Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: Robert E. Goozner & M. M. Labes (1979): Solute-Solvent Interactions in Discotic Mesophases, Molecular Crystals and Liquid Crystals, 56:3, 75-81

To link to this article: http://dx.doi.org/10.1080/01406567908071971

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 75-81
0140-6566/79/5603-0075-81$04.50/0

Printed in the United States of America

SOLUTE-SOLVENT INTERACTIONS IN DISCOTIC MESOPHASES

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(Received for publication August 13, 1979)

A 1:1 mixture of benzenehexa-n-heptanoate and benzenehexa-n-octanoate is used as a solvent for small non-mesogenic molecules. As opposed to the general expectation of depressions of phase transition temperatures by solute, enhancement, decreases, and maxima as a function of solute concentration are seen. Enthalpic changes parallel the transition temperature changes. Rod-disc interactions are also discussed.

The recent observation of thermotropic mesomorphism in the benzenehexa-n-alkanoates by Chandrasekhar et al[1] has triggered a number of studies of "discotic" mesophases.[2-5] Because of the similarity of such structures to compounds known to clathrate guest molecules in the solid state,[6-8] it seemed likely to us that relatively specific solute-solvent interactions might be possible in such phases. Indeed Chandresekhar et al[9] noted that the pure compounds mixed with up to about 10% (w/w) of benzene "also formed mesophases", in contrast with the marked phase suppression which would be typical in the usual rod-like mesogens.

In order to extend the liquid crystalline temperature range of these compounds, a 1:1 (mole %) mixture of benzenehexa-n-heptanoate and benzenehexa-n-octanoate was prepared. Fig. 1 presents the phase diagram and enthalpy of transitions for this binary system. The phase diagram reflects

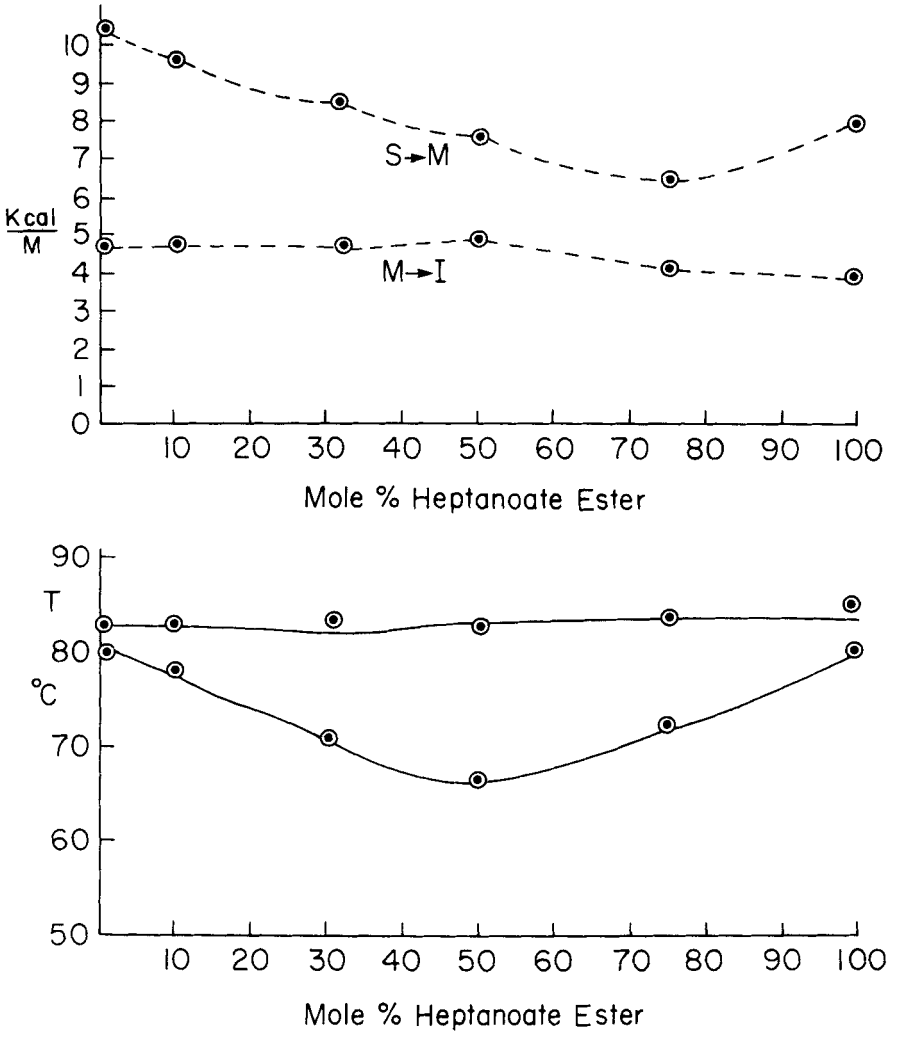

Figure 1. Phase diagram and enthalpies of transition of the binary system benzenehexa-n-heptanoate and -octanoate.

essentially ideal behavior of the binary system. X-ray data (Table I) is consistent with the ideality of the system.

Fig. 2 demonstrates the results of dissolving a number of representative small solute molecules in the 1:1 mixture. The subtlety of the behavior is best demonstrated by the 3 xylenes. o-Xylene enhances both the mesophase→isotropic (m→i) and solid→mesophase (s→m) transition temperatures, while p-xylene decreases these temperatures. m-Xylene is extremely insoluble (< 1%) in the same 1:1 mixture. An attempt was made to see specific structural effects in the x-ray patterns of the binary mixture doped with 13.5 mole % o-xylene, but our results only imply some reduction in ordering without any discrete effects on the lattice parameters. Chandresekhar et al[9] made similar observations regarding benzene dissolved in the individual alkanoate components.

