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 binary mixtures V. Mixtures of bimolecular smectics and linear mesogens

Gamal R. Saad

To cite this Article Saad, Gamal R.(1998) 'Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures V. Mixtures of bimolecular smectics and linear mesogens', Liquid Crystals, 25: 6, 655 — 660

To link to this Article: DOI: 10.1080/026782998205679

URL: http://dx.doi.org/10.1080/026782998205679

LIQUID CRYSTALS, 1998, VOL. 25, NO. 6, 655–660

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures
V. Mixtures of bimolecular smectics and linear mesogens

by GAMAL R. SAAD*, REFAAT I. NESSIM and MAGDI M. NAOUM
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

(*Received 20 January 1998; in final form 10 April 1998; accepted 14 May 1998*)

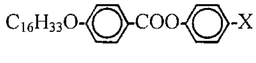
Two binary mixtures, prepared from either 4-cyanophenyl 4-hexadecyloxybenzoate (**Ib**) or 4-nitrophenyl 4-hexadecyloxybenzoate (**Ic**), with 4-carboxyphenyl 4-hexadecyloxybenzoate (**Ia**), were thermally characterized to construct the phase diagrams for the two systems **Ia/Ib** and **Ia/Ic**. Due to differences in the smectic layering between the individual components of each system, phase separation took place either in the solid or in the mesophase. A mathematical relation was derived to calculate the composition of each phase in the solid state. Another two phase diagrams were constructed for binary mixtures of the linear dimer molecule, 4-hexadecyloxybenzoic acid (**III**) with either the acid **Ia** or its isomeric derivative, 4-hexadecyloxyphenyl 4-carboxybenzoate (**II**).

1. Introduction

Liquid crystalline compounds and their mixtures offer unique opportunities to examine structure–properties relationships in their solid or liquid phases [1–5]. Binary mixtures of mesogens having similar structures exhibit a eutectic behaviour in their solid–mesophase transition temperatures, whereas their mesophase–isotropic transition temperatures vary linearly with composition [2, 4, 6]. On the other hand, mixtures of components possessing electronically different structures exhibit mesophase–isotropic transition temperatures which are strongly non-linear with composition [4, 7–15]. In the 4-substituted phenyl 4-hexadecyloxybenzoate series, the cyano and nitro substituents, having similar electronic properties, interact similarly with the mesogenic group of the molecule; consequently, their binary mixtures tend to show an ideal behaviour [4]. In such molecules, it is believed that the electron-withdrawing nature of the cyano or nitro substituent is responsible for the formation of the bimolecular smectic structure [16] as a result of molecular complexing either in the pure state or in their binary mixtures. Similarly, each of the two isomeric carboxylic acid derivatives, 4-carboxyphenyl 4-hexadecyloxybenzoate (**Ia**) and 4-hexadecyloxyphenyl 4-carboxybenzoate (**II**) possesses high transition temperatures due to the formation of linear dimer molecules in their condensed phases; because of the similar electronic factors occurring within the molecules of either component, their phase diagram exhibits an ideal behaviour [2].

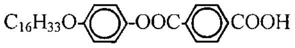
Conversely, binary mesophase systems in which a bimolecular smectic is mixed with one which significantly perturbs their molecular complexing would result in a non-ideal behaviour.

The objective in the present study is first, to investigate the effect of an admixture of the linear-dimer molecule (**Ia**) on the mesophase behaviour of either of the bimolecular smectic molecules **Ib** or **Ic**. Although these three derivatives differ only in one terminal substituent, **Ib** and **Ic** on the one hand and **Ia** on the other represent extremes in the mode of intermolecular association in their condensed phases.

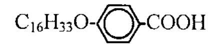


I_a X= COOH, I_b X= CN, I_c X= NO_2

The second aspect of this investigation is to examine the mesophase behaviour of the binary mixtures prepared from the simple alkoxybenzoic acid (**III**) as one component, and either of the two isomeric acids **Ia** or **II**, as a second component. Each of these three compounds forms a linear-dimer molecule through strong hydrogen bonding.



