Non-linear behaviour of smectic C phase in binary systems

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The mesophase behaviour has been characterized for binary mixtures formed from components of electron donating substituents. One of the chosen components shows a rich polymorphism existing either in nematic or nematic with smectic A and smectic B phases. An enhancement in smectic A phase has been observed between two components selected from this series. The other component which shows nematic and smectic C phases undergoes non-linear variation in smectic C-nematic transition curve. The phase diagrams have been constructed for the various systems in order to investigate the effect of change of polymorphism.

Mesogenic compounds and their mixtures offer unique opportunities to examine structure-property relationship in condensed phases. In general, the binary mixtures of these materials exhibit eutectic behaviour in their solid-mesophase transition temperatures whereas their mesophase-isotropic transition temperatures vary linearly with composition. However, non-linear behaviour has been reported for some mixtures when one of the compounds was chloro-mesogen. Non-linear behaviour has been observed for nematic, smectic A, smectic B and smectic E wherein complicated phase transition boundaries in phase diagrams are observed\(^6\). The deviation from the linear behaviour for other smectic phases, particularly smectic C and smectic I, have also been observed in the mixtures of terminally non-polar components\(^7\). In the present work, phase diagrams of binary mixtures of compounds I and II are described in which a discontinuous behaviour of smectic C phase belonging to II is observed by changing the polymorphic behaviour of compounds from the homologous series I.

Experimental

The polymorphism of the compounds used alongwith their transition temperature (°C) observed microscopically are as shown in (I) and (II).

Notes

**I**

4-n-Alkylloxy phenyl-4'-n-alkyl cyclohexyl carboxylate

\[
\text{C}_\text{n}H_{2n+1}\text{O} - \text{C}_\text{m}H_{2m+1}
\]

\(a: n=5, m=5, \text{Cr} 35.5\) (Sm A) N 5.0 I

\(b: n=5, m=6, \text{Cr} 32.3\) Sm B 35.6 Sm A 46.9 N 79.0 I

\(c: n=5, m=8, \text{Cr} 36.0\) Sm B 48.6 Sm A 64.4 N 78.9 I

\(d: n=7, m=8, \text{Cr} 44.0\) Sm B 67.0 Sm A 78.0 N 81.0 I

\(e: n=5, m=8, \text{Cr} 30.0\) N 60.0 I

(The compound Ie has two adjacent lateral fluor substituents in the phenyl ring)

**II**

2,3-Difluoro-4-n-octyloxy-4'-l4-n-pentyl cyclohexyl-phenyl benzate

\[
\text{C}_\text{n}H_{2n+1}\text{O} - \text{C}_\text{m}H_{2m+1}\]  

\(\text{Cr} 58.0\) Sm C 95.0 N 166.8 I

The isobaric phase diagrams were studied by microscopic observations of the transitions from room temperature until the field of view became dark, i.e., isotropic liquid, using contact as well as singular concentration methods. The contact preparations were made from two molten samples kept between the glass slide and cover slip and the effect of concentration gradient in the sample was observed. The concentrations prepared in the steps of 10 weight percent were thoroughly mixed and kept in the isotropic state on Koehler’s heating plate with intermediate stirring for about six hours to ensure complete homogeneity of the mixture. The Leitz POM with programmable Mettler FP 82 hot stage and Mettler FP 90 central processor was used to study the phase diagrams. The phase transitions were determined in the heating as well as cooling modes. The heating rate in the vicinity of the transition was maintained at 1 °C min\(^{-1}\). The different phases were identified by their characteristic textures.

Results and discussion

Five different members of the homologous series, Ia-e, of type I were taken in which the terminal alkyl group was varied. Barring the lowest member in the series, Ia, which shows only nematic phase and monotropic smectic phase, all other analogues
investigated contain in addition to nematic phase, the smectic A and smectic B phases. A lateral substitution of two fluoro substituents in the phenyl ring in 1e, now named as 1e, too exhibits only nematic phase. All these compounds have lower clearing temperature in which the range of mesomorphic phase is appreciable. The other component, II, is also difluoro substituted but has an additional phenyl ring (in comparison to I) which serves as bridging group in conjunction with carboxylate. This compound possesses nematic and smectic C phases, the clearing temperature being much higher.

