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Phase Diagrams of Binary Nematic Mesophase Systems II

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Phase Diagrams of Binary Nematic Mesophase Systems. II.†

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Temperatures and heats of transition are presented for two binary nematic mesophases: *p*-azoxyanisole plus *p*-anisalazine, and *p*-azoxyphenetole plus *p*-anisalazine. Temperatures of transition are also given for three additional binary mesophase systems: *p*-azoxyanisole plus *p*-[(*p*-methoxybenzylidene)amino]phenyl acetate, N-(ethoxybenzylidene)-*p*-butylaniline and *p,p'*-di-*n*-heptyloxyazoxybenzene. The phase diagrams are of the simple eutectic type with the formation of ideal comesophase solutions permitting prediction of the eutectic composition and temperature. The heats of transitions can be estimated with reasonable accuracy.

INTRODUCTION

Extensive studies of temperatures and heats of transition, specific heats and entropies have been reported for individual mesophase or liquid crystal compounds (see for example Ref. 1). Relatively few studies of similar studies on binary mesophase systems have appeared. A comprehensive review article for binary mesophase systems has been made.[2] This work reports both temperatures and heats of transition for two binary systems and temperatures of transition for three binary mesophase systems.

† Part XXXVII of a series "Order and Flow in Mesophases".

EXPERIMENTAL

The compounds studied were: (1) *p*-azoxyanisole (PAA), $CH_3O-C_6H_4-N=N(\rightarrow O)-C_6H_4-OCH_3$; (2) *p*-azoxyphenetole (PAP), $C_2H_5O-C_6H_4-N=N(\rightarrow O)-C_6H_4-OC_2H_5$; (3) *p*-anisalazine (AAA), $CH_3O-C_6H_4-CH=N-N=CH-C_6H_4-OCH_3$; (4) *p*-[(*p*-methoxybenzylidene)amino] phenyl acetate (MBAPA), $CH_3O-C_6H_4-CH=N-C_6H_4-OCCH_3$ (O); (5) N-(*p*-ethoxybenzylidene)-*p*-butyaniline (EBBA), $C_2H_5O-C_6H_4-CH=N-C_6H_4-C_4H_9$; and (6) *p,p'*-di-*n*-heptyloxyazoxybenzene (DHpAB), $C_7H_{15}O-C_6H_4-N=N(\rightarrow O)-C_6H_4-OC_7H_{15}$.

Compounds 1 through 5 are all nematic and compound 6 is both smectic and nematic, see Table I. Compounds 1, 2, 3, 4 and 6 were obtained from Eastman Organic Chemicals (Rochester, New York). Compound 5 was obtained from Vari-Light Corp. (Cincinnati, Ohio).

PAA, PAP, AAA, MBAPA and DHpAB were recrystallized three times from absolute ethanol. After solvent recrystallization PPA, PAP and DHpAB were further purified by zone refining, EBBA was used as received. The purification and purity determination techniques have been described in detail elsewhere.[3]

Phase transition temperatures and heats were measured by use of DTA and DSC techniques. The techniques have been described in Ref. 3.

RESULTS AND DISCUSSION

The temperature-composition phase diagrams of five binary systems are shown in Figures 1 through 5. All phase diagrams were of "the simple eutectic" type as described in Ref. 3. The area below the tie line at the eutectic temperature consisted of a mechanical mixture of the two pure components or the two terminal solid solutions which probably contain only a small amount of the second component. From the available data, the compositions of the terminal solid solutions can not be estimated. If the terminal solid solutions exist in each system, the compositions apparently have $< 5\%$ of the minor component.

Above the eutectic temperature and below the liquidus curves there are two phase regions with solid crystalline material in equilibrium with the nematic mesophase, Figures 1 through 4. Above the liquidus curves a single nematic comesophase exists until the transition temperature to the isotropic liquid is reached.

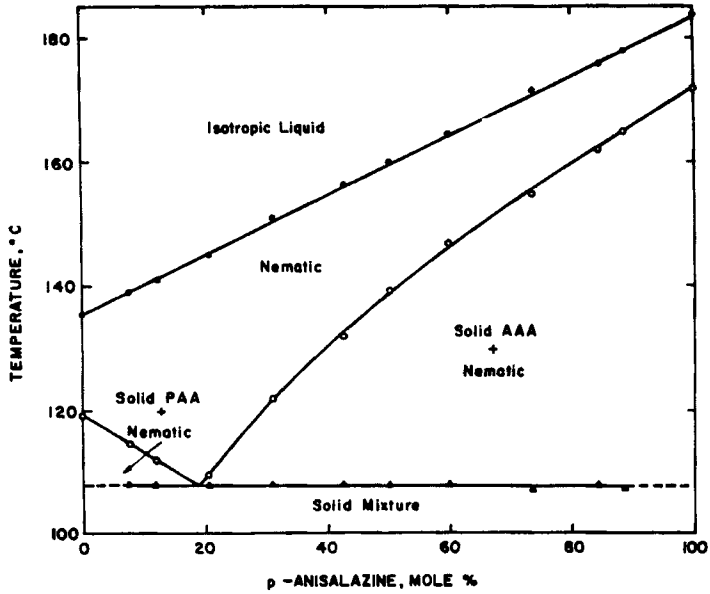

FIGURE 1 Phase diagram of *p*-azoxyanisole – *p*-anisalazine systems.