II



III

Differences in the mutual conjugation between the alkoxy and carboxyl groups will have a different effect on the polarity of the ester carbonyl group in the molecules of **Ia** and **II** and, consequently, their phase diagrams with compound **III** are expected to be different.

---

*Author for correspondence.

2. Experimental

2.1. *Materials and analyses*

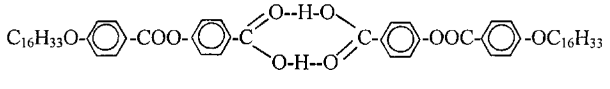
Compounds **Ia–c**, **II**, and **III** were prepared according to methods described before [2, 3]. Calorimetric investigations were performed with a differential scanning calorimeter, PL-DSC, England, with nitrogen as a purge gas. The typical heating rate was 10 K min^{-1}, and sample masses were 1–3 mg. The instrument was calibrated from the melting points of ultra-pure metals and a value of 28.45 J g^{-1} was used for the enthalpy of fusion (ΔH_m) of indium. Three samples were measured for each composition and the average values of ΔH were obtained and used for calculation. Transition temperatures were identified with a standard WL-polarized light microscope (C. Zeiss, Germany) attached to a FB 82 hot-stage equipped with a FB 80 central processor (Mettler, Switzerland).

2.2. *Phase diagrams*

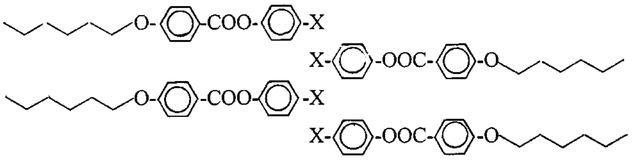
Mixtures of any two components, in known proportions, were prepared by fusion, thoroughly mixed, and cooled in air to room temperature. Transition temperatures were determined, both with the polarizing microscope and the DSC, and found to agree within 2°C. In the phase diagrams, constructed by plotting transition temperatures against composition, the symbols '○' denote solid–mesophase or mesophase–mesophase transitions, '□' mesophase–isotropic transitions, '×' solid–solid transitions, and '●' eutectic temperatures.

3. Results and discussion

Recalling the transition temperatures of the cyano derivative (**Ib**), with a mesophase stability $\Delta T = 96.3 - 83.2 = 12.6°\mathrm{C}$ [3], as well as the nitro analogue (**Ic**), with $\Delta T = 88.7 - 79.4 = 9.3°\mathrm{C}$ [3], and comparing with their carboxy analogue (**Ia**), revealed that *para* substitution with the carboxyl group greatly increases the stability of the mesophase, $\Delta T = 212.4 - 119.8 = 92.6°\mathrm{C}$, in comparison with the other two substituents, due to dimer formation in **Ia**.



On the other hand, comparison of the effect of CN and NO_2 groups, in the enantiotropes **Ib** and **Ic**, respectively, with other substituents such as $OCH_2C_6H_5$, $COOCH_2C_6H_5$, OH [1], Cl, or OCH_3 [3], on the mesophase stability of these compounds, revealed that there is a strong tendency in the cyano and nitro derivatives to lose molecular pairing [16]; an anti-parallel alignment of the cyano or nitro dipoles then occurs.



I_b X= CN, I_c X= NO_2

Each cyano or nitro group in a pair of molecules is located close to the opposite end of its neighbour, and the effective molecular length is therefore enhanced. This may explain the strong promotion of the mesophase stability effected by the introduction of the cyano or nitro group.

The binary phase behaviour of the carboxy-substituted derivative (**Ia**) with its isomeric form (**II**) has been thoroughly investigated in previous work [2] and the resulting phase diagram is reproduced in figure 1. In another paper [4], the binary phase behaviour of the mixtures of the two electronically similar analogues **Ib** and **Ic** was reported and their phase diagram is illustrated in figure 2. As can be seen from these figures, both mixtures are of a simple eutectic type in their solid–mesophase transitions, and possess linear mesophase–isotropic transition variation with composition. Such behaviour is attributed to similar electronic factors existing within the two molecules constituting the mixture.

