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

Effect of Molecular Structure on Mesomorphism. 13[1] Calorimetry of Smectic A Phase Diagrams Exhibiting Enhancement

Anselm C. Griffin [a] , Neal W. Buckley [a] , Julian F. Johnson [b] & Gail Bertolini [b]

[a] Department of Chemistry, University of Southern Mississippi, Box 8448, Southern Station, Hattiesburg, MS, 39401

[b] Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT, 06268

Version of record first published: 20 Apr 2011.

To cite this article: Anselm C. Griffin , Neal W. Buckley , Julian F. Johnson & Gail Bertolini (1981): Effect of Molecular Structure on Mesomorphism. 13[1] Calorimetry of Smectic A Phase Diagrams Exhibiting Enhancement, Molecular Crystals and Liquid Crystals, 73:1-2, 35-45

To link to this article: http://dx.doi.org/10.1080/00268948108076260

Mol. Cryst. Liq. Cryst., 1981, Vol. 73, pp. 35–45
0026-8941/81/7302–0035 $06.50/0

Printed in the United States of America

Effect of Molecular Structure on Mesomorphism. 13[1] Calorimetry of Smectic A Phase Diagrams Exhibiting Enhancement

ANSELM C. GRIFFIN and NEAL W. BUCKLEY

Department of Chemistry, University of Southern Mississippi, Box 8448, Southern Station, Hattiesburg, MS 39401

and

JULIAN F. JOHNSON and GAIL BERTOLINI

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT 06268

(*Received May 11, 1981*)

Three binary liquid crystal phase diagrams are presented for mixtures exhibiting enhancement of the smectic A-isotropic transition. Both temperature: composition and enthalpy: composition diagrams are given for each mixture. It is found that unambiguous assignment of temperature: composition diagrams are greatly facilitated when enthalpy:composition data is obtained concurrently.

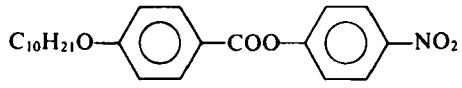
Most binary liquid crystalline (mesomorphic) mixtures exhibit mesophase-isotropic transition temperatures which are approximately linearly dependent on composition. In some cases, however, enhancement (increasing) of the mesophase-isotropic temperature in mixed systems is possible. Part 10[2] of this series discusses some aspects of molecular structure on enhancement and contains extensive bibliographies of previous experimental and/or theoretical investigations of enhanced mesophases.

Most of the reported phase diagrams are based on the determination of the various transition temperatures only, usually by microscopic or thermal measurements. This work reports both temperature:composition and enthalpy: composition phase diagrams.

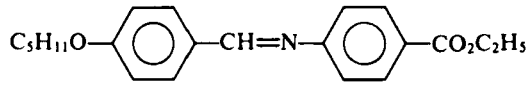
EXPERIMENTAL

There are three binary systems reported here and the compounds in each of these will be referred to as A and B for the first mixed system; C and B for the second system; and for the third system, D and E. These compounds have been described previously.[3]

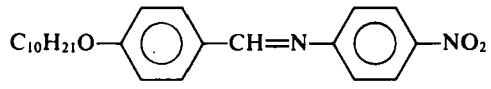
Mixture Components

I 

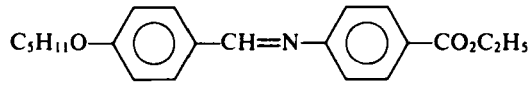
(A)



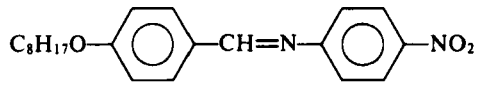
(B)

II 

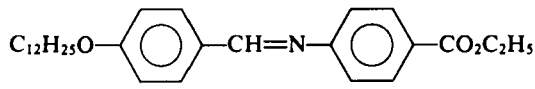
(C)



(B)

III 

(D)



(E)

The thermal analysis was performed using a DuPont Model 990 thermal analyzer with a DuPont DSC cell. A DuPont two-stage mechanical cooler was employed to insure linear cooling rates. The techniques were conventional; heating rates of 1° to 5°/min. were employed. The instrument was calibrated on the temperature scale using a series of pure compounds of known melting points. The calorie scale was calibrated using indium. The center of the peak temperature was read for both the calibration standards and on the thermograms to determine transition temperatures. The areas under the curves were determined by planimetry and in some cases by cutting out and weighing and the calibration factor used to convert this to calories.

