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Applicability of the Schroeder-van Laar relation to multi-mixtures of liquid crystals of the phenyl benzoate type

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Abstract

Eutectic binary, ternary, and quaternary mixtures of the enantiotropic cyano and nitro derivatives of the two series, 4-hexadecyloxyphenyl-4′-substituted benzoates ($\mathbf{I}_{a,b}$) and 4-substituted phenyl-4′-hexadecyloxy benzoates ($\mathbf{II}_{a,b}$) in presence and in absence of the monotropic methoxy derivative ($\mathbf{II}_c$) were prepared and their crystal-mesophase transition temperatures (T_E) were determined by DSC and identified with polarised-light microscopy. For mixtures of enantiotropes, the values of T_E obtained were found to be successfully correlated, by the Schroeder-van Laar equation, to the mole fraction χ_i, of each individual component. In each case of mixture containing the monotrope $\mathbf{II}_c$, as one component, very poor correlation was observed.

1. Introduction

Phenyl benzoate molecule represents a model compound to investigate the electronic interaction between the para substituent and the central benzoyl group. The effect of substituent on the phase behaviour of the two series of compounds, 4-hexadecyloxyphenyl-4′-substituted benzoates (**I**) and 4-substituted phenyl-4′-hexadecyloxy benzoates (**II**) has been thoroughly investigated [1] from the DSC and polarised-light microscopic analyses. Conjugative interactions within the molecule, which differ according to the electronic nature and bulkiness of the substituent as well as its location with respect to the ester carbonyl group, has led to a significant variation in the mesophase behaviour of the individual compounds [1], and consequently, to differences in the phase behaviour of their mixed systems [2–4]. Substituents with similar electronic nature (such as CN or NO_2 groups), whether they are attached to the benzoyl or phenolic moiety of the ester, resulted in compounds that gave, in their mixtures [2], phase diagrams of similar characteristics. That is, all diagrams exhibit eutectic behaviour in their crystal-mesophase transition temperatures (T_m), and a linear behaviour in their mesophase-isotropic transition temperatures (T_c). For these groups of compounds ($\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$) the mixture law, relating T_c to the polarisability anisotropy ($\Delta\alpha_X$) of a substituent of individual component in a binary, ternary, and quaternary mixture [5], was tested and the results were found to be in close proximity to those measured experimentally. These findings confirm the similarity between the electronic nature of the NO_2 and the CN groups from one hand, and that between their corresponding isomers in series **I** and **II**, from the other hand. However, non-linear behaviour has been reported for some mixtures of 4-substituted phenyl 4′-alkoxy benzoates when nitro esters were mixed with methyl or methoxy esters [2–6].

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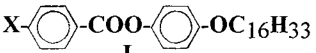
On the other hand, predicting the crystal-mesophase transition temperatures, T_m, of a mixture is quite a bit less straight forward. The solubility of compounds in a mixture, which behaves as a thermodynamically ideal system, follows the van't Hoff relation, which is conveniently recast into the Schroeder-van Laar equation [7–9]:

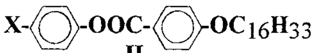
$$\ln \chi_i = -(\Delta H_i/R)[(1/T_E)-(1/T_i)] \qquad (1)$$

in which the eutectic melting point (T_E) is related to the mole fraction (χ_i), crystal-mesophase transition temperature (T_i), and the molar enthalpy of fusion (ΔH_i) of component "*i*" in a mixture. *R* is the gas constant. Deviations from ideal behaviour are sufficiently common and large to make this approach unreliable [10].

The aim of this investigation is to test the applicability of Eq. (1) to all possible eutectic binary, ternary, or quaternary mixtures formed from the four enantiotropes $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$, as well as of those formed from these enanti-otropes and the monotropic methoxy derivative $\mathbf{II}_c$.



$\mathbf{I}_{a\&b}$



$\mathbf{II}_{a\text{-}c}$

a) X = CN, b) X = NO_2 c) X = CH_3O

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

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

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–*n*, and $j \neq i$.

2. Experimental

The preparation and characterisation of compounds $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a\text{–}c}$ have been described in a previous paper [1]. Eq. (2) was used to estimate the eutectic compositions of the ternary and quaternary systems investigated. Eutectic (binary, ternary, and quaternary) mixtures were made by mixing the appropriate amounts of components, melting them together, stirring to give intimate mixture, and cooling to room temperature with stirring in air. Calorimetric investigations were made by using differential scanning calorimeter (PL-DSC, England) with nitrogen as a purge gas. Typical heating rate was 10 K min^{-1}, and sample masses were 2–3 mg. Transition temperatures were identified with a standard polarised-light microscope (C. Zeiss, Germany), attached to a FB 52 hot-stage equipped with a FB 80 central processor (Mettler, Switzerland).