3.1. *Mixtures of bimolecular smectic and linear-dimer molecules*

Since the intermolecular forces acting between molecules of the type **Ib** or **Ic** (bimolecular smectic layering) differ

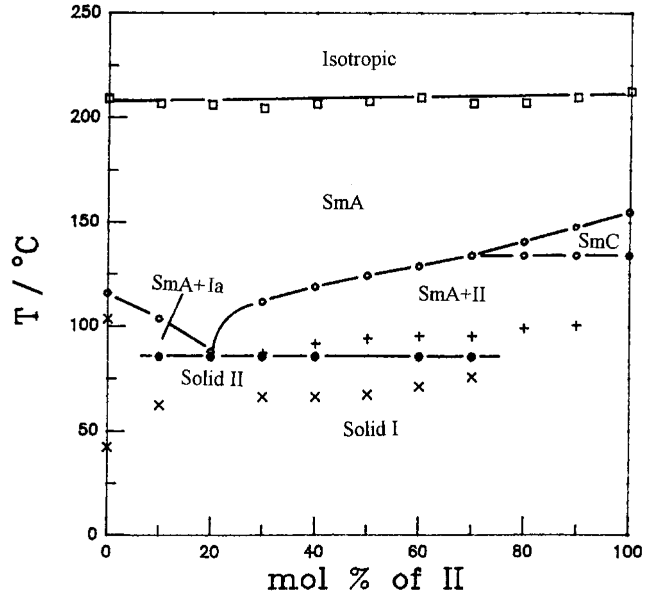


Figure 1. Phase diagram of the binary mixture **Ia**/**II**.

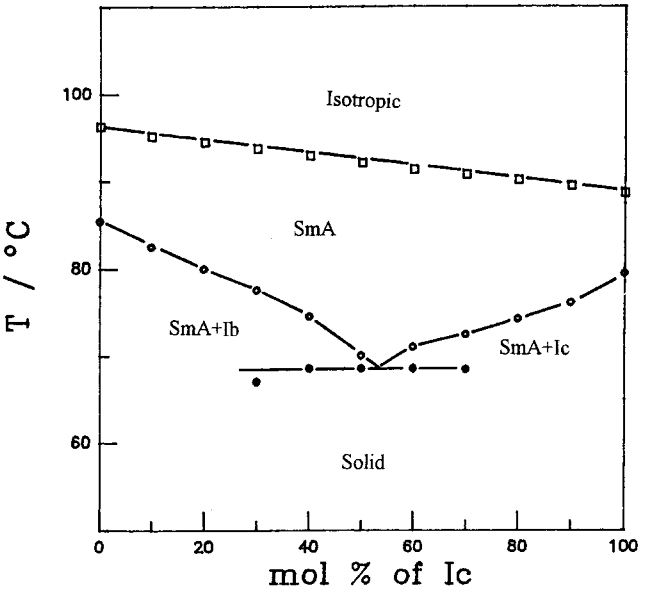


Figure 2. Phase diagram of the binary mixture **Ib/Ic**.

