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Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures VIII. Quaternary mixtures of enantiotropes

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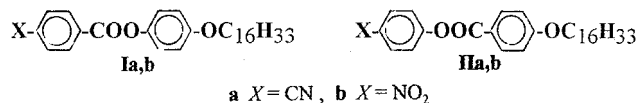
Transition temperatures of quaternary mixtures prepared from the cyano and nitro derivatives of the two series, 4-hexadecyloxyphenyl 4-substituted benzoates (**Ia,b**) and 4-substituted phenyl 4-hexadecyloxy benzoates (**IIa,b**) have been determined by DSC and the transitions identified with polarized light microscopy. The cyano and nitro derivatives, in both series, were used because their molecules are enantiotropic. The method described before for the ternary system was extended to elucidate the eutectic composition of the quaternary system from the knowledge of either the eutectic compositions of the four possible ternary mixtures or of those of the six individual binary systems. A general equation was deduced to calculate the eutectic composition of any multi-component system from values determined for their individual binary systems. T_c values of binary, ternary, or quaternary mixtures were related to the polarizability anisotropy, $\Delta\alpha_X$, of the individual $C_{Ar}-X$ bonds. The mixture law was successfully applied.

1. Introduction

In previous works [1–3], the effect of inverting the central $-\text{COO}-$ group and terminal substituents, X , on the mesophase behaviour of 4-hexadecyloxyphenyl 4-substituted benzoates (**I**) and 4-substituted phenyl 4-hexadecyloxybenzoates (**II**), as well as of their binary mixtures, was investigated. Molecules of **I** and **II** represent extremes in conjugative interactions between the terminal substituent and the remainder of the molecule. Substituents were chosen [1] to cover a wide range of intramolecular electronic interactions. It was further revealed [3] that the square root of the clearance temperature T_c , of the pure components, is related to the polarizability anisotropy, $\Delta\alpha_X$, of the $C_{Ar}-X$ bond. On the other hand, a new method [4] was adopted to estimate the eutectic compositions of the four ternary systems which could be prepared from the four enantiotropes **Ia,b** and **IIa,b** making use of the eutectic compositions of their corresponding individual binary mixtures.

The purpose of the present work is first to extend the latter investigation to examine the mesophase behaviour of the quaternary mixtures of these four enantiotropes. Secondly, it is to test the applicability of the relation derived by van der Veen [5], and examined further by Griffin [6] and Naoum *et al.* [3] to cover the binary

and ternary systems previously investigated [2–4], as well as their quaternary mixture.



2. Experimental

The preparation and characterization of compounds **Ia,b** and **IIa,b** have been described in a previous paper [1]. Calorimetric investigations were made using a differential scanning calorimeter (PL-DSC, England) with nitrogen as purge gas. Typical heating rate was 10 K min^{-1} , and sample masses were 2–3 mg. Transition temperatures were identified with a standard polarized light microscope (C. Zeiss, Germany), attached to a FB 52 hot stage equipped with a FB 80 central processor (Mettler, Switzerland).

Ternary mixtures were prepared by mixing the appropriate amounts of components, melting them together, stirring to give an intimate mixture, and then cooling to room temperature while stirring in air. The quaternary mixtures for the system (A/B/C/D) were prepared in two steps. First the eutectic mixture of the ternary system A/B/C was prepared, as a constant ratio mixture, then the component D was admixed to cover the whole D-composition range, i.e. from 0 to 100 wt % of D.

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Alternatively the eutectic mixture A/B/D was first prepared, to which the component C was added in amounts varying from 0 to 100 wt%. Similarly, the eutectics B/C/D or A/C/D were first prepared and the fourth component (A or B) was added. (A, B, C, D are general terms and do not represent specific compounds.)

Transition temperatures of the prepared mixtures were measured both 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 transition, '◇' denotes mesophase–isotropic transition, and '×' denotes eutectic temperatures.

