made using a differential scanning calorimeter (PL-DSC, England) with nitrogen as a purge gas. The typical heating rate was 10 K min^{-1}, and sample masses were 2–3 mg. Transition

*Author for correspondence;
e-mail: magdi@chem-sci.cairo.eun.eg

temperatures were identified with a standard polarized light microscope (C. Zeiss, Germany), attached to an FB 52 hot stage equipped with a FB 80 central processor (Mettler, Switzerland).

Binary, ternary, and quaternary mixtures were prepared as described before [4, 5]. Transition temperatures of the prepared mixtures were measured by DSC and polarized light microscopy and found to agree within 2–3°C.

In the phase diagrams, constructed by plotting transition temperatures versus composition, the symbol '○' denotes solid–mesophase transitions, '◇' denotes mesophase–isotropic transition, and '×' denotes eutectic and pretectic transition temperatures.

3. Results and discussion

3.1. *Ternary and quaternary mixtures of enantiotropes (**Ia**,**b** & **IIa**,**b**) and the monotrope (**IIc**)*

The composition and phase transition temperatures of the eutectic mixtures of the binary mixtures of compounds investigated are given in table 1 [1]. For ternary and quaternary systems, the compositions of the mixtures are represented by an equilateral triangle and a regular tetrahedron, respectively. In order to test the applicability of the method adopted to estimate the eutectic composition of the ideal ternary [4] and quaternary [5] mixtures (prepared from the bimolecular smectic molecules **Ia**,**b** and **IIa**,**b**) to other non-ideal systems, the monotropic derivative **IIc** was used as one component while the enantiotropes **Ia**,**b** and **IIa**,**b** constitute the other components.

3.1.1. *Ternary systems*

The composition triangle and phase diagrams of the six possible ternary combinations were constructed, and are reproduced in figures 1–6. In each case, the composition triangle is constructed by locating each of the eutectic compositions of the three individual

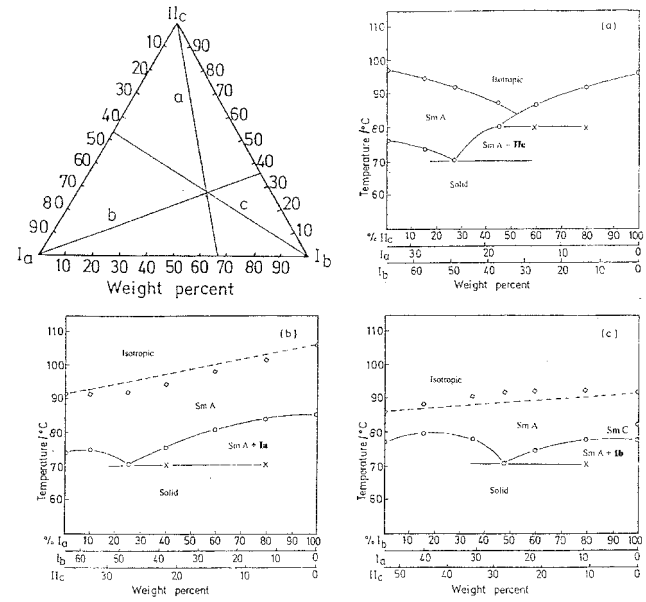


Figure 1. Composition triangle of the ternary system **Ia/Ib/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

binary mixtures on its corresponding side and connecting each one to the opposing apex (representing a pure component). The point of intersection of the three inner connecting lines (a, b, and c) gives the eutectic composition of the system concerned. For each composition triangle, i.e. a given ternary system, three phase diagrams covering the composition ranges represented by the inner lines a, b, and c, are produced.

As can be seen from figures 1–6, the eutectic composition of any ternary system can be safely determined either from any one of the phase diagrams a, b, or c, or from the point of intersection of the three inner lines inside the composition triangle. The composition and phase transition temperatures of the eutectic mixtures are collected in table 2, from which it can be seen that

Table 1. Eutectic composition (wt %), phase transition temperatures (°C), and T_c calculated by the mixture law for the binary systems investigated.