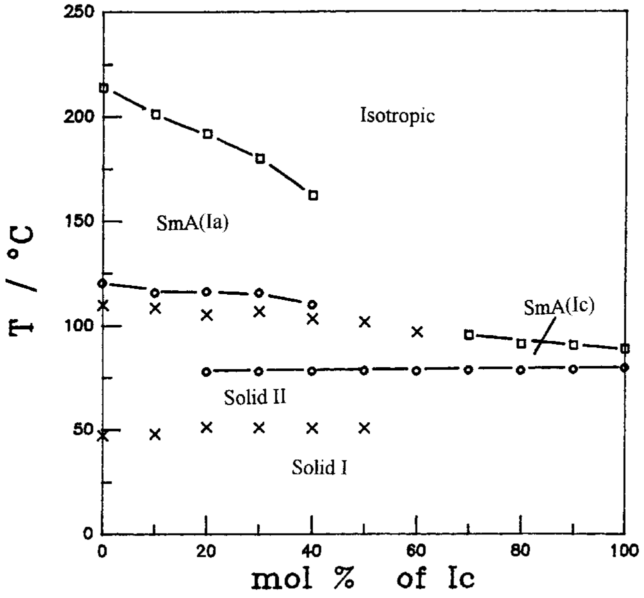


Figure 4. Phase diagram of the binary mixture **Ia/Ic**.

drastically from those occurring between molecules of the type **Ia** (linear-dimer association through strong hydrogen bonding), the mesophase behaviours of the electronically different components, **Ia/Ib** or **Ia/Ic**, are expected to deviate considerably from ideal. The phase diagrams constructed for these two systems are illustrated in figures 3 and 4, respectively. Examination of these figures reveals that there exists phase separation in either the solid or in the meso phases. It may be further noticed from the same figures that in both systems the melting point of component 1 (either the cyano or the nitro derivative) is not significantly affected by the gradual increase of component 2 (the carboxy analogue). Conversely, the melting point of component 2, in the neighbourhood of 110°C, is found to decrease with the increase of the amount of component 1. These findings indicate that mixing of the two components leads to the separation of two phases in the solid state; that is phase 1, which melts first, is composed of pure component 1, and phase 2, that melts later, is a mixture of the two components. The composition of the latter phase depends on the total composition of the mixture; thus its melting point decreases as the content of component 1 (having the lower melting point) in the mixture is increased.

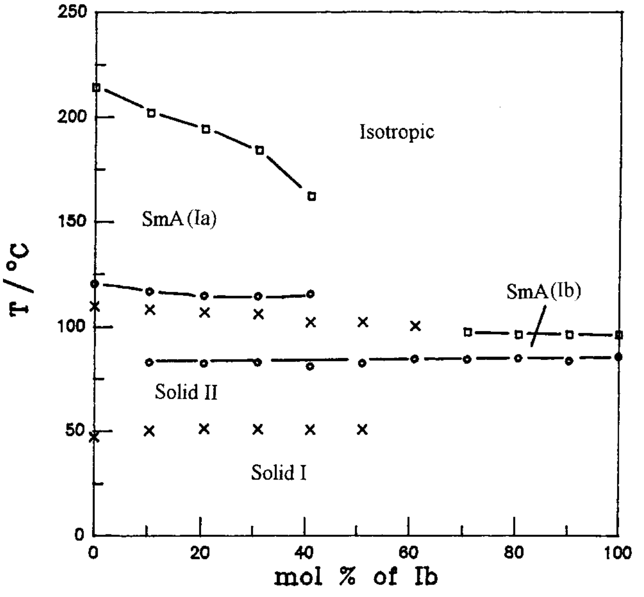


Figure 3. Phase diagram of the binary mixture **Ia/Ib**.

This conclusion may be confirmed by calculating the composition of each phase, with respect to the two components 1 and 2, in the following manner. Suppose that in 1 g of the mixture the total weight fractions of components 1 and 2 are W_1 and W_2, respectively. At the melting point of phase 1 (of lower melting point), let m_1 and m_2 be the masses (in grams) of the liquid (phase 1) and the solid (phase 2), respectively. Since the total mass of the mixture is taken as 1 g, then

$$m_1 + m_2 = 1 \text{ (g)}. \qquad (1)$$

Let us assume that the total composition of the mixture is such that the two components are differently distributed between the two phases; then, if we denote w_{11} as the weight fraction of component 1 in phase 1, w_{12} that of component 1 in phase 2, w_{21} that of component 2 in phase 1, and w_{22} that of component 2 in phase 2, we may write