The calibration constant to convert results from the DSC cell to calories was determined in duplicate on a weekly basis using a sapphire disc. The calibration constant was calculated at 6 different temperatures between −40° and 150°C. Only a very small drift from week to week was observed.

The thermal history of the samples was kept constant in that after weighing into the hermetic pans and sealing, the pans were stored at room temperature until ready for use. Immediately before the beginning of each run, the sample was placed in the instrument and the instrument was cooled to −45°C and maintained isothermally at this temperature for one hour. The temperature was programmed to at least 15° above the last transition. Not more than one of these measurements was performed on a given sample in a single 24-hour period. At least two reproducible cycle runs, that is from the initial to the final down to the initial up to the final and back to the initial −45° temperature, were obtained for each sample.

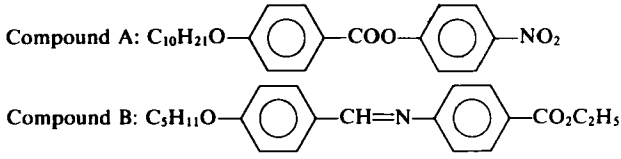
The heats of transition for the samples were obtained using the time base rate selector which controls the X axis of the DuPont 990 recorder. This permitted a more accurate determination of transition heats as the transition curve could easily be enlarged to decrease planimetry area. Again, at least two time base measurements were made for each sample.

In general, the precision of the enthalpy measurements increased as the transition heat became larger. For the smaller transition heats on the average the ΔH values were reproducible to within ±5% or better.

Samples were weighed on a microbalance and were typically two to five milligram samples. During measurements the sample chamber was purged with dry nitrogen. A minimum of two runs per sample and usually three or more

TABLE I

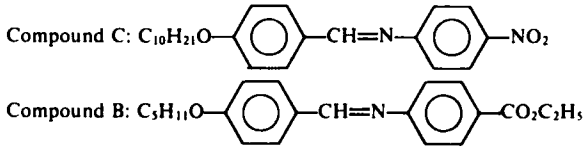
Thermal Data for Binary System I



Composition (mole % B)	Transition Temperatures (°C) and Associated Transition Enthalpies (in parentheses) in cal/avg. mole	Total Heat (cal/avg. mole)
11.8	57.8 (9267), 84.0 (534)	9801
14.7	53.8 (9765), 83.0 (539)	10304
18.8	56.0 (9428), 84.6 (582)	10010
27.5	57.2 (5820), 60.9 (1133), 89.7 (582)	7535
42.0	56.6 (2098), 66.0 (3964), 94.7 (748)	6810
45.2	54.0 (1099), 66.4 (5362), 94.4 (890)	7351
55.7	63.6 (1526), 67.8 (4832), 99.3 (1003)	7361
56.2	60.3 (954), 66.2 (5447), 96.7 (1031)	7432
69.4	64.3 (6260), 100.4 (1159)	7419
75.0	63.2 (6837), 99.2 (1286)	8123
82.5	62.9 (4898), 66.9 (1938), 100.0 (1242)	8078
85.0	60.9 (3866), 66.6 (3337), 97.6 (1341)	8544
0 (cpd. A)	61.4 (10100), 79.4 (560)	10660
100 (cpd. B)	75.0 (7400), 96.6 (1400)	8800