Preliminary data indicate that rod-like mesogens mixed with these disc-like materials show several of the features suggested by Alben[10] in a theoretical study of rod-disc interactions. When small amounts of rods are added to the discotic phase, dm→i/dc (the derivative of the change in the mesophase→isotropic phase transition temperature with concentration) decreases with increasing length of the dissolved rod. Small amounts of disc-like mesogens do not strongly suppress the nematic-isotropic transition of conventional nematics if their molecular length is sufficient. The enthalpies of the nematic-isotropic transitions of rods are also strongly suppressed by discs. For example, when p-(trans-4-n-propylcyclohexyl)benzonitrile, a nematic liquid crystal of a calculated length of 13.8 Å, is used to dope the 1:1 discotic mixture, the m→i transition temperature is strongly depressed with dm→i/dc = -60. When the mixture is

Table I. Molecular Spacings (Å) in the Mesophase via X-ray Diffraction

Compound				Designation
Benzenehexa-n-heptanoate	Benzenehexa-n-octanoate	1:1 Heptanoate/octanoate	13.5 M% o-xylene/1:1 mixture	
4.6	4.6	4.6	4.6	intermolecular spacing along C_6 axis
14.6	15.9	15.6	16.6	d_{100}
8.7	9.1	8.8	9.0	d_{110}
7.6	7.8	7.7	7.7	d_{200}
17.4	18.2	17.6	18.0	lattice constant

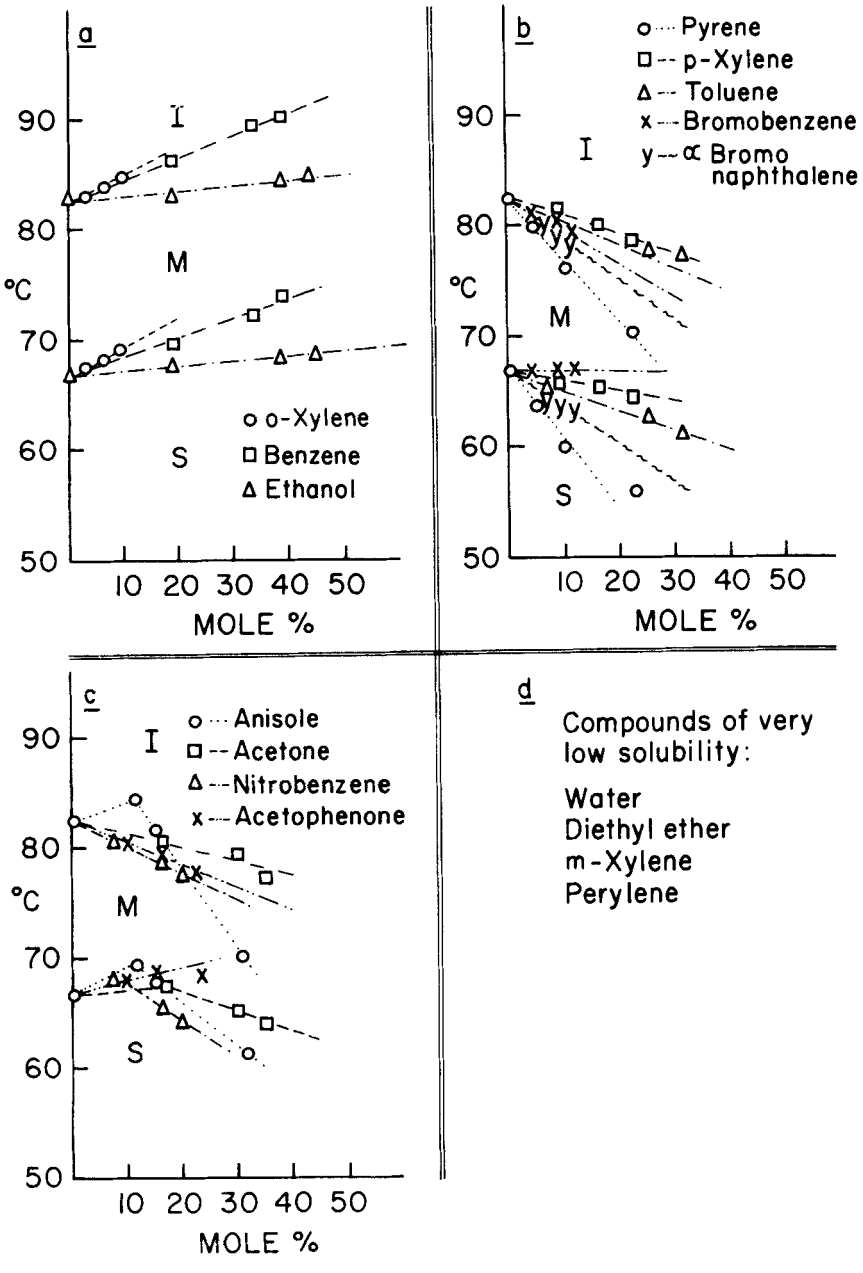

Figure 2. Solute behavior in the 50-50 binary mixture.

doped with S-(4-cyanophenyl)4-(2-methylbutoxy)-thiobenzoate, a nematic liquid crystal of a calculated length of 23.1 Å, the m→i transition is only moderately depressed with dm→i/dc = -20. Finally, when the mixture is doped with 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl-carboxylate, a nematic with a calculated molecular length of 35.0 Å, the m→i transition was observed to have second order characteristics with dm→i/dc ∿ 0. In the last example, the molecular geometries approach those discussed by Alben.[10]

It is clear that the discotic mesophases show strong structural effects with dissolved solutes. Further studies are underway to elucidate the nature of these interactions.

Acknowledgment: This work was supported by the National Science Foundation under Grant No. DMR77-07811.

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