$$w_{11}+w_{21}=1 \quad (2)$$

$$w_{12}+w_{22}=1 \quad (3)$$

and

$$w_{11}m_1+w_{12}m_2=W_1\ (\mathrm{g}) \quad (4)$$

$$w_{21}m_1+w_{22}m_2=W_2\ (\mathrm{g}). \quad (5)$$

Substituting for m_2 by $(1-m_1)$ in equation (4) we get

$$m_1=(W_1-w_{12})/(w_{11}-w_{12}). \quad (6)$$

Similarly, substituting by $(1-m_2)$ for m_1 in equation (5) we get

$$m_2=(W_2-w_{21})/(w_{22}-w_{21}). \quad (7)$$

Since pure component 2 has no transition peaks in the region of the melting of phase 1, and at the same time the melting point of component 1 is independent of the total composition of the mixture (W_1) [see again figures 3 and 4], then, if ΔH_1(pure) is the enthalpy change per gram accompanying the melting of pure component 1, and ΔH_1(mix) is that measured for the same transition of a mixture having the total composition W_1, we see that for the enthalpy changes accompanying the melting of phase 1

$$w_{11}m_1\Delta H_1(\mathrm{pure})=\Delta H_1(\mathrm{mix}). \quad (8)$$

Substituting for m_1 from equation (6) into (8) we obtain

$$W_1w_{11}/(w_{11}-w_{12})-w_{12}w_{11}/(w_{11}-w_{12})$$
$$=\Delta H_1(\mathrm{pure})/\Delta H_1(\mathrm{mix})=\Delta_1. \quad (9)$$

Thus, by plotting the value Δ_1 as a function of the total weight fraction W_1, a straight line would be obtained with

$$\mathrm{slope}=-w_{11}/(w_{11}-w_{12}),$$

and

$$\mathrm{intercept}=w_{12}w_{11}/(w_{11}-w_{12})$$

from which we can calculate w_{12} and w_{11} as

$$w_{12}=-(\mathrm{slope/intercept})$$

$$w_{11}=(\mathrm{slope}\times w_{12})/(\mathrm{slope}-1).$$

Alternatively, w_{12} can be calculated by putting $\Delta_1=0$ in equation (9), i.e. the intercept with the abscissa. In this case $w_{12}=W_1(\Delta_1=0)$.

Similarly, if the melting point of phase 2 does not change significantly with mixture composition, then, substituting for m_2 from equation (7) in the equation

$$w_{22}m_2\Delta H_{12}(\mathrm{pure})=\Delta H_1(\mathrm{mix})$$

we get

$$W_2w_{22}/(w_{22}-w_{21})-w_{21}w_{22}/(w_{22}-w_{21})$$
$$=\Delta H_2(\mathrm{pure})/\Delta H_2(\mathrm{mix})=\Delta_2 \quad (10)$$

where ΔH_2(pure) is the enthalpy change accompanying melting of component 2 and ΔH_2(mix) is that measured for the same transition of a mixture having the total weight fraction W_2.

As can be seen from figures 3 and 4, the melting point of phase 1 is constant throughout the whole composition range of the mixture and, hence, equation (9) is applicable. The correlations obtained for the binary mixtures **Ia/Ib** and **Ia/Ic** are represented in figures 5 and 6, respectively. Regression analysis was applied to both lines in order to calculate the slope and intercept and, hence, the composition of each phase at this temperature. The results obtained, as given in the table, indicate that at the melting point of component 1, phase 1 is composed of pure component 1 while phase 2 is a mixture of component 2 with a small amount of component 1. Increasing the temperature to that corresponding to the melting point of phase 2 results in an increase of the miscibility of each component in the other; consequently a decrease in the melting point of component 2 and an increase in the clearance point of component 1 were observed, in such a way that the two transition peaks overlap in regions of mixed components. In this case, equation (10) could not be applied.