TABLE II

Thermal Data for Binary System II



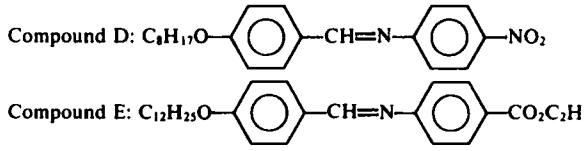
Composition (mole % B)	Transition Temperatures (°C) and Associated Transition Enthalpies (in parentheses) in cal/avg. mole	Total Heat (cal/avg. mole)
16.2	43.6 (1287), 52.9 (5330), 59.0 (uncertain), 96.8 (548)	7165
23.8	44.3 (2968), 50.0 (4543), 54.4 (264), 97.5 (566)	8341
39.8	44.5 (7161), 98.7 (643)	7804
53.5	43.8, 47.1 (7151), 100.6 (866)	8017
66.1	43.6 (4850), 56.2 (2068), 100.6 (963)	7881
83.9	42.8 (2123), 67.8 (4676), 100.3 (1233)	8032
0 (cpd. C)	63.3 (9820), 95.3 (620)	10440
100 (cpd.B)	75.0 (7400), 96.6 (1400)	8800

were made and the results averaged to give the values shown in Tables I, II, and III.

The identification of the phase types was performed by polarized light microscopy using a Reichert Thermovar polarizing microscope along with a Mettler FP5/52 microfurnace. The phase types were identified by optical textures using a contact preparation of two pure materials, one a standard reference.

TABLE III

Thermal Data for Binary System III



Composition (mole % E)	Transition Temperatures (°C) and Associated Transition Enthalpies (in parentheses) in cal/avg. mole	Total Heat (cal/avg. mole)
9.4	59.6 (696), 89.3 (7427), 93.6 (471)	8594
27.0	60.0 (2855), 83.4 (5129), 103.4 (807)	8791
41.7	60.3 (3544), 78.2 (5213), 108.0 (1066)	9823
52.6	61.4 (6808), 71.7 (1995), 109.7 (1290)	10093
69.1	61.2 (8775), 110.4 (1516)	10291
86.0	60.1 (3302), 67.2 (5284), 105.7 (1666)	10252
0 (cpd. D)	92.2 (10700), 85.9 (200), 83.5 (140)	10700
100 (cpd. E)	71.5 (10500), 99.0 (1610)	12110

In the enthalpy:composition diagrams for these mixtures the enthalpy is given in units of calories per average mole. The 'average mole' is calculated in the following manner:

Average mole = (mole % component 1) * (molecular weight of component 1) + (mole % component 2) * (molecular weight of component 2)

This has been described earlier[3] and is we feel a quantity more closely related to molecular properties than is the conventional calories per gram.

DISCUSSION

Figure 1 is a plot of the temperature of transition versus composition for binary mixture I, Figure 2 is a plot of the heats of transition versus composition, again for binary mixture I.