The phase diagram constructed for the mixture II/1a, shown in Fig. 1, exhibits gradual variation of solid-mesophase transition temperature with composition and linear dependence of its mesophase (nematic)-isotropic transition temperature. Also, 1e being the only compound, nematogenic in nature, shows a similar behaviour with II as shown in Fig. 2. In both the cases, smectic C-nematic transition curve does not exceed beyond 40% of 1a or 1e. This behaviour indicates that polymorphy of individual component (1a or 1e) being same exert similar effects and retain similar and strong intermolecular interactions in the mesophase, whether it is nematic or smectic.

Figure 3 represents phase diagram for the binary mixture of II/1b. We observe, from the side of component II, as a result of successive addition of 1b, an increase in the nematic phase range accompanied with a little non-linear variation in the smectic C-nematic transition temperature.

The phase diagram of II/1c, (Fig. 4), characterizes the feature of smectic C phase in different steps. Firstly, a rapid decrease in the transition temperature as one moves up to about 45% of 1c (as was the case in Figs 1 and 2). Secondly, a slight enhancement at around 60% of 1c followed again by a rapid decrease in smectic C-nematic transition curve, simultaneously extending its region of existence even upto high concentrations of 1c. A similar behaviour is seen in the system II/1d in which the variation of smectic C behaviour fashions in a non-linear approach.

An attempt was made to observe the phase diagram behaviour amongst the various components of series I and to study its effect on the polymorphic behaviour of II. For this purpose, the phase diagram of the system 1a/1c (Fig. 5) reveals, surprisingly, a maximum in smectic A-nematic transition temperature. The smectic A phase appearing from low concentration of
The curve also shows a minimum in smectic A-nematic which is observed at 1:1 concentration of the components. Therefore, an equimolar concentration of \( \text{Ia:le} \) showing phase properties similar to those used in the series \( \text{Ib-d} \) was prepared whose polymorphic behaviour varied as \( \text{Cr 25.0 Sm B 27.0 Sm A 30.0 N 76.0 I} \). It was used as one of the components to observe the behaviour with respect to \( \text{I} \). Consequently, such a situation is represented in Fig. 6. A gradual variation of smectic C-nematic is suddenly followed by a maximum on smectic C-nematic phase transition in a narrow concentration range. The maximum of smectic \( C \) is also shifted from equimolar ratio of the present components but appears nearly in the same range in which such a behaviour is observed for the other systems.

With respect to the solid-mesophase transition, all the systems were supposed to show eutectic behaviour which, however, could not be achieved under normal conditions. In all these cases, as is to be expected, mesophase (nematic)-isotropic curve varies linearly with composition.

The various phase diagrams, thus, reflect the features of smectic \( C \) phase in the mixed system. When a donor component (alkyl- or alkyloxy-) shows smectic \( C \) phase, it has been observed that this phase is strongly depressed in the mixtures containing electron withdrawal components such as terminal-CN, -NO\(_2\) or -CNS but an enhancement and then depression when instead of -CN etc., the other component has terminal substituents as R-CO- or R-COO\(^-\). In the present case, all the phase diagrams are constructed for the binary systems composed from \( \text{le} \) suffers a non-linear composition dependence which can be called an "induced" or "enhanced" smectic \( A \) phase.
electron donating substituted derivatives. Since there is no difference in the electronic nature between the components, the curves should have behaved in a linear manner. Generally, in the phenyl benzoate systems, the liquid crystallinity is more persistent as mutual conjugation between substituent and ester group is increased. The existence of multimesogenic nature in the higher members of I series makes the behaviour of smectic C-nematic curve in an abnormal way. The non-linear behaviour is not observed when the component chosen is either Ia or Ie. It can be concluded that in Figs 3, 4 and 6, the alkyl chain length and rich polymorphism may have an influence on the non-linear behaviour of smectic C phase. Another unique feature to be observed is the enhancement of smectic A phase in Fig. 5. The enhancement usually appears in mixtures with electron withdrawing and releasing groups or between polar and non-polar components. The similar electronic behaviour, that is, polar-polar or non-polar-non-polar is least responsible for this phenomenon. One tool to account for mesogenic behaviour is computer simulation. Appropriately focussed computer simulation studies can, no doubt, give a unique insight into molecular ordering and phase behaviour and can provide systematically structure-property information. Although, the literature shows results on liquid crystal phases and chemically induced liquid crystal phases, we have not carried out any such studies of the model systems. Such a system or similar ones, thus, need extensive dynamic studies.

References