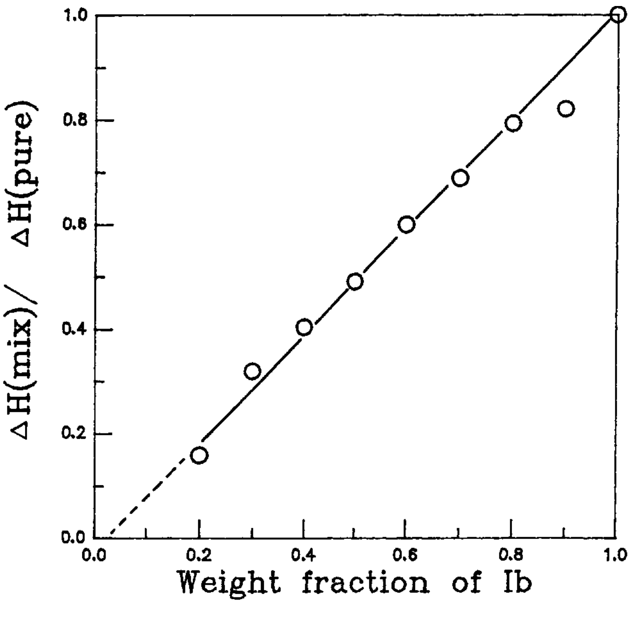


Figure 5. Variation of $\Delta_1[=\Delta H(\mathrm{mix})/\Delta H_1(\mathrm{pure})]$ with weight fraction of **Ic** in the binary mixture **Ia/Ic**.

Table. Regression analyses based on figures 5 and 6 for the determination of phase composition at the first transition temperature (T).

Binary system	T °C	Slope	Intercept	Correlation coefficient	Standard deviation	w_{11}	w_{12}
Ia/Ib	84	1.013	−0.013	0.998	±0.007	0.997	0.013
Ia/Ic	78	1.042	−0.042	0.998	±0.006	0.985	0.040

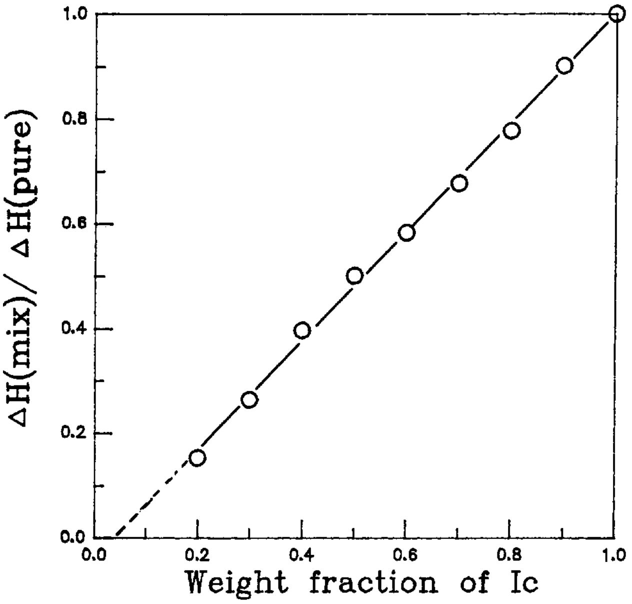


Figure 6. Variation of $\Delta_l[=\Delta H(\text{mix})/\Delta H_l(\text{pure})]$ with weight fraction of **Ic** in the binary mixture **Ia/Ic**.