Transition temperatures of the mixtures prepared, were measured both by DSC and polarised-light microscopy and found to agree within 2–3°C.

3. Results and discussion

The transition temperatures, T_m and T_c, for compounds of the two series in the pure state, as reported before [1], are summarised in Table 1. As can be seen

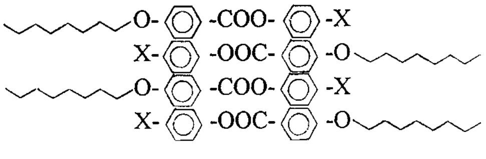
Table 1
Transition temperatures (°C) for compounds $\mathbf{I}_{a\text{–}c}$ and $\mathbf{II}_{a\text{–}c}$

Substituent X	Compound no.	T_m (°C)	T_c (°C)	Compound no.	T_m (°C)	T_c (°C)
CN	$\mathbf{I}_a$	88.2	106.8	$\mathbf{II}_a$	85.4	96.3
NO_2	$\mathbf{I}_b$	82.4	91.7	$\mathbf{II}_b$	79.4	88.7
OCH_3	$\mathbf{I}_c$	90.9	–	$\mathbf{II}_c$	96.1	(75)*

* On cooling.

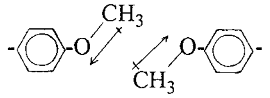
from this table, the methoxy derivative $\mathbf{I}_c$ is not mesomorphic. Its corresponding isomer $\mathbf{II}_c$ is monotropic which possesses its smectic phase on cooling at 75°C. The cyano and nitro analogues in both series were found to be enantiotropic.

In the two series, 4-hexadecyloxyphenyl-4′-substituted benzoates, **I**, and 4-substituted phenyl 4′-hexadecyloxy benzoate, **II**, the cyano and nitro substituents, having comparable electronic properties, interact similarly with the mesogenic portion of the molecule, and hence, their binary mixtures showed ideal solution behaviour [2]. In such molecules, bimolecular smectic structures [11,12] is believed to be formed as a result of molecular complexing, either in the pure state or in their binary [2], ternary, or quaternary [5] mixtures.



where X = CN or NO_2.

Conversely, in the monotropic methoxy derivative ($\mathbf{II}_c$), 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 linear association with end-to-end orientation of the mesophase.



The effect of the methoxy groups in $\mathbf{I}_c$ and $\mathbf{II}_c$ is explicable in terms of shielding effect of the oxygen lone-pair by an insulator, the methyl group. The repulsive forces involving the oxygen lone-pairs are thereby substantially reduced; the lack of strong repulsive forces simply allows a close approach of the neighbouring molecules, thus increasing bonding forces. These strong forces will be associated with high melting points and melting enthalpies [1] in such a way that no mesophase is detected on heating. In these compounds melting of the crystals occurs at a higher temperature than does the breakdown of the mesomeric forces and there is insufficient molecular anisotropy to cause the formation of a mesophase.

Any mesophase system [6] in which a bimolecular smectic is mixed with one which perturbs their molecular complexing would result in a non-ideal thermal behaviour. Such a perturbation would be found in mixing compounds with electron-rich aromatic rings (which can successfully compete with molecular complexation) with an electron-deficient ring of another molecule. Thus, the A–B interactions are considerably different from the A–A or B–B interactions. In such cases, non-linear thermal behaviour is found. Likewise, one should expect that mixtures of compounds with similar smectic layering characteristics, such as $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$, should exhibit ideal thermal behaviour.

The relationship between the clearing temperature (T_c) of an ideal liquid–crystal mixture and those of its components is closely related by the equation

$$T_{c(\text{mix})} = \sum \chi_i T_{c(i)}, \tag{3}$$

where χ_i represents the mole fraction of component "i". This relation is only applicable for mixtures of components of electronically similar molecular structure, such as the cyano and nitro analogues of series **I** and **II**. There have been occasional observations of significant deviations from this relationship as in case of nitro analogues when mixed with the electron-donating methoxy analogues [2,3,6].

