

THERMODYNAMIC ASPECTS OF POLYMORPHISM IN LIQUID CRYSTALS

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ABSTRACT

Thermodynamic aspects of the polymorphism of liquid crystals are reviewed to enable a classification to be drawn up on the basis of miscibility criteria in binary systems. Liquid-crystalline modifications are classified as nematic and several types of smectic modifications. Structural investigations so far seem to confirm this scheme. The topology of binary isobaric phase diagrams is examined and the interpretation of intermediate mixed phases discussed. Quantitative thermodynamic data on solutes in liquid-crystalline phases seem to reflect the degree of order of modification. Transition enthalpies and entropies are reported on and it is concluded that polymorphism of liquid crystals gives opportunity for extending thermodynamic investigations to various mixed phases and their transition processes.

INTRODUCTION

Liquid crystals are states of condensed matter. Using the conventional criteria of thermodynamics they are characterized as phases. The term 'liquid crystal' or 'crystalline liquid' refers to phenomenological characteristics. The anisotropy of their properties has been used to distinguish these states from 'normal' isotropic liquids, although many properties show a behaviour typical for liquids. In other cases it is not strictly possible to make a clear distinction between this state and the solid state. However, the conventional notation represents well the most essential features and functions of these states.

The formation of liquid-crystalline states can be observed in organic one-component systems within a range of pressure and temperature which is typical for the individual compounds. Adding a second and further components, the formation of a homogeneous mixture is frequently observed (mixed liquid crystals, liquid-crystalline mixtures or solutions). If the second component also forms a liquid-crystalline phase, the formation of a complete series of liquid-crystalline mixtures can take place. These systems are called thermotropic liquid crystals.

A large group of liquid-crystalline states comprises the lyotropic liquid crystals which originate from the interaction of an organic component with a solvent which itself does not form liquid-crystalline states, e.g. with water. Liquid-crystalline structures are here generated by a specific interaction with the solvent. Typical examples are amphiphile substances capable

of specific interactions with a certain type of solvent, e.g. soaps, many surfactants and lipids.

In order to discuss the fundamental problems of liquid-crystalline phases a consideration of thermotropic liquid crystals is of wider generality, as the treatment can refer to monocomponent systems. Essential knowledge can then be transferred to lyotropic systems, which will not be considered in this paper. Liquid-crystalline lyotropic systems play some role in the wide field of the chemistry of colloids and interfaces and are of some importance to membranology, particularly in connection with the structure and function of biological membranes.

SOME FUNDAMENTAL FACTS*

Thermotropic liquid crystals are formed by substances which are composed of molecules displaying a strong anisotropy of shape. This can be found in organic molecules of noncyclic, isocyclic and heterocyclic nature, if the sub-units are arranged suitably in a bond system which gives the molecules the necessary stiffness. *Table 1* gives some examples. Combined with this anisotropy of shape there is, normally, a strong anisotropy of polarisability. Further, according to the type of structure, there are electric moments arranged at definite angles to the longitudinal axis of the molecules. These properties are decisive for the intermolecular interaction.

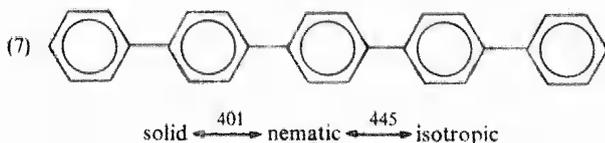
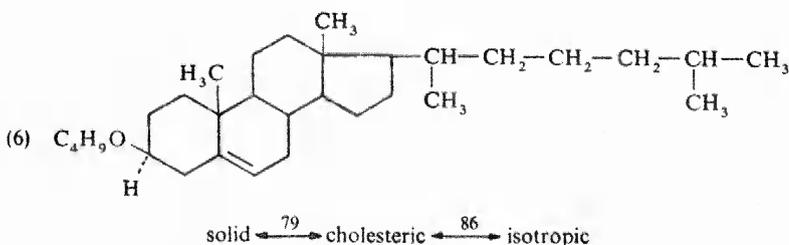
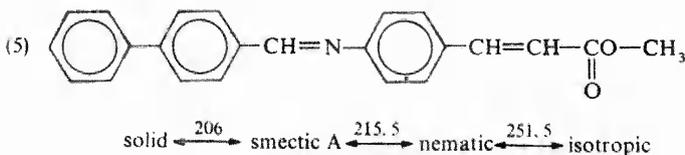
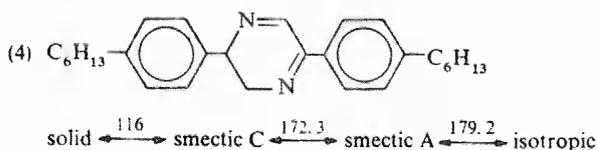
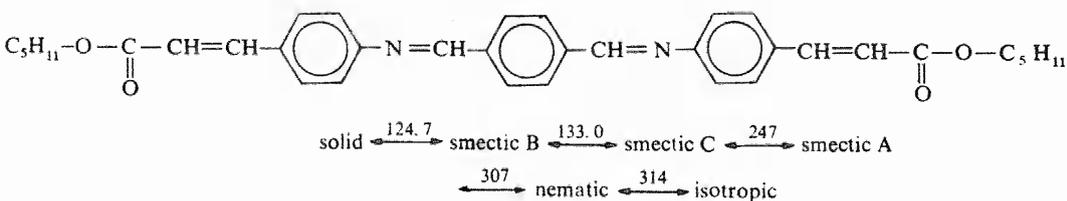
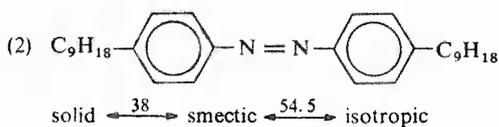
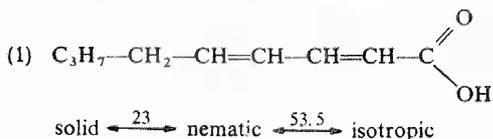
Table 1 also shows the characteristic phase behaviour of these compounds. Melting of the solid leads to liquid-crystalline states which transform at a higher temperature (clearing point) into the isotropic liquid. Several liquid-crystalline states can occur as polymorphous modifications. Two main forms of liquid crystals are distinguished, i.e. nematic and smectic liquid crystals. In *Figure 1* the most significant features of these structures are represented schematically. The nematic state is characterized by the fact that the longitudinal axes of the molecules are oriented parallel to each other, within a certain range of thermal fluctuation, and determine in this way a preferential direction (*Figure 1a*). But the molecular positions are distributed at random. In the smectic states the molecules are arranged in layers with their longitudinal axes aligned more or less parallel. It seems that no strong geometrical relation between the molecular axes in adjacent layers exists and in part the layers can be shifted one against the other. The orientation of the molecules can differ in the individual layers; their longitudinal axes can be oriented orthogonal to the layers or tilted against the layer planes (*Figure 1b*), both without a strong geometrical arrangement of the lateral intermolecular distances. Arrangements of molecules of higher order are known, with hexagonal packing of the longitudinal axes, which again can be oriented either orthogonal or tilted against the layer planes (*Figure 1c, d*).