	Component					Transition temperature		
System	**Ia**	**Ib**	**IIa**	**IIb**	**IIc**	T_m	$T_{c(meas)}$	$T_{c(calc)}$
Ia/Ib	33.0	67.0	—	—	—	76.2	97.1	97.8
Ia/IIa	42.0	—	58.0	—	—	74.8	99.8	100.1
Ia/IIb	35.0	—	—	65.0	—	69.9	94.3	95.1
Ib/IIa	—	60.0	40.0	—	—	70.4	95.0	94.7
Ib/IIb	—	53.0	—	42.0	—	64.9	90.8	91.3
IIa/IIb	—	—	43.5	56.5	—	68.7	91.5	92.2
Ia/IIc	47.0	—	—	—	53.0	77.4	86.5	87.7
Ib/IIc	—	64.0	—	—	36.0	74.0	91.5	85.7
IIa/IIc	—	—	55.0	—	45.0	72.0	86.0	85.1
IIb/IIc	—	—	—	60.0	40.0	78.5	90.5	82.1

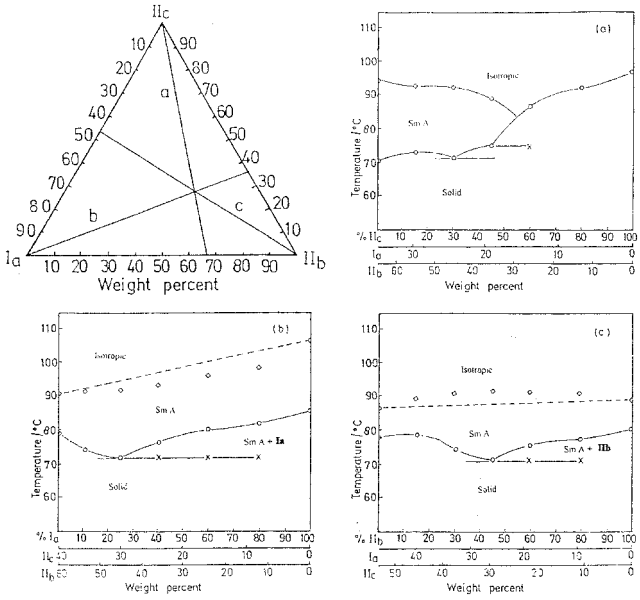


Figure 2. Composition triangle of the ternary system **Ia/IIb/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

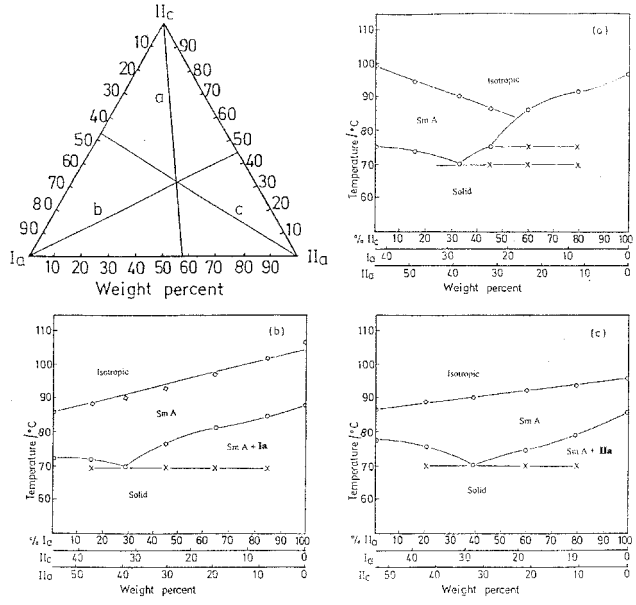


Figure 3. Composition triangle of the ternary system **Ia/IIa/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

