EFFECT OF MOLECULAR STRUCTURE ON MESOMORPHISM. 6. NON-LINEAR

THERMAL BEHAVIOR IN SOME BINARY LIQUID CRYSTAL SYSTEMS

Anselm C. Griffin, Thomas R. Britt, Neal W. Buckley, Richard F. Fisher, Stephen J. Havens

Department of Chemistry, University of Southern Mississippi; Hattiesburg, Mississippi 39401 U.S.A.

and

D. Wayne Goodman

National Bureau of Standards
Gaithersburg, Maryland 20760 U.S.A.

Most binary mesophase systems exhibit mesophase-isotropic transition temperatures which are linearly dependent on composition. There are however exceptions. Demus (1) reported non-linear behavior for some mixtures when one component was a chloro mesogen. Dave (2) found similar behavior with chloro and nitro liquid crystals and postulated a structural rationale based on dipolar characteristics of the constituent molecules. Schroeder and Schroeder (3) reported in 1968 that non-mesomorphic nitro-terminated anils enhanced (4) the smectic phase of di-n-hexyloxazoxybenzene. These authors suggested a loose dimeric association of the nitro anils as part of a molecular explanation for this enhanced smectic phase.

In more recent times Labes (5,6) and Oh (7) have found that cyano-terminated liquid crystals are often successful in promoting enhanced mesomorphic behavior in mixed liquid crystals. Labes (5,6) favors a charge transfer interaction as the reason for such non-ideal solution behavior while Oh (7) prefers a lamellar structure of constituent molecules. One of us (8) has recently studied 4-nitrophenyl 4'-decyloxybenzoate by x-ray diffraction and postulated an explanation for the non-linear behavior of mixtures containing the compound based on the bimolecular smectic structure (9) of this nitro
ester. The alkyl cyanobiphenyls studied by Labes (5,6) and Oh (7) also have bimolecular smectic phases. The purpose of this work was to further probe the relationship between smectic layer structure and non-linear thermal behavior in binary mesophase systems.

In order to test this theory (8) we decided to use four mesogens; x-ray data for each of them has been previously reported. We chose two unimolecular smectogens ("unimolecular" in the sense that the x-ray spacing \( d \) is equal to or less than the measured extended molecular length, \( l \)); and two bimolecular smectogens ("bimolecular" in the sense that \( d \) is greater than \( l \)). Compounds 1 and 3 have unimolecular smectics; compounds 2 and 4 have bimolecular smectics. Values for \( d \) and \( l \) are shown below in Figure 1 along with structures for these compounds. It was intended to form binary systems by admixture of each of these aforementioned compounds with three compounds which themselves differ only in the electronic nature of one terminal group. In this way it was possible to examine both the effect of smectic layer arrangement and also the electronic effects of terminal groups on non-linear thermal behavior of binary mesophases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>( d (\text{\AA}) )</th>
<th>( l (\text{\AA}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{C}_4\text{H}_9\text{O} - \text{O} - \text{CH=N} - \text{O} - \text{C}_2\text{H}_5 )</td>
<td>17.3</td>
<td>21.5</td>
</tr>
<tr>
<td>2</td>
<td>( \text{C}<em>6\text{H}</em>{17}\text{O} - \text{O} - \text{O} - \text{CN} )</td>
<td>31</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>( \text{C}_2\text{H}_5\text{O} - \text{O} - \text{CH=N} - \text{O} - \text{CO}_2\text{C}_2\text{H}_5 )</td>
<td>19.9</td>
<td>21.3</td>
</tr>
<tr>
<td>4</td>
<td>( \text{C}<em>{10}\text{H}</em>{21}\text{O} - \text{O} - \text{COO} - \text{O} - \text{NO}_2 )</td>
<td>31.4</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Figure 1. The four smectogens used in phase studies along with x-ray \( d \) values and molecular lengths \( l \) as measured from Dreiding stereomodels.
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EXPERIMENTAL