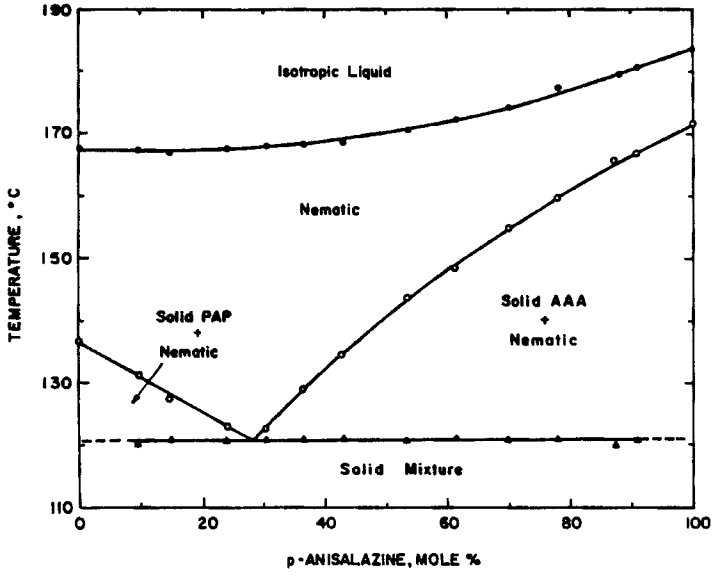

FIGURE 2 Phase diagram of *p*-azoxyphenetole – *p*-anisalazine system.

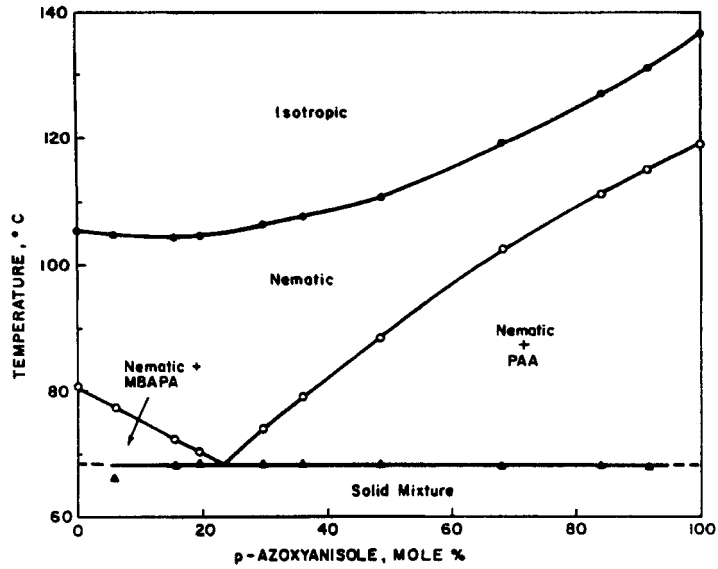

FIGURE 3 Phase diagram of *p*-azoxyanisole – *p*-[(*p*-methoxybenzylidene)-amino]phenyl acetate system.

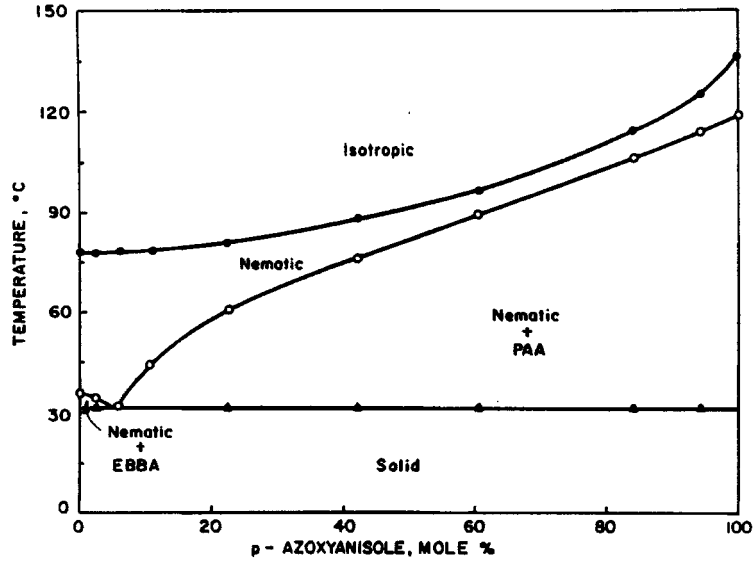

FIGURE 4 Phase diagram of *p*-azoxyanisole – N-(*p*-ethoxybenzylidene)-*p*-butylaniline system.