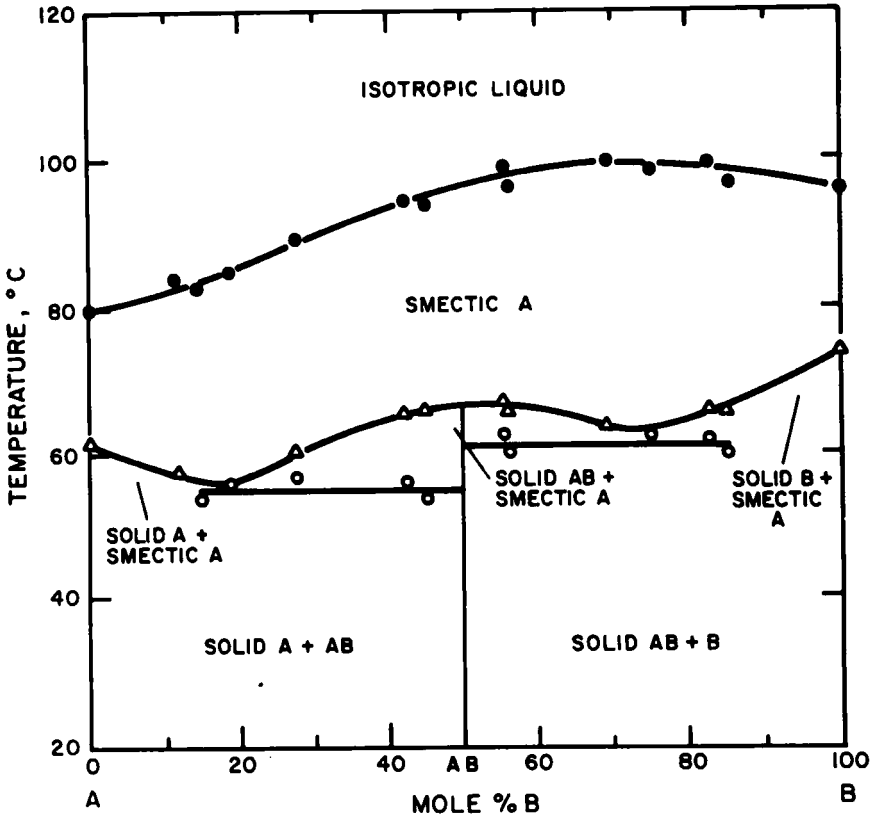


FIGURE 1 Temperature:composition phase diagram for Mixture I.

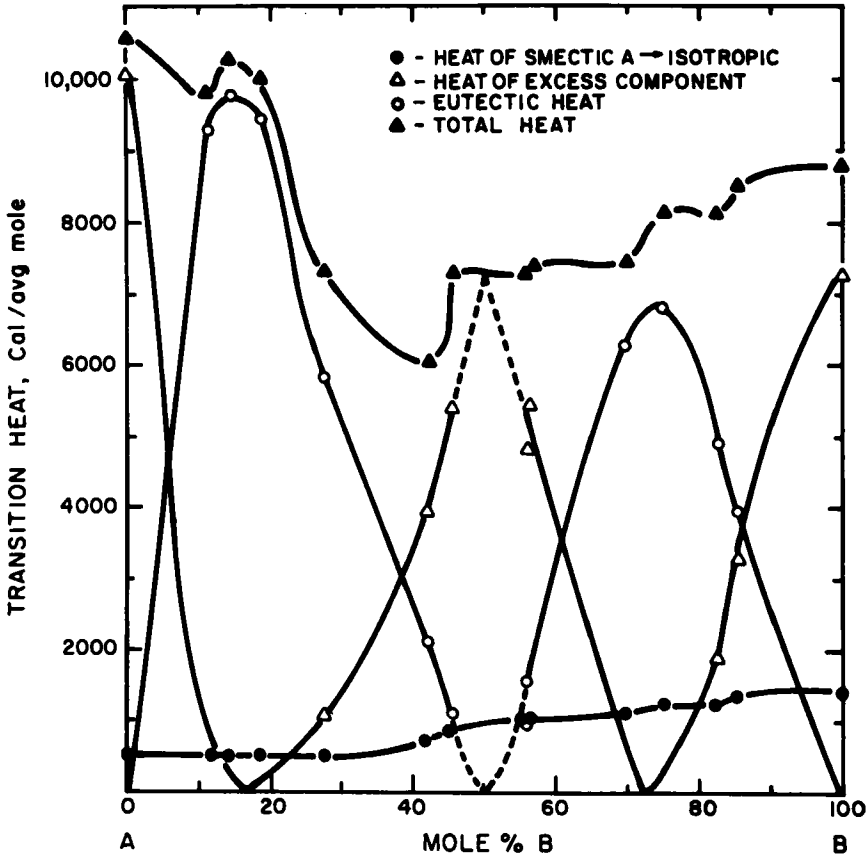


FIGURE 2 Enthalpy:composition diagram for Mixture I.