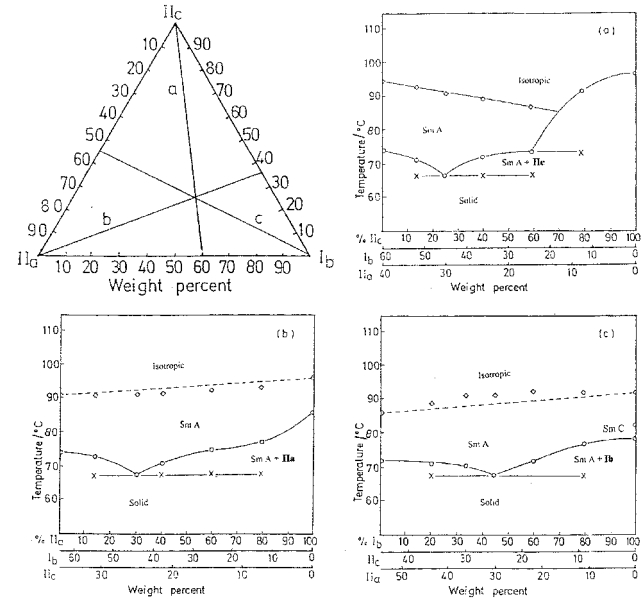


Figure 4. Composition triangle of the ternary system **Ib/IIa/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

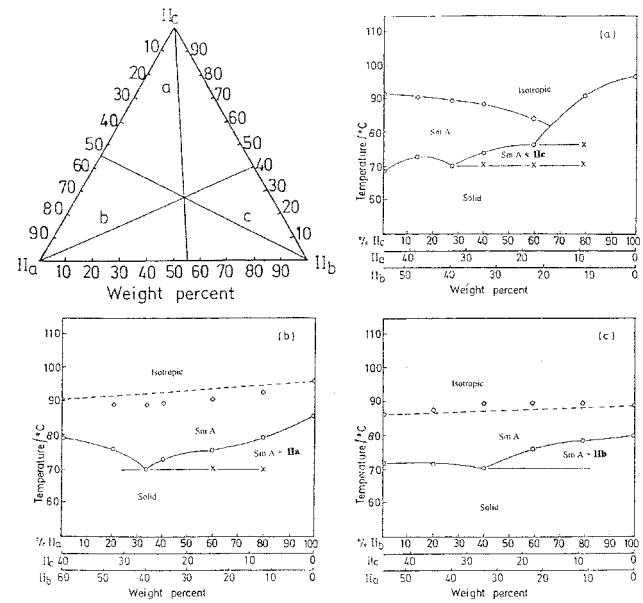


Figure 5. Composition triangle of the ternary system **IIa/IIb/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

the mesophase ranges ($\Delta T = T_c - T_m$) for the systems investigated decrease in the order:

	Ib/IIb/IIc >	**Ib/IIa/IIc** >	**Ia/Ib/IIc** =	**IIa/IIb/IIc** ≈	**Ia/IIa/IIc** >	**Ia/IIb/IIc**	
ΔT	23.3	22.7	20.5	20.5	20.4	19.6	°C

It can be further seen from figures 1–6 that the gradual addition of a nitro compound (**Ib** or **IIb**) to the eutectic mixtures of a cyano compound (**Ia** or **IIa**) with the methoxy derivative (**IIc**) results in an enhancement of the mesophase–isotropic transition temperatures, T_c (figures 1, 2, 4, and 5, curve c). The reverse also seems true: that is, the addition of the cyano compound (**Ia** or **IIa**) to the eutectic mixture of the methoxy and nitro compounds results in T_c values lower than those expected from the linear dependences (compare curve b in the same group of figures). This may be attributed to the stronger forces

Table 2. Eutectic composition (wt %), phase transition temperatures (°C), and T_c calculated by the mixture law for the ternary and quaternary systems investigated.

