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RELATIONSHIPS BETWEEN MISCIBILITY GROUPING AND SMECTIC MESOPHASE STRUCTURE

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Abstract:

Classification of smectic liquid crystal mesophases has been based on the concept of comiscibility between like phases. Based on thermodynamic principles this categorization scheme is not related directly to the structures of the phases. The elucidation of the structures of the various smectic modifications has shown that each miscibility group possesses a set of structural parameters common to all examples of that group. Also present are structural factors which form subsets of the miscibility group. These two sets of structural characteristics are defined for each miscibility group.

INTRODUCTION:

The concept of classification by comiscibility of like smectic phases was first introduced by Sackmann and Demus in 1966.[1] It has been, for the most part, a very successful method of identifying smectic modifications. However, as more structural studies are undertaken and new phases defined, classification by microscopy methods has become difficult, even for experienced observers. This has led to many misnomers and misunderstandings concerning the true relationships between phase structure and miscibility groupings.

Over recent years detailed investigations have been slowly clarifying which structural features define a miscibility group.[2–6] These properties can be termed the *primary* structural parameters. *Secondary* structural parameters also exist, but these do not define separate miscibility groups but rather subsets of that group, for example, the helical arrangements in optically active smectic systems such as S_C^* (see later).

In the following sections these primary and secondary parameters will be defined and used to distinguish between the various miscibility groups.

DISCUSSION:

The concept of miscibility is based on thermodynamic principles and sequencing of smectic mesophases.[1] The thermodynamic ordering of smectic phases was relatively simple until the recent discovery of the new smectic phases I,F,J,(G′),K(H′) and hexatic B.

The present list is therefore complicated by the fact that certain phase sequences have not yet been established in pure materials. From the current information the following tabulation can be made:

Iso Liq –A–D–C– B hex –I–B cryst –F–J–G–E–K–H–crystal

This thermodynamic sequencing is obviously not based on structural ordering, i.e., as the groups are descended from left to right they do not necessarily become more ordered on approaching the crystalline state. For example, the hexatic smectic F phase occurs below the crystal B phase on cooling. This is observed for the material N-(4′-n-pentyloxybenzylidene)-4-n-hexylaniline (50.6) which possesses a A-C-B cryst-F-G phase sequence.[7]

When the thermodynamic phase sequencing is coupled to miscibility studies the resulting combination becomes a very powerful tool in phase classification. These united principles, rather than structural studies, have been responsible for the majority of discoveries of new miscibility groups and their introduction into the general classification scheme.

However, it can be argued that like phases which are comiscible should also possess identical primary structural parameters in order for comiscibility to occur. Thus, phases of similar structures should be comiscible and therefore share a common group letter. Structural investigations have provided a description of each of the phases, and therefore the problem is reduced to one in which the primary parameters have to be defined in order to describe the separate miscibility groups.

However, an important distinction must be drawn first between the more ordered (crystal) and the more fluid (liquid crystal) phases.[8] Many structural investigations are now revealing true long range positional ordering of the molecules in the more ordered mesophases. The temptation has been to describe these phases as crystalline in nature. However, in x-ray studies of these modifications only low order reflections are observed, and there is intense diffuse scattering indicating that considerable disorder is present. The fact that usually not more than five orders of reflection are observed indicates that the layer distribution function is not sharp, and is therefore different from that of a typical crystal. A better perspective of this situation is that these phases are essentially disordered solids which possess certain liquid crystal properties, for example comiscibility, microscopic textures etc. Thus, these phases; J,G,H,K,E, and B cryst (L) can be termed *smectic crystal phases*.

Where the positional correlation length of the molecules is only short range the phases can be denoted *smectic liquid crystal phases*. This definition encompasses the A,C,B hex, and F phases. The I phase generally has been classed as a hexatic phase, but it may not fit either of these definitions as recent evidence indicates that its structure possibly consists of stacks of two-dimensional crystals. However, this observation has been limited only to members of the TBBA series.[9]

The crystalline to the liquid crystalline state can generally be defined by the transition that possesses the largest heat of transition in the melting process of the material. Both smectic crystal and smectic liquid crystal phases can and do occur above this temperature making them enantiotropic, and indicating that the smectic crystal phases are not true crystals.

The primary and secondary structural parameters can then be listed as follows:

(1) *Primary Structural Parameters*

(a) Molecular orientation - The long axes of the molecules can be either tilted or orthogonal on average to the layer planes.

(b) Positional in-plane correlations - The correlation length of the positions of the molecules can be either short range or long range.

(c) Layer packing order - The packing of the molecules can be random, hexagonal or base centered rectangular in type.

(d) Layer correlations - The positions of the molecules in adjacent layers on top of one another can be ordered (long range) or disordered (short range).

(e) Bond orientational ordering[10] - This is the extent of the registry of the packing net on moving from layer to layer, and within the layer.