The binary phase diagram for mixture I is seen in Figure 1. This mixture clearly exhibits compound formation in the solid state with concommitant double eutectic behavior. A maximum in the melting curve of the addition compound occurs at or about 50:50 mole percent composition. Smectic A is the only mesophase seen in this mixture and the $S_A \rightarrow I$ temperature is mildly enhanced. The enthalpy: composition diagram, Figure 2, reveals conclusively the double eutectic and shows an irregularly shaped total heat curve.

Referring to Figure 3, the phase diagram for mixture II is of the simple eutectic type. The only mesophase is a clearly identifiable smectic A. However, below about 40 mole % of B there is a narrow region composed of an unidentified phase. Importantly, the smectic A to isotropic liquid transition shows a distinct maximum indicating enhancement. The transition heat data empha-

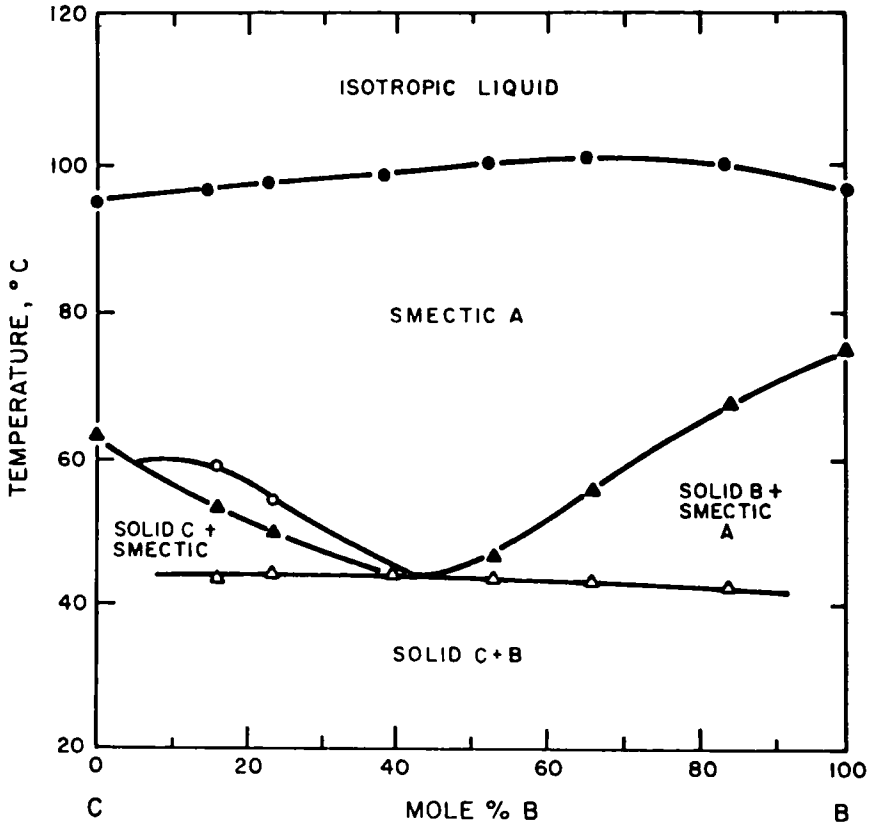


FIGURE 3 Temperature:composition phase diagram for Mixture II.

size the presence of the eutectic at about 40 mole % B, and include a small, but we believe real, local maximum in the total heat as shown in Figure 4.