Synthesis:

Compounds 1 and 3 were obtained by reacting equimolar quantities of the appropriate aldehyde and aniline in absolute ethanol. The reaction solution was stirred at room temperature for 16 hours and then cooled at 0° in an ice-water mixture. The resulting solid was collected by vacuum filtration and crystallized from absolute ethanol to constant transition temperatures. Agreement with literature data when available was excellent. Compound 2 was obtained as a gift from Dr. Robert Cox, IBM, San Jose, CA, and was used as received. Compound 4 has been previously reported by us (8). Compounds A, B, and C were synthesized using the method described above for the preparation of 1 and 3. The homologous series of ethyl 4-n-alkoxybenzylidene-4′-aminobenzoates (10) were synthesized as 1 and 3. Our transition temperatures are very close to those in the literature (10) and are the temperatures used in calculations described later.

Mixture Preparation:

Binary mixtures were prepared by the Kofler contact procedure (11) and phase diagrams were constructed by polarized light microscopy of these mixtures using a hot stage. It should be noted that 50:50 mole percent compositions were examined for the phase diagrams to insure a degree of accuracy for the composition coordinate. For evaluation of the effect of alkoxy chain length, mixtures were examined in two ways: (1) by packing one component in a glass melting point capillary tube; fusing; then packing the second component on top of the first. Enhanced mesophases were observed at the interface of the two components in a Thomas-Hoover melting point apparatus (2) by conventional microscopy to determine the type of liquid crystal phase which is enhanced. Regions of mixed composition were seen in the phase diagrams, but were not included in the diagrams in an effort to facilitate readability.

RESULTS AND DISCUSSION

Mixtures of A:

The four phase diagrams for binary mixtures of compound A with compounds 1-4 are shown below in figure 2.

Compound A itself exhibits only an enantiotropic smectic A phase, K59959I. We find that mixtures of A with compounds 1 and 3 (hereafter referred to as A-1 and A-3, respectively) exhibit marked non-linearity in the mesophase-isotropic transition temperatures as one scans the composition coordinate. Mixture A-1 shows an enhanced
nematic phase in the region of 50:50 mole percent composition, some 28° above the N-I temperature of the only nematogenic component, 1. There is also definite non-linearity in the S-N temperatures in the region of the diagram near pure 1. Mixture A-3 also shows a mixture-induced nematic phase of higher N-I temperature than either pure component even when neither pure component is enantiotropically nematogenic.

Mixtures of A with compounds 2 and 4, the bimolecular smectics, on the other hand, show ideal solution behavior. In summary, compound A exhibits non-linear behavior with unimolecular smectics and linear behavior with bimolecular smectics.
MIXTURES OF B:

Compound B is a most unusual smectogen. It has an enantiotropic smectic phase, K66577.5I. Gray (12) has recently reported an analogous compound, 4-n-hexyloxybenzylidene-4'-trifluoromethylaniline, and found it to possess no mesophase. We (13) have, however, prepared numerous members of this homologous series including the hexyloxy member and found them to be smectogenic. Evidence for a smectic phase and other data for these compounds will be reported in the near future. Although this smectic phase does flow it is extremely viscous. It exhibits a most intriguing variety of microscopic textures (mosaic, homeotropic, and rodlike). We are here describing this smectic as $S_2$ due to our current uncertainty as to its appropriate smectic classification.

In mixtures with compounds 1 and 3, compound B promotes and enhances an enantiotropic smectic A ($S_1$) mesophase, even in mixtures with compounds which themselves do not possess an enantiotropic $S_1$ phase. The usual linear behavior is found for mixtures B-2 and B-4. For compound B we find non-linear behavior with unimolecular smectics and linear behavior with bimolecular smectics.