(f) Tilt orientation - in monoclinic phases (J,G,I,F,H and K) the tilt can be to a corner of the net or to the side of the net.

(g) Molecular association - bilayers and monolayers are possible where there are strong intermolecular interactions. This does not refer to stacking sequences of layers, see 2(a).

(h) In-plane density modulation.

(2) *Secondary Structural Parameters*

(a) Stacking positions - ABC, AB or AA stacking is possible in some hexagonal phases. Changes between these variations occur with change in temperature, but they do not induce separate miscibility groups.

(b) Layer rippling - This may or may not occur in examples of phases of the same miscibility group.

(c) Helical structures - In optically active systems the I^*,F^* and C^* phases possess a helical arrangement of the tilt director perpendicular to the layer planes. These phases are all comiscible with their achiral analogues.

(d) Permanent Polarization - In optically active systems where a helical arrangement of the tilt direction is not usually observed, as in some G^*,J^*,H^* and K^* phases a permanent polarization still persists.[11] These phases are however comiscible with their achiral analogues.

The history of the coding letters for smectic phases is very confusing and too complex to go into in depth here. However, recent studies have shown that the B phase can be divided into two separate groups B cryst. (L) and B hex.[12] These groups have been shown to occur together in pure materials and therefore are immiscible and are therefore separate classes of smectic phases. Similarly, as with I and F, G and G'(J), and H and H'(K) phases are distinguished by differing tilt directions. The G and G'(J) phases have been shown to occur in a pure material so

Miscibility code letter		axiality	molecular orientation	molecular packing	bond orientational ordering	in-plane positional ordering	phase type	molecular rotation
A	1	uniaxial	orthogonal	random	short range	short range	-	free
C	1	biaxial	tilted	random	short range	short range	-	free
B(B hex)	11	uniaxial	orthogonal	pseudo hexagonal	long range	short range	hexatic	6-fold coordinated
I	16	biaxial	tilt to apex of hexagon	pseudo hexagonal	long range	short range	hexatic	6-fold coordinated
F	17	biaxial	tilt to side of hexagon	pseudo hexagonal	long range	short range	hexatic	6-fold coordinated
L(B cryst)	11	uniaxial	orthogonal	hexagonal	long range	long range	crystal	6-fold coordinated
J(G')	14	biaxial	tilt to apex of hexagon	pseudo hexagonal	long range	long range	crystal	6-fold coordinated
G	15	biaxial	tilt to side of hexagon	pseudo hexagonal	long range	long range	crystal	6-fold coordinated
E	18	biaxial	orthogonal	orthorhombic	long range	long range	crystal	oscillation through 180°
K(H')	14	biaxial	tilted	c centered monoclinic	long range	long range	crystal	oscillation through 180°
H	15	biaxial	tilted	c centered monoclinic	long range	long range	crystal	oscillation through 180°

TABLE 1

miscibility code letter	molecular packing	layer correlation	in-plane positional ordering	tilt direction	bond orientational ordering	helical order	phase type
C^*	random	none	short range	tilted	short range	yes	-
I^*	pseudo hexagonal	none	short range	to apex	long range	yes	hexatic
F^*	pseudo hexagonal	none	short range	to side	long range	yes	hexatic
J^*	pseudo hexagonal	long range	long range	to apex	long range	no	crystal
G^*	pseudo hexagonal	long range	long range	to side	long range	no	crystal
$K^{*\dagger}$	herringbone	long range	long range	tilted	long range	no	crystal
$H^{*\dagger}$	herringbone	long range	long range	tilted	long range	no	crystal

TABLE 2

† Molecular packing is of a c centered monoclinic type.

miscibility code letter	layering structure	molecular packing	molecular orientation	in-plane density modulation
A_2[20]	bilayer	random	orthogonal	-
A_1[20]	monolayer	random	orthogonal	-
$\tilde{A}$[21]	bilayer	random	orthogonal	long range
Ad	interdigitated bilayer	random	orthogonal	-
C_2	bilayer	random	tilted	-
C_1	monolayer	random	tilted	-
$\tilde{C}$[22]	bilayer	random	tilted	long range

TABLE 3

they obviously have separate identities.[13] Thus, G′ is now denoted J. The H and H′ phases have not yet been discovered together in one material or been shown to be immiscible in mixtures. However it is believed that a similar situation to G and J will operate with these phases producing two groups H and K.

Tables 1-3 list the structural features of all of the smectic phases defined so far. Table 1 lists the properties of normal smectogens, Table 2 the properties of optically active smectogens, and Table 3 the features of smectogens which possess a strong terminal dipole group (eg CN or NO_2).[20–22]

CONCLUSION:

The tables list the present structural parameters which possibly define each miscibility group as denoted by its common group letter. Further detailed structural investigations will no doubt add to these features, but it appears that miscibility criteria are still required in order to define which parameters are necessary to describe a particular smectic group.

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