The same information for binary system III, that is transition temperature and ΔH as functions of composition, are shown in Figures 5 and 6, respectively. The temperature phase diagram is again of the simple eutectic type with a smectic A composition. Compound D does not exhibit a mesophase in the pure state on heating; on cooling it shows monotropic nematic and smectic A phases. The diagram shows a marked enhancement for the smectic A to isotropic liquid transition. The transition heats again show the eutectic behavior with the total heats apparently exhibiting one maximum and two minima. There is no ready explanation at the moment for this behavior. An important consideration in Figure 5 is that the smectic A-isotropic enhancement is produced by the nonmesomorphic component. The nitro containing Schiff's base

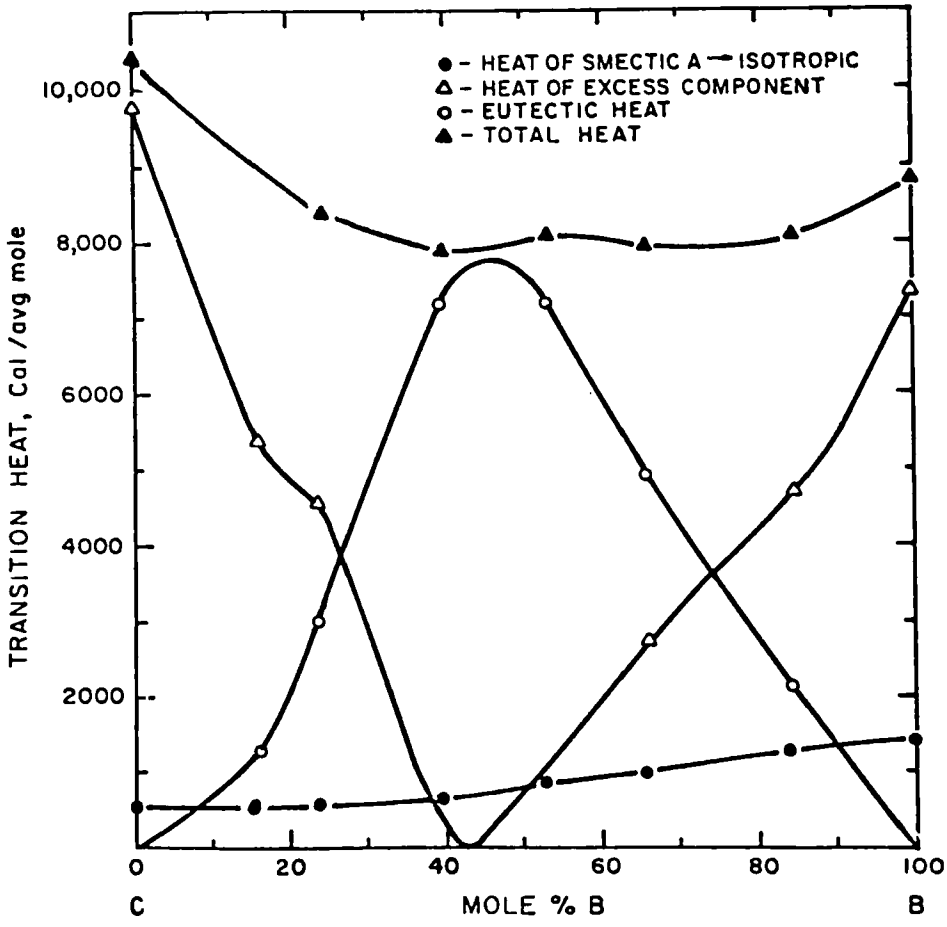


FIGURE 4 Enthalpy:composition diagram for Mixture II.

compound is the one promoting the enhanced phase when it itself has no enantiotropic mesophase. This is reminiscent of some earlier work by Schroeder and Schroeder on similar mixtures.[4] The eutectic composition for binary system III appears to be very close to a two-to-one molar ratio, two parts of component E, one part component D whereas the complex composition in binary system I appears to be very close to a one-to-one molar ratio of the pure components. The phase transitions in all drawings are shown as occurring at a single temperature. In reality as is well known, the phases must co-exist over a short spindle region. The thermal, DSC, method detects only one transition because the temperature range of the spindle is relatively narrow.[5] Optically the co-existence of two phases is observed but it is difficult to assign tempera-