System	Component					Transition temperature		
	Ia	**Ib**	**IIa**	**IIb**	**IIc**	T_m	$T_{c(meas)}$	$T_{c(calc)}$
Ia/Ib/IIc	25.0	48.0	—	—	27.0	71.5	92.0	90.8
Ia/IIa/IIc	28.5	—	39.0	—	32.5	70.0	90.4	90.95
Ia/IIb/IIc	24.5	—	—	45.5	30.0	72.0	91.6	88.0
Ib/IIa/IIc	—	45.0	30.0	—	25.0	68.5	91.2	88.9
Ib/IIb/IIc	—	40.5	—	36.0	23.5	68.2	91.5	86.8
IIa/IIb/IIc	—	—	32.9	40.1	27.0	70.2	90.7	86.5
Ia/Ib/IIa/IIc	18.1	36.7	24.7	—	20.5	67.1	93.5	92.0
Ia/Ib/IIb/IIc	16.6	34.0	—	30.0	19.4	67.2	93.0	90.1
Ia/IIa/IIb/IIc	18.6	—	26.0	33.6	21.7	68.2	92.0	90.3
Ib/IIa/IIb/IIc	—	32.1	21.7	28.0	18.2	58.5	92.0	89.0

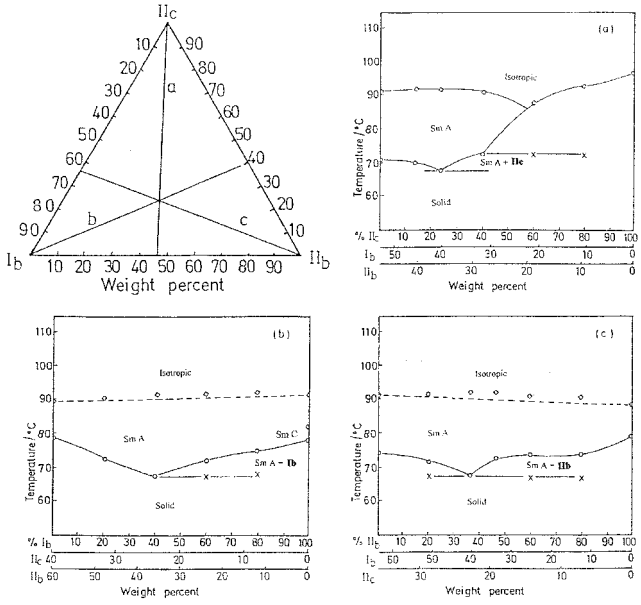


Figure 6. Composition triangle of the ternary system **Ib/IIb/IIc**, and ternary phase diagrams for the composition ranges represented by the inner lines a, b, and c.

of association between the nitro-substituted derivatives and the methoxy analogue compared with those occurring between the cyano and methoxy derivatives. These findings are in accordance with the behaviour of the binary mixtures studied before [1]. The T_c values of the binary mixtures of the methoxy and cyano derivatives were found to vary almost linearly with composition, while enhanced dipole–dipole interactions, due to the bulkiness and non-linearity of the nitro group, led to a positive deviation from linear behaviour [1]. Furthermore, the enthalpies of clearance (ΔH_c) for the eutectic binary mixtures of the systems concerned (in kJ mol^{-1}) were determined experimentally by the DSC and also calculated from the mixture law:

$$\Delta H_c(\text{calc}) = \sum \chi_i \Delta H_{c(i)}$$

where χ_i is the mole fraction of component i and $\Delta H_{c(i)}$ its enthalpy of clearance. The results are given in table 3 from which it can be seen that the calculated ΔH_c values match the measured ones for the eutectic mixtures of the methoxy and cyano derivatives; whereas the measured ΔH_c values are greater than the calculated values in the case of the nitro/methoxy mixtures. In addition, the clearance enthalpies are greater in the latter case compared with the former. These findings together support the assumption that stronger forces of association occur between the nitro and methoxy analogues than between the cyano and methoxy derivatives.