MIXTURES OF C:

Compound C has both enantiotropic smectic and nematic phases, K66575N771. Behavior of C in binary mixtures is completely the reverse of that of compounds A and B in mixtures. Mixtures C-2 and C-3 show non-linear, non-ideal thermal behavior exhibiting $S_1$ phases having enhanced $S_1$ transition temperatures. In mixtures C-1 and C-3 one finds ideal, linear behavior. Thus for mixtures of compound C with unimolecular smectics we find linear thermal behavior; for mixtures of C with bimolecular smectics we find non-linear thermal behavior.

From observation of these phase diagrams two points are prominent:

1. A relationship exists between smectic layering of constituent molecules and non-linear thermal behavior in binary liquid crystal systems.
2. The molecular explanation for observation (1) lies in an electronic phenomenon not a geometric one. This is apparent as the only structural difference in molecules A, B, and C is in the nature of one small, terminal substituent.

The first point is obvious from a general examination of the three sets of phase diagrams. We feel that non-linear behavior (which arises when $Y-Z$ interactions are significantly different from interactions between the pure components $Y-Y$ and $Z-Z$) is to be anticipated when smectics of different layering arrangements are mixed. From this postulate we predict that compounds A and B will exhibit x-ray photographs in which $d$ is greater than 1, i.e. a bimolecular smectic. Likewise we predict C to have a $d$ less than 1, i.e. a unimolecular smectic phase.
Figure 3. Set of phase diagrams for binary mixtures of B. Compounds 1 and 3 are unimolecular smectics; compounds 2 and 4 are bimolecular smectics.

From a consideration of terminal groups which promote non-linear thermal behavior, -CN, -NO₂, and -CF₃; we believe that it is the electron-withdrawing effect of these substituents which is responsible for this behavior. Bimolecular smectics are we feel a result of molecular complex formation (14,15) in the pure components. The analogy with Neubert's domino model (16) for nematics is noted. As an extension of this model, we feel that for the cyano and nitro compounds 2 and 4, the most satisfactory model is a bimolecular one such as that shown schematically below in figure 5. Cladis et al. (17) have recently proposed a similar model to account for re-entrant nematic phases. It should be noted that the driving force for molecular association in our model is \pi-molecular complexation, whereas they favor attraction between hydrocarbon chains as the dominant factor.
The schematic is proposed to explain the unusual d-spacings in compounds 2 and 4. It also provides a molecular rationale consistent with the electronic character of cyan and nitro groups and with Labes'(6) finding that donors such as p-aminobiphenyl (no hydrocarbon chain) can promote non-linear thermal behavior in mixed systems.

Binary mesophase systems in which a bimolecular smectic is mixed with one which significantly perturbs the molecular complexing of the pure bimolecular smectic will, we predict, exhibit non-linear thermal behavior, i.e. (non-ideal solution behavior). An example of such perturbation would be found in the addition of compounds (solute) with electron rich aromatic rings which can successfully compete for molecular complexation with an electron deficient ring of a solvent molecule. Thus Y-Z interactions are considerably different than Y-Y or Z-Z interactions, or the concentration weighted
sum of Y-Y + Z-Z interactions. Indeed in such cases, system A-1 as an example, non-linear thermal behavior is found. Likewise one should expect that compounds with similar smectic layering characteristics, i.e., 2 and 4, should when mixed with each other exhibit thermal behavior which is linear with concentration. This is experimentally found to be the case (18).