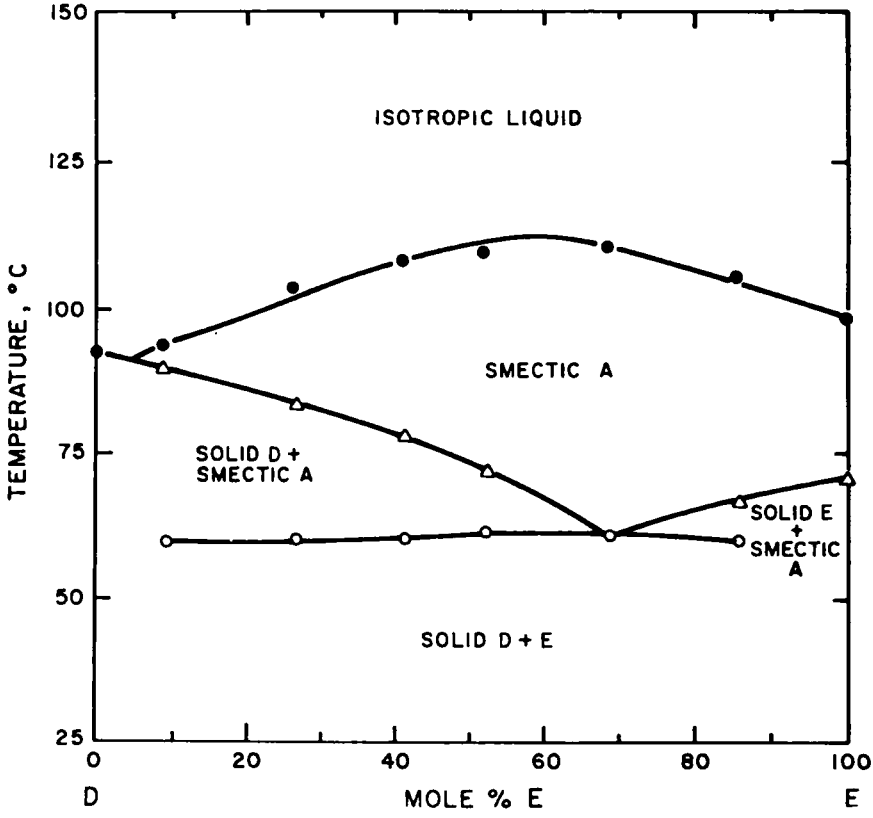


FIGURE 5 Temperature:composition phase diagram for Mixture III.

ture precisely enough to warrant drawing the transitions as a spindle rather than as a single curve.

It is clear from this data that use of enthalpy: composition diagrams in conjunction with optical characterization to determine binary phase diagrams is attractive due to the ease in following enthalpy curves to determine transitions involving solid phases which are often difficult to unambiguously characterize with only optical data at hand. For example it is difficult to describe with confidence the phase diagram in mixture I without the enthalpy: composition curves which fully support the claim of molecular compound formation.

The fact that the solid phase behavior can be drastically different in mixtures differing only slightly in component structure is evident in comparing mixtures I and II. Both mixtures contain component B as a one component. In spite of the fact that both component A (mixture I) and component C (mixture II) are nitro containing decyloxy phenyl ethers, the imine (Schiff's base) linkage connecting the aromatic rings leads to simple eutectic behavior (mixture