A common feature of figures 1–6 (curve a) constructed by the gradual addition of the monotrope **IIc** to a mixture of two enantiotropes, is the pretectic transition temperature around 75°C. At this temperature, crystals of one solid modification, precipitated at the beginning of solidification, interact with the liquid of a definite composition to form new crystals of solid solution. This transformation occurs at a constant temperature (as do eutectic transformations) and is called a *pretectic transformation*. This property characterizes the mixtures containing compound **IIc** in proportions above the eutectic composition, indicating the existence of two solid modifications with transition at about 75°C. On the other hand, the SmC mesophase (figures 1c, 4c, and 6b),

Table 3. Eutectic composition (mol %), measured $(\Delta H_c)_{meas.}$ and calculated $(\Delta H_c)_{calc.}$ enthalpies of clearance for the eutectic binary mixtures (A/B).

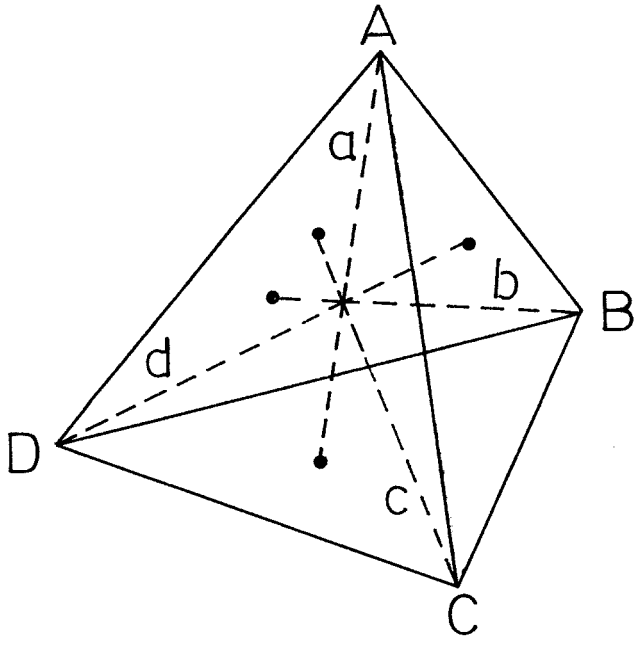
System (A/B)	mol % **IIc**	$(\Delta H_c)_{meas.}$ /kJ mol^{-1}	$(\Delta H_c)_{calc.}$ /kJ mol^{-1}
Ia/IIc	52.73	3.17	3.04
Ib/IIc	36.73	4.36	3.87
IIa/IIc	44.73	3.09	3.08
IIb/IIc	40.76	3.88	2.99

which forms at 78.2°C and changes to SmA at 82.4°C, disappears on the addition of less than 20% of the eutectic mixture of the other two components.

Furthermore, it can be deduced from table 2 that the composition of the eutectic mixtures is richer in the component which has the lower melting point.

3.1.2. *Quaternary systems*

To determine the eutectic composition of a quaternary system, each of the four possible ternary combinations is located on the corresponding face of the composition tetrahedron. Each vertex (representing one component) is then connected to the point (on the opposite face) representing the eutectic composition of the other three components (●). The point of intersection of the four inner connecting lines (a, b, c, and d) corresponds to the eutectic composition of the quaternary mixture.