Since clearing temperature, T_c, of a single component was related by van der Veen [13] to the polarisability anisotropy ($\Delta\alpha_X$) of the Ar–X bond by the equation

$$T_c = (\Delta\alpha_M + \Delta\alpha_X)^2, \tag{4}$$

where $\Delta\alpha_M$ is the anisotropy of polarisability for all the molecular structure except the terminal substituent X, Naoum et. al [5] have used such an equation together with Eq. (3) to relate the clearing temperatures of binary, ternary, and quaternary mixtures of compounds $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$ to the polarisability anisotropy of the Ar–X bonds of their individual components. The results they obtained, which were in good agreement with the experimental values, reflect the ideal thermal behaviour of these mixed systems. This ideal behaviour has encouraged us to test the applicability of the Schroeder-van Laar equation to the eutectic melting temperatures (T_E) of such ideal systems. Eq. (1) can be re-written in the linear form

$$\ln\chi_i = (\Delta H_i/RT_i) - (\Delta H_i/R)(1/T_E) \tag{5}$$

Table 2
Eutectic composition (mol%) and eutectic melting point (T_E, °C) of mixtures of enantiotropes $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$

System	$\mathbf{I}_a$ (%)	$\mathbf{I}_b$ (%)	$\mathbf{II}_a$ (%)	$\mathbf{II}_b$ (%)	T_E(meas)	$(1/T_E) \times 10^3$	T_E (calc)
$\mathbf{I}_a/\mathbf{I}_b$	33.7	66.3	–	–	70.4	2.911	70.3
$\mathbf{I}_a/\mathbf{II}_a$	42.0	–	58.0	–	74.0	2.881	74.2
$\mathbf{I}_a/\mathbf{II}_b$	35.7	–	–	64.3	72.0	2.897	71.5
$\mathbf{II}_a/\mathbf{I}_b$	–	58.5	41.5	–	68.0	2.931	67.2
$\mathbf{II}_a/\mathbf{II}_b$	–	–	45.8	54.2	68.7	2.925	69.0
$\mathbf{I}_b/\mathbf{II}_b$	–	53.0	–	47.0	66.0	2.949	66.1
$\mathbf{I}_a/\mathbf{I}_b/\mathbf{II}_a$	22.8	45.7	31.5	–	63.2	2.973	63.4
$\mathbf{I}_a/\mathbf{I}_b/\mathbf{II}_b$	21.1	21.5	–	37.4	62.5	2.979	61.9
$\mathbf{I}_a/\mathbf{II}_a/\mathbf{II}_b$	23.8	–	34.0	42.2	64.0	2.966	64.2
$\mathbf{I}_b/\mathbf{II}_a/\mathbf{II}_b$	–	38.7	27.1	34.2	60.5	2.997	60.5
$\mathbf{I}_a/\mathbf{I}_b/\mathbf{II}_a/\mathbf{II}_b$	16.4	32.3	22.7	28.6	57.3	3.026	57.5

from which it can be seen that $\ln \chi_i$ is linearly related to $1/T_E$ with slope $-\Delta H_i/R$ and intercept $\Delta H_i / RT_i$. That is, the enthalpy of fusion of component "i" is given by the slope of the regression line multiplied by the gas constant R, and the melting temperature of the same component is deduced by dividing the slope by the intercept. The method is acceptable if the values of T_i and ΔH_i calculated from the linear regression are in fair agreement with those determined experimentally. Thus eutectic binary, ternary, and quaternary mixtures of compounds $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$ were prepared and their melting temperatures determined by DSC. The results obtained are given in Table 2, and the data were used to plot, individually, the natural logarithm of the mole fraction of each single component against the reciprocal of the eutectic melting point of the mixture containing this component. The four lines obtained for components $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$are represented graphically in Figs. 1–4, respectively. The correlations given in these figures were further analysed by the method of least squares to give acceptable values for T_i and ΔH_i for each component with good correlation coefficient as deduced from Table 3.

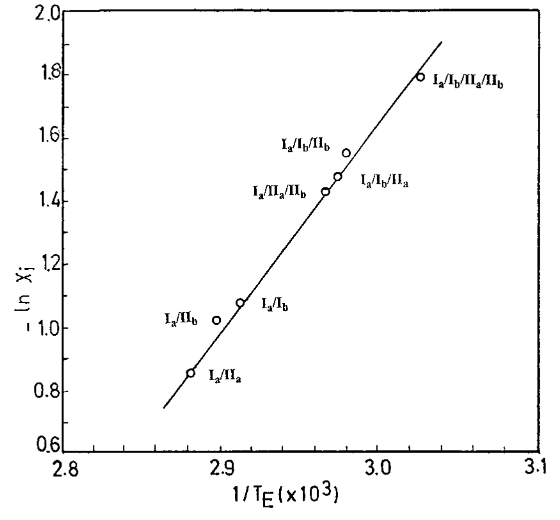


Fig. 1. Dependence of the mixture eutectic melting point on the mole fraction of component $\mathbf{I}_a$ in various binary, ternary, and quaternary mixtures.