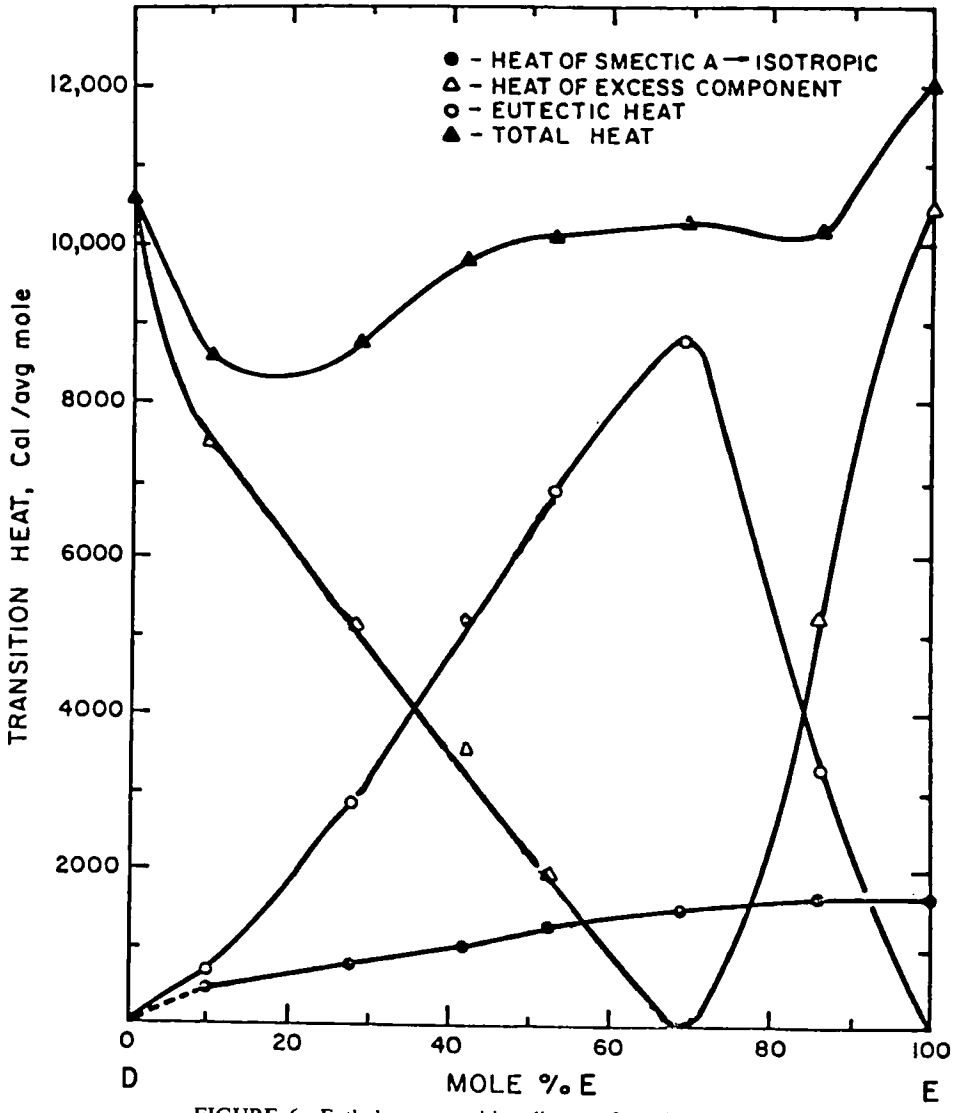


FIGURE 6 Enthalpy:composition diagram for Mixture III.

II) whereas the ester linkage (mixture I) in an otherwise identical molecule leads to formation of a molecular compound and totally different solid phase behavior.

Acknowledgments

This work was supported in part by a grant from the National Science Foundation (DMR 7805284). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References

1. For part 12 in this series see A. C. Griffin and T. R. Britt, *J. Am. Chem. Soc.*, accepted for publication.
2. A. C. Griffin, N. W. Buckley, S. J. Havens, J. F. Johnson, G. J. Bertolini and L. Thomas in 'The Physics and Chemistry of Liquid Crystal Devices', G. J. Sprokel, ed., Plenum Press, NY, NY, 1980, p. 305.
3. R. J. Cox, J. F. Johnson and A. C. Griffin, *Mol. Cryst. Liquid Cryst.*, in press.
4. J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).
5. R. J. Cox and J. F. Johnson, *IBM J. Res. Develop.*, **22**, 51 (1978).