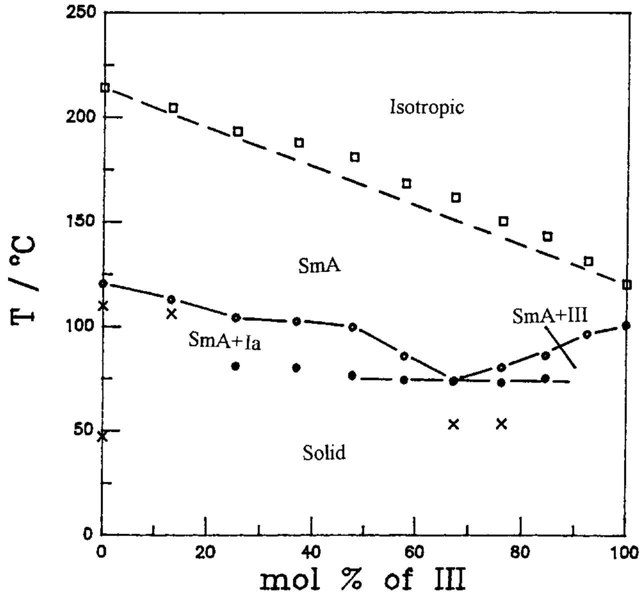


Figure 7. Phase diagram of the binary mixture **Ia/III**.

3.2. *Mixtures of 4-hexadecyloxybenzoic acid with **Ia** and **II***

The phase diagrams of the two binary systems **III/Ia** and **III/II** are given in figures 7 and 8, respectively. As can be seen from these figures, both systems are of a simple eutectic type, possessing their eutectic compositions at about 67 and 85 mol % of **III**, respectively. The eutectic mixture of the first system melts at about 73°C having a liquid crystalline range of 86°C. The corresponding values for the latter system are 94 and 46°C, respectively, indicating that the mesophase of the binary system **III/Ia** is more stable than that of the **III/II** binary system.

Generally, the stability of a mesophase is greater the greater the lateral adhesion between the rod-shaped molecules in question; this is augmented by the increase in the polarity and/or the polarizability of the mesogenic part of the molecule. In 4-hexadecyloxybenzoic acid (**III**) there is a mutual conjugation between the alkoxy oxygen and the acid carbonyl group; this should increase the

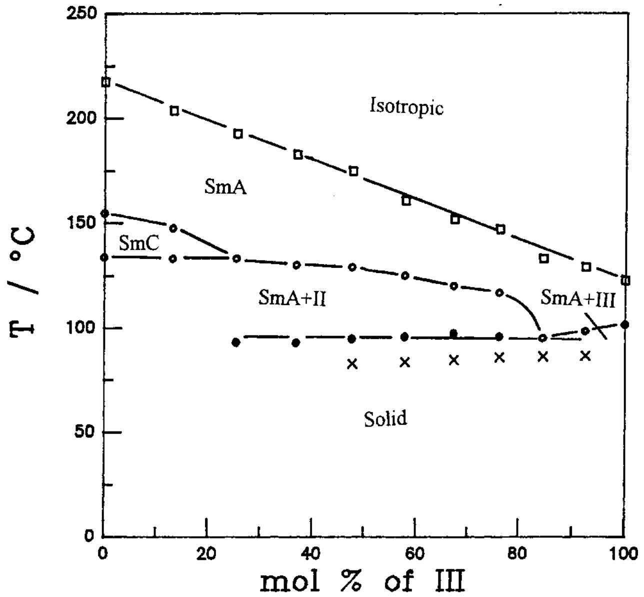
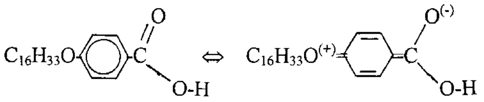
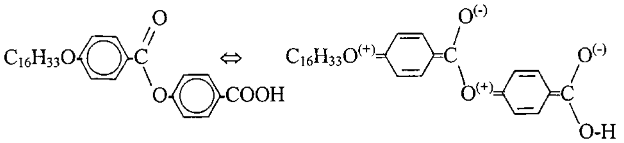


Figure 8. Phase diagram of the binary mixture **II/III**.

polarity of the carboxyl group and so stabilize the hydrogen bond and the mesophase ($\Delta T = 131 - 102 = 29°C$).



Similarly, in 4-carboxyphenyl 4-hexadecyloxybenzoate (**Ia**) the mutual conjugation between the alkoxy oxygen and the ester carbonyl group should increase the polarity of the carbonyl oxygen that helps to stabilize the mesophase ($\Delta T = 92.6°C$).