3. Results and discussion

3.1. Quaternary mixtures of enantiotropes

Eutectic compositions and phase transition temperatures of the binary [2] and ternary [4] mixtures of the compounds investigated are given in the table. Generally, the phase diagram of a binary system is constructed by plotting transition temperature versus composition in a two-dimensional representation. For a ternary system, the composition is represented by an equilateral triangle, while transition temperatures are plotted on the third dimension. In the triangle of composition, each apex represents one pure component, and each side covers the full composition range of a binary mixture made from any two of the three components. The ternary mixtures are given by points enclosed within the area of the triangle.

Correspondingly, the composition of a quaternary system is represented by a regular tetrahedron. In this case, each vertex of the composition tetrahedron represents a pure component, each of the six edges covers a possible binary combination, and the four faces of the tetrahedron give the four ternary combinations.

Quaternary mixtures are given by points inside the volume of the tetrahedron.

To detect the eutectic composition of a quaternary system, the eutectic composition of each of the four ternary systems is located on its corresponding face of the tetrahedron of composition; if we connect each vertex representing one component with the opposite point representing the eutectic composition of the other three components, we would get the point of intersection of the four inner connecting lines (*a*, *b*, *c*, and *d*) as the eutectic composition of the quaternary system.

As in the case of ternary systems [4], this idea can be verified experimentally by constructing the four individual phase diagrams by plotting transition temperature versus the selected composition range represented individually by the four inner connecting lines *a*, *b*, *c*, and *d*. In each case, the eutectic composition of these four selected ranges of quaternary mixtures would be individually determined. These four values are expected to coincide with one another and with the point of intersection inside the tetrahedron of quaternary composition.

The four enantiotropes **Ia,b** and **IIa,b** were used to realize this idea. Quaternary mixtures for the system **Ia/Ib/IIa/IIb** were prepared and the phase diagrams covering the quaternary composition ranges given by the inner lines *a*, *b*, *c*, and *d*, were constructed and represented graphically in figures 1(*a–d*), respectively. The eutectic composition of the ternary mixtures, as given on each face of the composition triangle were constructed from the corresponding ternary phase diagram [4]. As can be seen from figure 1, the eutectic composition of the quaternary system **Ia/Ib/IIa/IIb** can be determined from any one of the four phase diagrams 1(*a–d*). Transition temperatures and the eutectic composition of the quaternary system are included in the table, from which it can be seen that the range of mesophase

Table Eutectic composition (wt fraction), phase transition temperatures (°C), and T_c calculated by the mixture law, of the mixtures investigated.

System	Ia	Ib	IIa	IIb	T_m	T_c (meas.)	T_c (calc.)
Ia/Ib	0.33	0.67	—	—	76.2	97.1	97.8
Ia/IIa	0.42	—	0.58	—	74.8	99.8	100.1
Ia/IIb	0.35	—	—	0.65	69.9	94.3	95.1
Ib/IIa	—	0.60	0.40	—	70.4	95.0	94.7
Ib/IIb	—	0.53	—	0.47	64.9	90.8	91.3
IIa/IIb	—	—	0.435	0.565	68.7	91.5	92.2
Ia/Ib/IIa	0.225	0.465	0.310	—	60.5	96.5	97.2
Ia/Ib/IIb	0.206	0.418	—	0.376	62.5	94.2	94.5
Ia/IIa/IIb	0.235	—	0.335	0.430	58.8	94.8	95.4
Ia/IIa/IIb	—	0.390	0.265	0.345	61.0	92.8	92.8
Ia/Ib/IIa/IIb	0.160	0.328	0.221	0.291	57.6	94.6	94.9