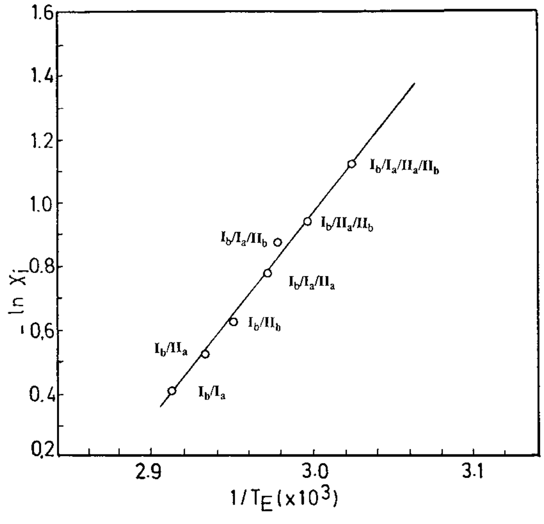


Fig. 2. Dependence of the mixture eutectic melting point on the mole fraction of component $\mathbf{I}_b$ in various binary, ternary, and quaternary mixtures.

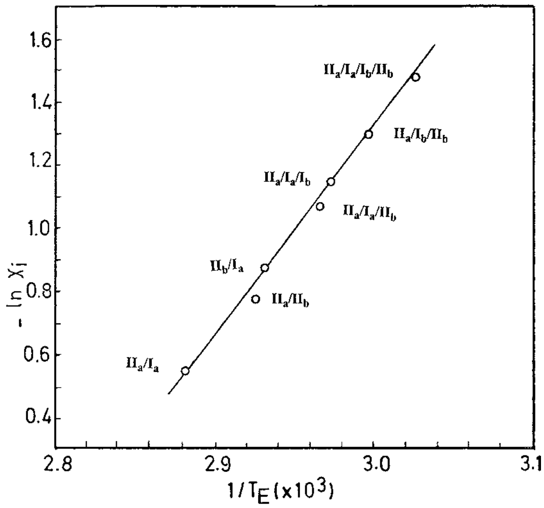


Fig. 3. Dependence of the mixture eutectic melting point on the mole fraction of component **II**$_a$ in various binary, ternary, and quaternary mixtures.

Table 3

Calculated and measured melting points (T_m,°C) and enthalpies (ΔH, kJ mol^{-1}) of fusion of compounds **I**$_{a,b}$ and **II**$_{a,b}$ and the corresponding correlation coefficient (r) of Eq. (5)

Compound	$T_{m(meas)}$	$T_{m(calc)}$	$\Delta H_{(meas)}$	$\Delta H_{(calc)}$	r
I$_a$	88.2	90.5	50.0	53.2	0.998
II$_a$	82.4	78.2	60.2	53.2	0.998
I$_b$	85.4	84.0	60.1	54.9	0.997
II$_b$	79.4	79.7	54.5	54.9	0.999

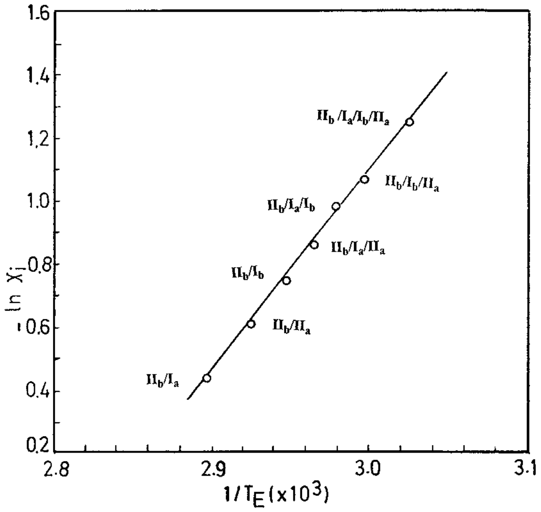


Fig. 4. Dependence of the mixture eutectic melting point on the mole fraction of component **II**$_b$ in various binary, ternary, and quaternary mixtures.