Thus, quaternary mixtures of the systems containing **IIc** as one component and the other three from the four enantiotropes **Ia**,**b** and **IIa**,**b** were prepared and the transition temperatures (T_m and T_c) were determined. These systems are **Ia/Ib/IIa/IIc**, **Ia/Ib/IIb/IIc**, **Ia/IIa/IIb/IIc**, and **Ib/IIa/IIb/IIc**. At this stage, it is believed that one of the four phase diagrams is enough to elucidate the eutectic composition of the quaternary systems under investigation. Thus, a phase diagram, covering the quaternary composition range given by one of the inner lines a, b, c, or d, was constructed (for each system) and represented graphically in figures 7–10, respectively. Transition temperatures and composition of the eutectic mixtures were determined and the results are included in table 2, from which it can be seen that

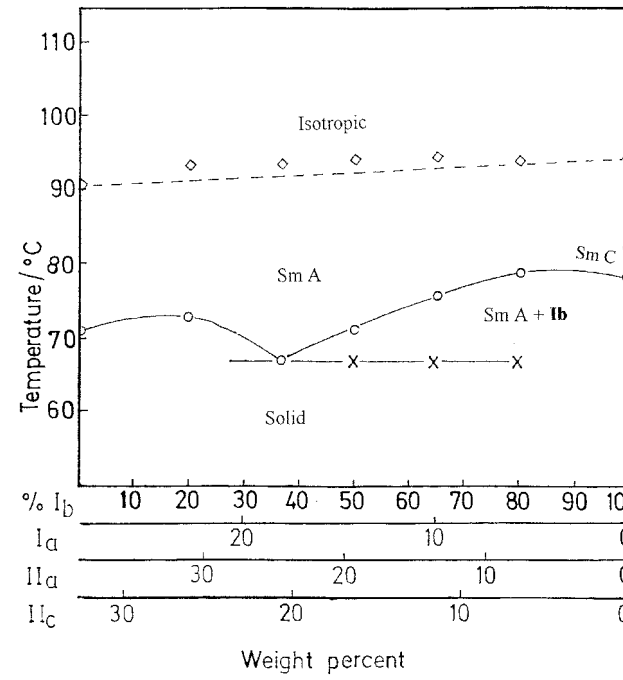


Figure 7. Quaternary phase diagram of the system **Ia/Ib/IIa/IIc**, covering the quaternary composition range prepared by the addition of **Ib** to the eutectic ternary mixture of the system **Ia/IIa/IIc**.

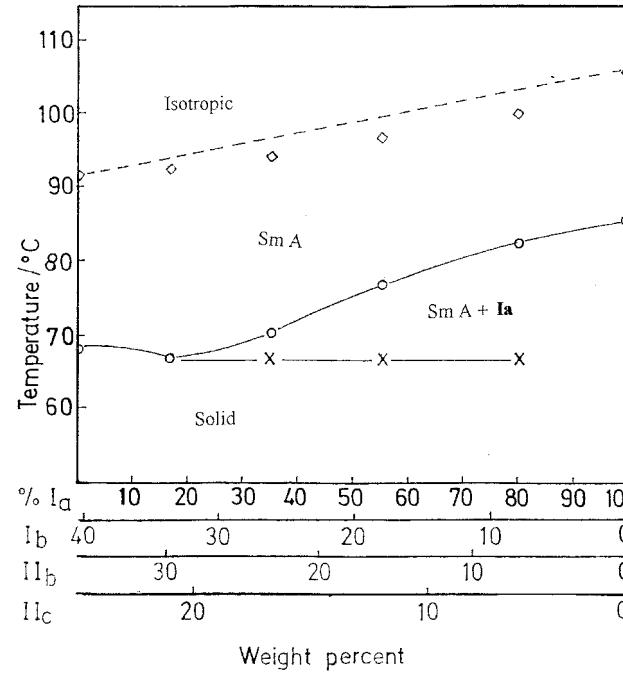


Figure 8. Quaternary phase diagram of the system **Ia/Ib/IIb/IIc**, covering the quaternary composition range prepared by the addition of **Ia** to the eutectic ternary mixture of the system **Ib/IIb/IIc**.