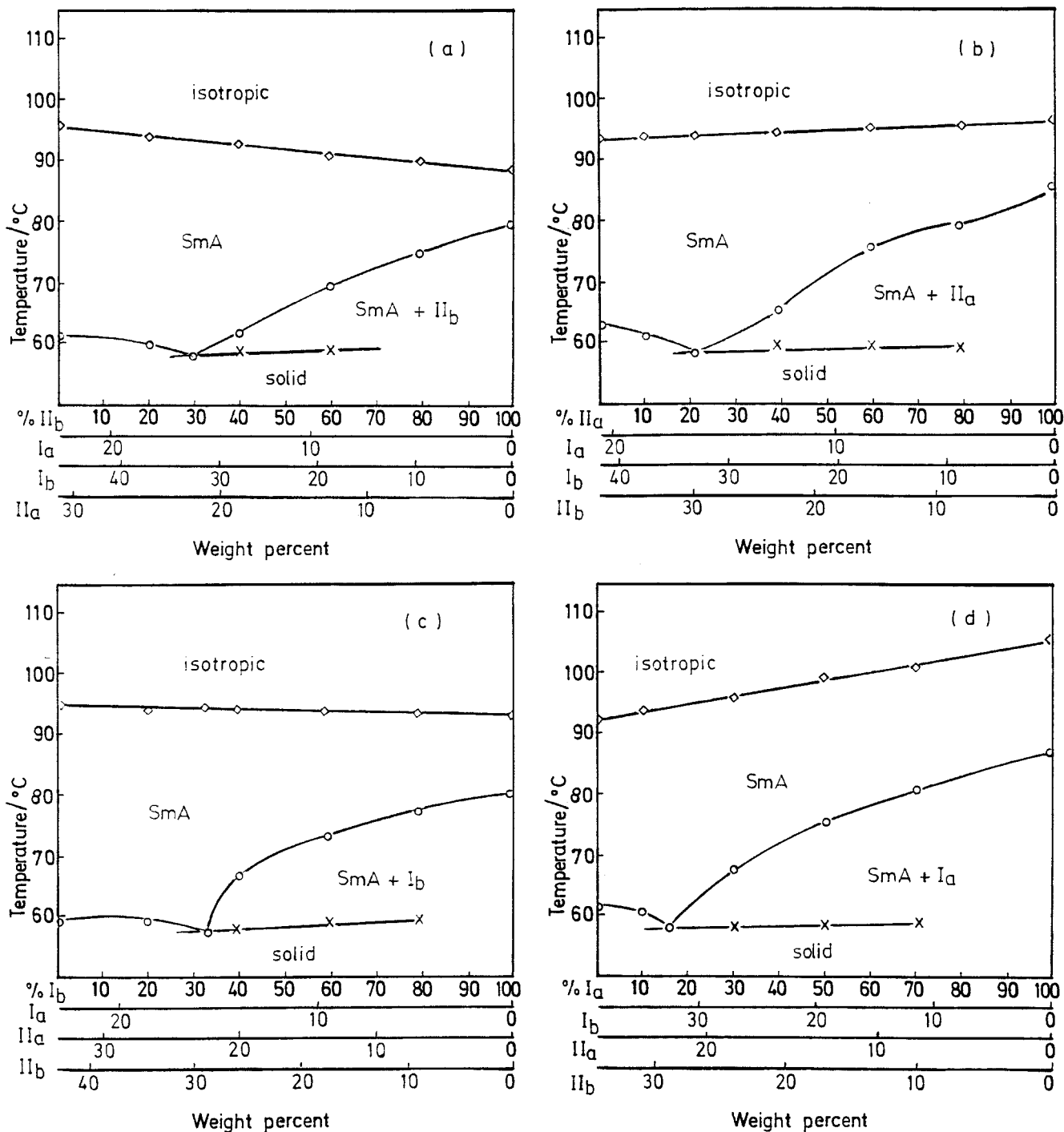


Figure 1. Ternary Phase diagrams of the system **Ia/Ib/IIa/IIb** covering the composition ranges represented by the inner lines *a*, *b*, *c* and *d* of the composition tetrahedron.

stability is further increased to 37°C; also, that the composition of the eutectic mixture is again richer in the component that has the lower melting point. This finding is in accordance with that observed before for the binary [2] and ternary [4] systems. That is, the mixture is found to have its eutectic composition shifted

toward the component according to the order:

$$Ib > IIb > IIa > Ia.$$

A very important observation can be deduced from the results given in the table. That is, the ratio between the weight fractions of any two components in a binary

system, i.e. $(C_A/C_B)_{AB}$, remains unchanged in the ternary, $(C_A/C_B)_{ABC}$, or in the quaternary, $(C_A/C_B)_{ABCD}$, systems, i.e.