For the system PAA-DHpAB (see Figure 5), a eutectic occured at 67.5° C and 81 mole% DHpAB. The phase transition in the left side of the eutectic is similar to the systems in which both components are the nematogenic compounds. The phase regions in the right side of the eutectic, however, are more complicated. There are four transitions at the high concentration side of DHpAB (80 to 100 mole%): (a) transition from the crystalline solid mixture to a two phase region, the smectic mesophase and excess pure DHpAB solid, (b) transition from the two phase region to the smectic mesophase, (c) transition from the smectic mesophase to the nematic mesophase, and (d) transition of the nematic mesophase to an isotropic liquid. The phase transitions between the eutectic composition and 88 mole% DHpAB are proposed to be the same as those in the left side of the eutectic. The smectic-nematic transition temperatures lie on a sharply falling curve which merges with the liquidus curve at 88 mole% DHpAB and 69.5°C. This indicates that the layer structure of the smectic mesophase is broken into the nematic structure as the concentration of PAA increases. Figure 5 also indicates that the nematic mesophase and smectic mesophase are not continuously miscible.

The nature of all phase diagrams investigated in this study was examined by use of the Schröder-von Laar equations.[3] A comparison of calculated and measured results shows excellent agreement.

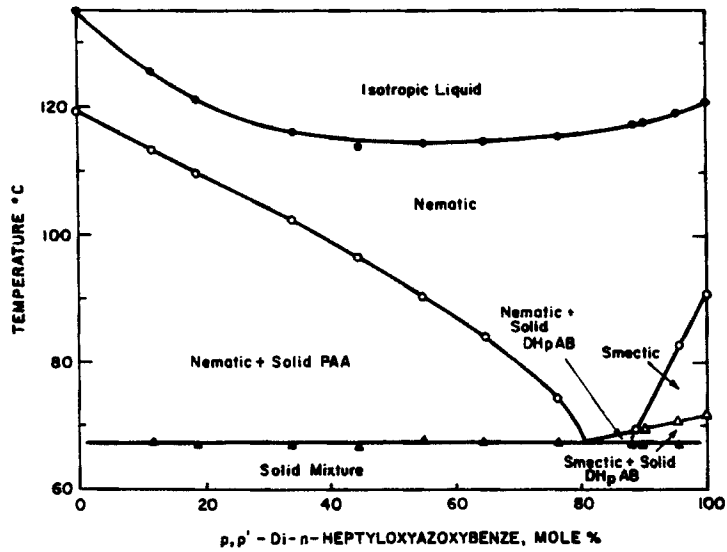

FIGURE 5 Phase diagram of *p*-azoxyanisole – *p,p'*-di-*n*-heptyloxyazoxybenzene system.

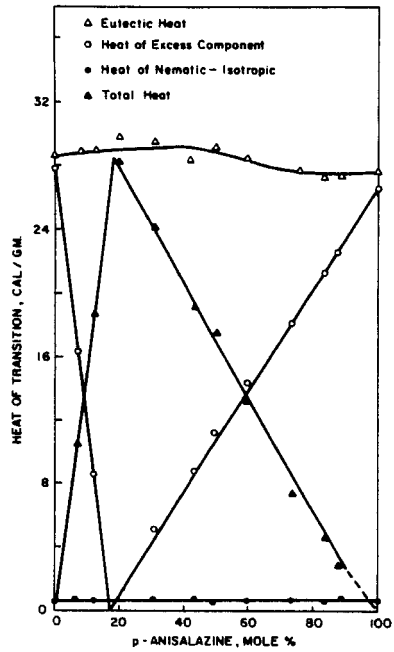

FIGURE 6 Transition heats of *p*-azoxyanisole – *p*-anisalazine system.

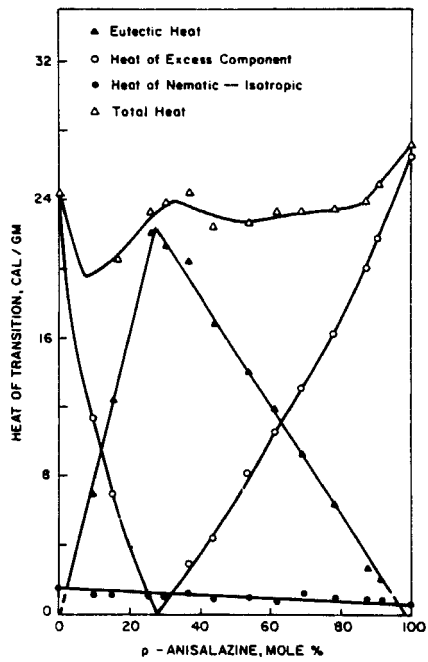

FIGURE 7 Transition heats of *p*-azoxyphenetole – *p*-anisalazine system.

Figures 6 and 7 show the heat-composition phase diagrams for the systems PAA-AAA and PAP-AAA. The behavior of these phase diagrams is similar to that described in Ref. 3.

References

1. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals* Academic Press, Inc., New York, 1962.
2. Hsu, E. C-H., Haberfeld, J. L. and Johnson, J. F., to be published.
3. Hsu, E. C-H., and Johnson, J. F., *Mol. Cryst. Liq. Cryst.*, 20 177 (1973).