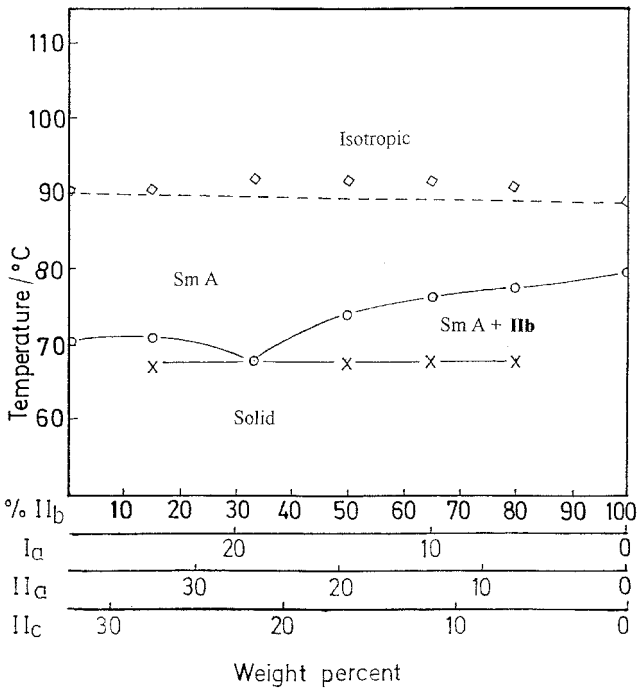


Figure 9. Quaternary phase diagram of the system **Ia/IIa/IIb/IIc**, covering the quaternary composition range prepared by the addition of **IIb** to the eutectic ternary mixture of the system **Ia/IIa/IIc**.

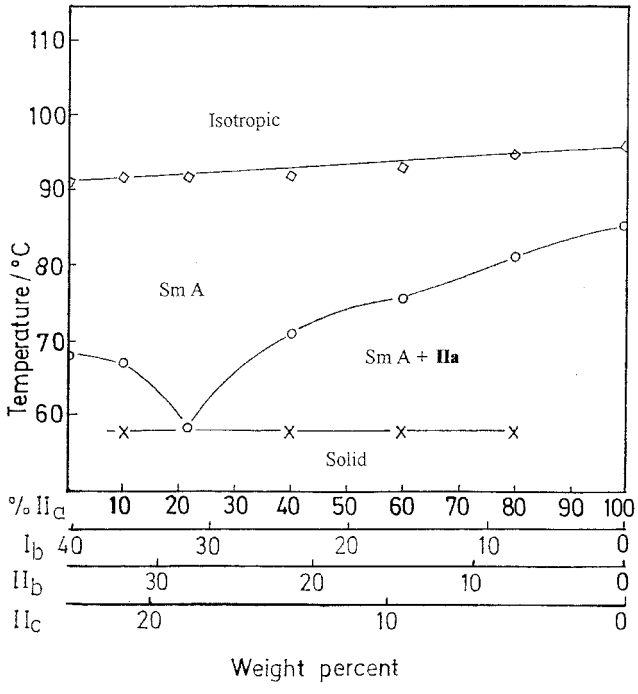


Figure 10. Quaternary phase diagram of the system **Ib/IIa/IIb/IIc**, covering the quaternary composition range prepared by the addition of **IIa** to the eutectic ternary mixture of the system **Ib/IIb/IIc**.

the mesomorphic ranges for the four systems studied decrease in the order:

	Ib/IIa/IIb/IIc >	**Ia/Ib/IIa/IIc** >	**Ia/Ib/IIb/IIc** >	**Ia/IIa/IIb/IIc**	
ΔT	33.5	26.4	25.8	23.8	°C

And again, the composition of the eutectic mixture is richer in the component that has the lower melting point, decreasing in the order:

	Ia >	**IIc** >	**IIa** >	**IIb** >	**Ib**	
T_m	88.2	(96.1)	85.4	79.4	78.2	°C

For the monotrope **IIc**, T_m on cooling (63.5°C) is less than that of **Ia** (79.1°C).