We have also examined the effect of alkoxy chain length as it relates to enhancement of the smectic A phase in mixtures. Figure 6 allows a comparison of trifluoromethyl and nitro as terminal groups in elevating the \( S_{A} \rightarrow I \) temperature in binary mesophases since the only difference in the molecules is in the terminal group. The alkoxy chain length of a homologous series of ethyl 4-n-alkoxybenzylidene-4'-aminobenzoates (10) is plotted against maximum mesophase-to-isotropic transition temperatures when the homologues are each mixed separately with both the trifluoromethyl and nitro compounds. These plotted temperatures represent values which are higher than mesophase-isotropic temperatures of either pure component and are the direct result of mixing the two components. It is easily seen that alkoxy chain length does have a significant influence on the \( S_{A} \rightarrow I \) temperature. It is a perturbation on a larger theme. The effect is different for the two types of terminal groups, nitro and trifluoromethyl. For the nitro compound one finds nematic behavior until the alkoxy chain length reaches five carbons while the trifluoromethyl compound exhibits smectic behavior even at low carbon chain number. In addition the curves differ radically as chain length is increased.
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\[ C_{10}H_{21}O\(\text{CF}_3 \)CH=\text{N}\(\text{CF}_3 \) \]
\[ C_{10}H_{21}O\(\text{NO}_2 \)CH=\text{N}\(\text{NO}_2 \) \]

![Graph showing the effect of molecular structure on mesomorphism](image)

Figure 6. Comparison of effectiveness of trifluoromethyl and nitro as terminal groups in elevating the \( S_A^{+}I \) temperature in binary mesophase systems.

Using figure 7 below a comparison between ester vs Schiff's base linkages is possible. Again we have used a common homologous series to probe the differences. The two curves are remarkably similar indicating that the alkoxy chain length exerts a similar effect for both molecules being compared. Transition from enhanced nematic to enhanced smectic behavior occurs at identical carbon number. In both cases the maximum \( S_A^{+}I \) occurs at an alkoxy chain length of ten carbons, an identical alkoxy length to that of the two nitro compounds being compared. The even-odd alternation is reminiscent of such alternation in stability constants for charge-transfer complexes of fluoranil: n-alkylbenzene mixtures (19).

Figure 8 below shows data for comparison of ester vs. Schiff's base linkage in terms of the degree of enhancement of the \( S_A^{+}I \) temperature. For this comparison we have taken the mean of the \( S_A^{+}I \)
temperatures for each of the two pure components and subtracted this value from the observed $S_A$ maximum as indicated in the previous figure. We have found that the stoichiometry of maximum $S_A$ temperature is 50:50 mole percent for these systems. Thus, we are justified in using the mean as described above.

This is similar in principle to the Job plot (20) used in molecular complex chemistry. The mean value described above yields a number which would be expected if one encountered ideal solution behavior, i.e. a linear variation of thermal behavior with composition. The numbers plotted in the figure above ($\Delta T$) represent the degree of non-linearity of the mixture. The curves are strikingly similar in shape with the ester curve lying above the Schiff's base curve; both curves maximizing at an alkoxy chain length of about ten carbon atoms. One possible explanation for the fact that the ester curve is above the Schiff's base curve is that the molecules comprising the ester mesophase are more available for intermolecular charge transfer interactions than Schiff's base molecules due to the less efficient intramolecular charge transfer interaction in

Figure 7. Comparison of ester vs. anil linkage in elevating $S_A$ temperature in binary mesophase systems.
the ester molecules. Intramolecular charge transfer interactions should reduce the inherent Lewis acidity and basicity of aromatic rings within the same molecule due to conjugative interactions between the rings. As the Schiff's base molecules are more efficiently π-conjugated than the esters, they will not participate to as great an extent in an intermolecular complex; thus, the lower curve for the Schiff's bases. Although an increase in dipolar character should result from an intramolecular charge transfer interaction, it is apparently of less consequence than the stabilization due to molecular complex formation.

It should be noted that arguments concerning structure-property relationships in the mesophase based on temperatures alone are to be used with the utmost caution. Calorimetric studies, in which one obtains the quantities ΔH and ΔS for these transitions, are in progress.
REFERENCES


9. The term "bimolecular smectic" is used to describe a molecular arrangement in which d>δ. It is our feeling that "bimolecular" used to describe one smectic layer in which two molecules must participate, is preferable to "bilayered" smectic which might be interpreted as two layers.


13. A. C. Griffin and N. W. Buckley, to be published.


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18. A. C. Griffin, unpublished work.