$$(C_A/C_B)_{AB} = (C_A/C_B)_{ABC} = (C_A/C_B)_{ABD} = (C_A/C_B)_{ABCD} \quad (1)$$

$$(C_A/C_C)_{AC} = (C_A/C_C)_{ABC} = (C_A/C_C)_{ACD} = (C_A/C_C)_{ABCD} \quad (2)$$

$$(C_B/C_C)_{BC} = (C_B/C_C)_{ABC} = (C_B/C_C)_{BCD} = (C_B/C_C)_{ABCD} \quad (3)$$

and so on.

These relations can be deduced either from the method adopted in the preparation of the ternary or quaternary mixtures, or by simple geometrical deduction from the triangles and/or tetrahedron of composition. Equations (1–3), together with the relations:

$$(C_A + C_B)_{AB} = 1 \quad (4)$$

$$(C_A + C_B + C_C)_{ABC} = 1 \quad (5)$$

$$(C_A + C_B + C_C + C_D)_{ABCD} = 1 \quad (6)$$

can be used to estimate the eutectic composition of any multi-component system as a function of the alternative binary composition. By simple algebra, these previous equations could be solved to give, for the ternary system A/B/C, the equations:

$$(C_A)_{ABC} = 1/[-1 + 1/(C_A)_{AB} + 1/(C_A)_{AC}] \quad (7)$$

$$(C_B)_{ABC} = 1/[-1 + 1/(C_B)_{AB} + 1/(C_B)_{BC}] \quad (8)$$

$$(C_C)_{ABC} = 1/[-1 + 1/(C_C)_{AC} + 1/(C_C)_{BC}]. \quad (9)$$

Similar relations can be derived for the quaternary A/B/C/D system:

$$(C_A)_{ABCD} = 1/[-2 + 1/(C_A)_{AB} + 1/(C_A)_{AC} + 1/(C_A)_{AD}] \quad (10)$$

$$(C_B)_{ABCD} = 1/[-2 + 1/(C_B)_{AB} + 1/(C_B)_{BC} + 1/(C_B)_{BD}] \quad (11)$$

$$(C_C)_{ABCD} = 1/[-2 + 1/(C_C)_{AC} + 1/(C_C)_{BC} + 1/(C_C)_{CD}] \quad (12)$$

$$(C_D)_{ABCD} = 1/[-2 + 1/(C_D)_{AD} + 1/(C_D)_{BD} + 1/(C_D)_{CD}]. \quad (13)$$

From equations (7–13) a general formula for a multi-component system can be deduced which has the form:

$$(C_i)_n = 1/\left[(2-n) + \sum_{j=1}^n (1/(C_i)_{ij}) \right]; \quad j \neq i. \quad (14)$$

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

Equation (14) was used to calculate the eutectic compositions of the ternary and quaternary systems investigated and the results were found to be in a fair agreement with those determined experimentally. Hence, this method allows a rapid cursory evaluation of the potential mixture utility for higher component systems.

3.2. Dependence of T_c of mixtures on the polarizability anisotropy of the aryl-X bond

In the phenyl benzoate molecule, liquid crystallinity is more persistent as the mutual conjugation between the *para*-substituent and the ester carbonyl group and/or the ester oxygen atom is increased. A change in the extent of conjugation will alter both polarizability and the resultant dipole moment of the whole molecule. A decrease in the polarizability will lead to a decrease in the dispersion forces, and consequently to a decrease in the thermal stability of the liquid crystalline phase; that is, to a decrease in the anisotropic–isotropic transition temperature, T_c , of the mesophase. Van der Veen [5] has used a relation to study the dependence of T_c on the anisotropy of polarizability of bonds to small, compact terminal substituents, i.e. of the $C_{Ar}-X$ bond, on the basis of molecular statistical theory by Maier and Saupe [7]. With some assumptions, van der Veen arrived at a relation which could be applied to any mesomorphic series of compounds differing only in their terminal substituents. This relation has the form:

$$T_c = \Delta\alpha_M^2 + 2\Delta\alpha_M\Delta\alpha_X + \Delta\alpha_X^2. \quad (15)$$

The term $\Delta\alpha_M$ is the anisotropy polarizability ($\alpha_{\parallel} - \alpha_{\perp}$) for all the molecular structure except the terminal substituent X, $\Delta\alpha_X$ is the polarizability anisotropy of the $C_{Ar}-X$ bond.