In order to verify the eutectic composition of a ternary or a quaternary mixture, Naoum [5] has recently deduced a general formula for a multi-component system which relates its eutectic composition to those of its possible individual binary combinations. This relation has the form:

$$(C_i)_n = 1 \Big/ \left[(2-n) + \sum_{j=1}^{n} (1/(C_i)_{ij}) \right], \quad j \neq i \qquad (1)$$

where $(C_i)_n$ is the eutectic weight-fraction of component i in the multi-component system of n components, and $(C_i)_{ij}$ is the eutectic weight-fraction of component i in the binary system i/j, where i and j take the values of 1 to n, and $j \neq i$.

Equation (1) was used to estimate the eutectic compositions of the ternary and quaternary systems investigated and the results were found to be close to the experimentally determined values. These findings also reveal the applicability of equation (1) to non-competitive mixtures.

3.2. *Dependence of T_c values of mixtures on the polarizability anisotropy of the C_{Ar}–X bonds*

The relation derived by van der Veen [7] to study the dependence of clearance temperatures, T_c, on the anisotropy of polarizability, $\Delta\alpha_x$, of bonds to small, compact terminal substituents, was extended later by Naoum [5] to cover binary, ternary, and quaternary mixtures. In series **I**, since group polarizabilities are not perturbed by the electronic interaction between substituents and the *para*-situated –CO– group, $\Delta\alpha_x$ values were calculated from measurements on substituted benzenes. Conversely, in series **II**, since mesomeric interactions take place between the substituents and the *para*-oxygen atom, $\Delta\alpha'_x$ values were calculated using data for substituted anisoles. The two linear dependences were analysed by the method of least squares to give the two regression lines for series **I** and **II**, respectively:

$$T_c^{1/2}(\mathbf{I}) = 17.06 + 0.565 \times 10^{24} \Delta\alpha_X \qquad (2)$$

$$T_c^{1/2}(\mathbf{II}) = 17.50 + 0.335 \times 10^{24} \Delta\alpha'_X. \qquad (3)$$

Equations (2) and (3) were used to calculate the anisotropic–isotropic transition temperatures, T_c, for a multi component system using the mixture law:

$$T_c(\text{mix}) = \sum X_i T_{c(i)} \quad (4)$$

$$T_c(\text{mix}) = \sum X_i (\Delta\alpha_{\mathbf{M(I)}} + \rho_{\mathbf{I}} \Delta\alpha_{X(i)})^2 \quad (5)$$

where X_i is the mole fraction of component i, $\Delta\alpha_{\mathbf{M(I)}}$ is the polarizability anisotropy of the molecular structure (**I** or **II**) excluding the substituent X, $\Delta\alpha_{X(i)}$ and $\rho_{\mathbf{I}}$ are the polarizability of the C_{Ar}–X bond and the slope of the regression line of the concerned series, respectively. The values of $\Delta\alpha_X$ and $\Delta\alpha'_X$ for the compounds investigated are given elsewhere [9].

Some systems studied before [1] are known to give ideal behaviour with compositions in their binary mixtures, therefore the equation deduced by Naoum [5] was found to be fairly applicable to such systems. The results are included in table 1 for ideal binary systems. Hence, we tried to use equation (5) to calculate the T_c values for the eutectic mixtures of the binary, ternary and quaternary systems containing the monotrope $\mathbf{II_c}$ as one component. The results obtained are added to tables 1 and 2, as appropriate. As can be seen from these tables for mixtures containing at least one of the two nitro derivatives, the calculated values are almost always less than those found experimentally. These findings reflect the possibility of complex formation between the electron-deficient derivatives, i.e. the nitro analogues, and the electron-rich methoxy derivative. Conversely, for the mixtures containing $\mathbf{II_c}$ as one component and the cyano derivatives as the other components, the difference is so small that these systems may be considered to behave ideally. These results agree with the previous findings that the addition of a cyano derivative to a mixture of the methoxy and nitro derivatives will destroy the complex formed between the latter two compounds.

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