On the other hand, T_E data for the eutectic mixtures (Table 4) comprises the monotropic derivative (**II**$_c$) are plotted in Fig. 5 as a function of its mole fraction in binary, ternary, and quaternary mixtures with the enantiotropes **I**$_{a,b}$ and **II**$_{a,b}$. The solid line in Fig. 5 represents the theoretical regression based on Eq. (5) using the experimental ΔH_i (= 67 kJ mol^{-1}) and T_i (= 96°C) values for the methoxy derivative (**II**$_c$).

Table 4

Eutectic composition (mol%) and eutectic melting point (T_E,°C) of mixtures containing the monotrope **II**$_c$

System	**II**$_c$ (%)	**I**$_a$ (%)	**II**$_a$ (%)	**I**$_b$ (%)	**II**$_b$ (%)	T_E	$(1/T_E) \times 10^3$	$-\ln \chi_{\mathbf{II}a}$
II$_c$/**I**$_a$	53.0	47.0	–	–	–	86.6	2.780	0.635
II$_c$/**I**$_b$	36.0	–	64.0	–	–	73.8	2.882	1.022
II$_c$/**II**$_a$	45.0	–	–	55.0	–	71.5	2.901	0.799
II$_c$/**II**$_b$	40.0	–	–	–	60.0	79.0	2.840	0.916
II$_c$/**I**$_a$/**I**$_b$	27.0	25.0	48.0	–	–	71.6	2.901	1.309
II$_c$/**I**$_a$/**II**$_a$	32.5	25.0	–	39.0	–	70.0	2.914	1.124
II$_c$/**I**$_a$/**II**$_b$	30.0	24.5	–	–	45.5	71.3	2.903	1.204
II$_c$/**I**$_b$/**II**$_a$	25.0	–	45.0	30.0	–	60.0	3.002	1.386
II$_c$/**I**$_b$/**II**$_b$	23.5	–	40.5	–	36.0	68.0	2.931	1.448
II$_c$/**II**$_a$/**II**$_b$	27.0	–	–	32.9	40.1	73.9	2.881	1.309
II$_c$/**I**$_a$/**I**$_b$/**II**$_a$	20.5	18.1	36.7	24.7	–	67.1	2.939	1.585
II$_c$/**I**$_a$/**I**$_b$/**II**$_b$	19.4	16.6	34.0	–	30.0	67.2	2.938	1.640
II$_c$/**I**$_a$/**II**$_a$/**II**$_b$	21.7	18.6	–	26.0	33.6	68.2	2.930	1.528
II$_c$/**I**$_b$/**II**$_a$/**II**$_b$	18.2	–	32.1	21.7	28.0	58.5	3.015	1.704

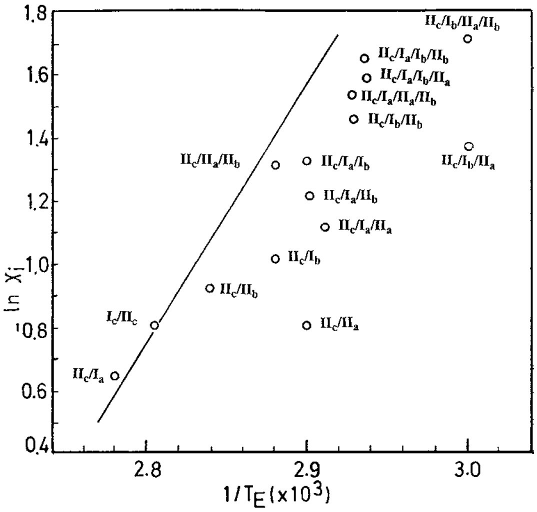


Fig. 5. Dependence of the mixture eutectic melting point on the mole fraction of component $\mathbf{II}_c$ in various binary, ternary, and quaternary mixtures.

As can be seen from Figs. 1–5, Eq. (5) is fairly applicable in case of mixtures of molecules having electronically similar structures, i.e., $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$ as well as that of the binary mixture containing the two methoxy derivatives $\mathbf{I}_c$ and $\mathbf{II}_c$ (44 mol% II_c and $T_E = 83.5°C$), while significant deviations were observed in case of mixtures of molecules possessing different molecular layering, e.g. $\mathbf{II}_c$ when mixed with one or more components of the bimolecular smectic molecules $\mathbf{I}_{a,b}$ and $\mathbf{II}_{a,b}$.

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