Conversely, in 4-hexadecyloxyphenyl 4-carboxybenzoate (**II**), such mutual conjugation is lacking; this is in addition to the competitive interaction between the two carbonyl groups on the one hand, and the two oxygen atoms on the other hand, through the intervening phenylene rings, thus leading to a lower mesophase stability ($\Delta T = 83.7°C$) for compound **II** as compared with compound **Ia**.

From the above discussion, the increased polarity in the two molecules (as a result of conjugation) of the binary mixture **III/Ia** would lead to greater lateral association between molecules of the individual components of the mixture. This is evidenced by the enhancement observed in their mesophase–isotropic transition temperatures, as seen in figure 7. In the other mixture, the reverse was found to be the case, that is a linear behaviour is observed between the less polar molecule (**II**) and the acid **III**, as can be seen from figure 8.

4. Conclusions

Generally, the mesophase behaviour of a binary mixture is greatly influenced by differences existing in the electronic nature of its individual components as well as by the type of intermolecular association in the condensed phases. Consequently, mixing of the two hydrogen-bonded dimer molecules in **Ia/III** or **II/III** results in phase diagrams of simple eutectic type in their solid–mesophase transition temperatures, while the mesophase–isotropic transition temperatures vary gradually with composition. Differences occurring in the conjugative interactions between molecules of **Ia** (in the first mixture) and its isomeric analogue **II** (in the second) affect slightly the linearity of the composition dependence of the latter transition.

Conversely, mixing of the hydrogen-bonded dimer molecule **Ia** with either of the two bimolecular smectics **Ib** or **Ic** results in phase diagrams that show a complete phase separation in the solid phase. Increasing the temperature above the melting point of the low melting component (**Ib** or **Ic**) increases the miscibility of each component in the other.

References

[1] Naoum, M. M., Seliger, H., and Happ, E., 1997, *Liq. Cryst.*, **23**, 247.

[2] Naoum, M. M., Hohne, G., Seliger, H., and Happ, E., 1997, *Liq. Cryst.*, **23**, 653.

[3] Naoum, M. M., Saad, G. R., Nessim, R. I., Abdel Aziz, T. A., and Seliger, H., 1997, *Liq. Cryst.*, **23**, 789.

[4] Naoum, M. M., Saad, G. R., Nessim, R. I., and Abdel Aziz, T. A., 1998, *Liq. Cryst.*, **23**, 789.

[5] Naoum, M. M., Nessim, R. I., Saad, G.R., and Abdel Aziz, T. A., 1998, *Liq. Cryst.*, **25**, 73.

[6] Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (New York: Academic Press).

[7] Griffin, A. C., and Johnson, J. F., 1977, *J. Am. chem. Soc.*, **99**, 4359.

[8] Sackmann, H., and Demus, D., 1963, *Z. phys. Chem.*, **224**, 177; Sackmann, H., and Demus, D., 1965, *Z. phys. Chem.*, **230**, 285.

[9] Dave, J. S., Patel, P. R., and Vasanath, K. L., 1966, *Ind. J. Chem.*, **4**, 505.

[10] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. org. Chem.*, **35**, 2711.

[11] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. Am. chem. Soc.*, **92**, 1582.

[12] Steinstrasser, R., 1972, *Angew. Chem.*, **84**, 636.

[13] Steinstrasser, R., *Z. Naturforsch.*, **27**, 774.

[14] Park, W., Bak, C. S., and Labes, M. M., 1975, *J. Am. chem. Soc.*, **97**, 4398.

[15] Griffin, A. C., Fisher, R. F., and Havens, S. J., 1978, *J. Am. chem. Soc.*, **100**, 6329.

[16] Leadbetter, A. J., Richardson, R. M., and Collin, C. N., 1975, *J. Phys. Fr.*, **36**, 37; Leadbetter, A. J., Durrant, A. L. J., and Rugman, M., 1975, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 231.