In equation (15), van der Veen assumed that if $\Delta\alpha_M$ is much larger than $\Delta\alpha_X$, T_c should show a linear dependence on $\Delta\alpha_X$, i.e.

$$T_c \approx 2\Delta\alpha_X. \quad (16)$$

Later, Naoum *et al.* [3] showed that equation (15) can be re-written as:

$$T_c^{1/2} \approx \Delta\alpha_M + \Delta\alpha_X. \quad (17)$$

Thus, if $T_c^{1/2}$ values are plotted against $\Delta\alpha_X$ a straight line is expected with an intercept equal to $\Delta\alpha_M$. In series I, since the group polarizabilities are not perturbed by the electronic interaction between the substituent (NO_2 or CN) and the *para*-situated $-\text{CO}-$ group, $\Delta\alpha_X$

of the $C_{Ar}-X$ bonds were calculated [3] from measurements on substituted benzenes. Conversely, taking into consideration the mesomeric interactions in series **II** between the substituent (NO_2 or CN) and the *para*-oxygen atom, $\Delta\alpha'_X$ values were calculated using data for substituted anisoles [3]. That is, in series **I** correlation was made between $T_c^{1/2}$ and $\Delta\alpha_X$, while for series **II**, $\Delta\alpha'_X$ values were used instead. The two linear dependences were analysed by the method of least squares to give the two regression lines (18) and (19) for series **I** and **II**, respectively:

$$T_c^{1/2}(\mathbf{I}) = 17.06 + 0.565 \times 10^{24} \Delta\alpha_X \quad (18)$$

$$T_c^{1/2}(\mathbf{II}) = 17.50 + 0.335 \times 10^{24} \Delta\alpha'_X. \quad (19)$$

Equations (18) and (19) can be used to calculate the anisotropic–isotropic transition temperatures for a multi-component system using the mixture law:

$$T_c(\text{mix}) = \sum X_i [\Delta\alpha_{M(\mathbf{I})} + \rho_{\mathbf{I}} \Delta\alpha_{X(i)}]^2 \quad (20)$$

where X_i is the mole fraction of component i , $\Delta\alpha_{M(\mathbf{I})}$ is the polarizability anisotropy of the molecular structure (**I** or **II**) except 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.

Equation (20) was used to calculate the T_c values for the binary, ternary, and quaternary systems investigated, and the results obtained are included in the table; these were found to agree within 0.6°C with the experimental results. These findings reflect the applicability of such relations to our investigated compounds where no compound formation was observed between them in their mixtures. This inference is in accordance with the previous conclusion [2] and there is a great similarity between the cyano and nitro group on the one hand, and between their parent molecules in series **I** and **II** on the other, in regards to their molecular interactions

in the pure and mixed states. That is, the mode of interaction between molecules of the cyano and nitro analogues in the **I/I** or **II/II** systems does not differ greatly from that relating to the **I/II** and **II/I** systems.

4. Conclusion

Cyano and nitro substituents, whether they are attached to the benzoyl or phenolic moiety of the phenyl benzoate molecule, resulted in compounds that gave in their binary, ternary, or quaternary mixtures, phase diagrams that exhibit eutectic behaviour in their solid–anisotropic transition temperatures, and linear dependences in their mesophase–isotropic transition temperatures. For any multi-component system composed of these four derivatives, it was found that for eutectic mixtures the ratio between any two components is that of their binary mixture. This finding has helped us to deduce a general formula for the calculation of the eutectic composition of a multi-component system. On the other hand, a general equation can also be deduced which relates clearing temperatures of eutectic mixtures to the polarizability anisotropy of substituents attached to its individual components.

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