If the molecules contain asymmetric atoms, the asymmetry of their force fields is transferred into the molecular aggregation. In nematic states the preferential direction shows a successive rotation (indicated in *Figure 1e* by showing the orientations of plane nematic regions separated by certain distances): a screw axis appears as a new preferential direction perpendicular

* For reviews see references 1-4.

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Table 1. Some substances having liquid crystalline behaviour (transition temperatures in °C)



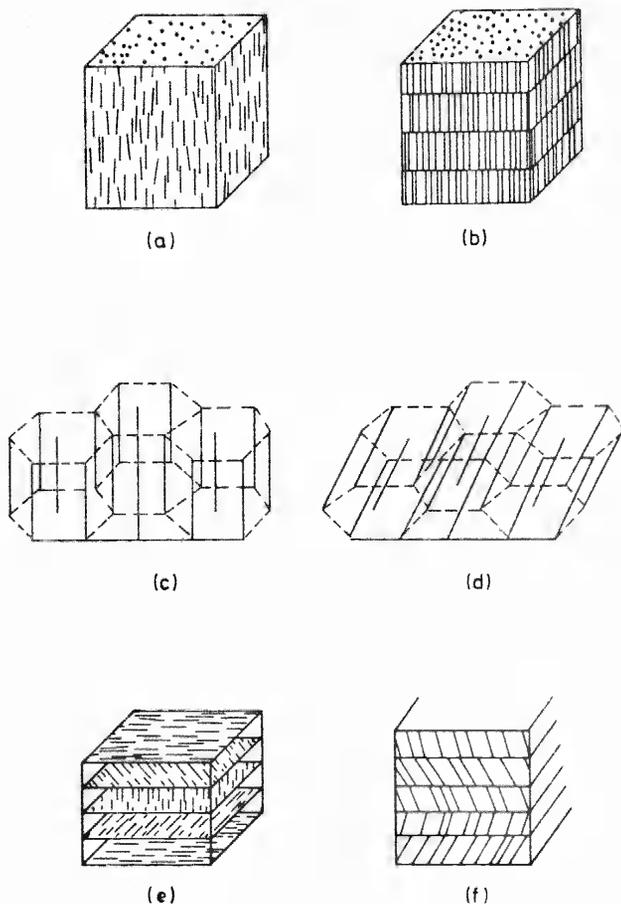


Figure 1. Scheme of structures of liquid crystals: (a) nematic structure; (b) smectic structure; (c, d) hexagonal orientation of molecules in smectic layers; (e) twisted nematic structure; (f) twisted smectic structure.

to the longitudinal axes. Such states are characterized by particular optical properties, e.g. large optical rotation of light, and are referred to as cholesteric or twisted nematic modifications. In tilted smectic states such a twisting may also occur, arising from a successive rotation of the angles of the long axes to the planes of the layers, progressively advancing from layer to layer (Figure 1f).

The molecular arrangements of the various liquid-crystalline modifications are also responsible for the different optical phenomena of microscopic samples which can be observed in polarized light (textures). Some examples of textures can be seen in Figure 2. The observation of textures helps in identifying the modifications and their transformations in single- and multi-component systems.

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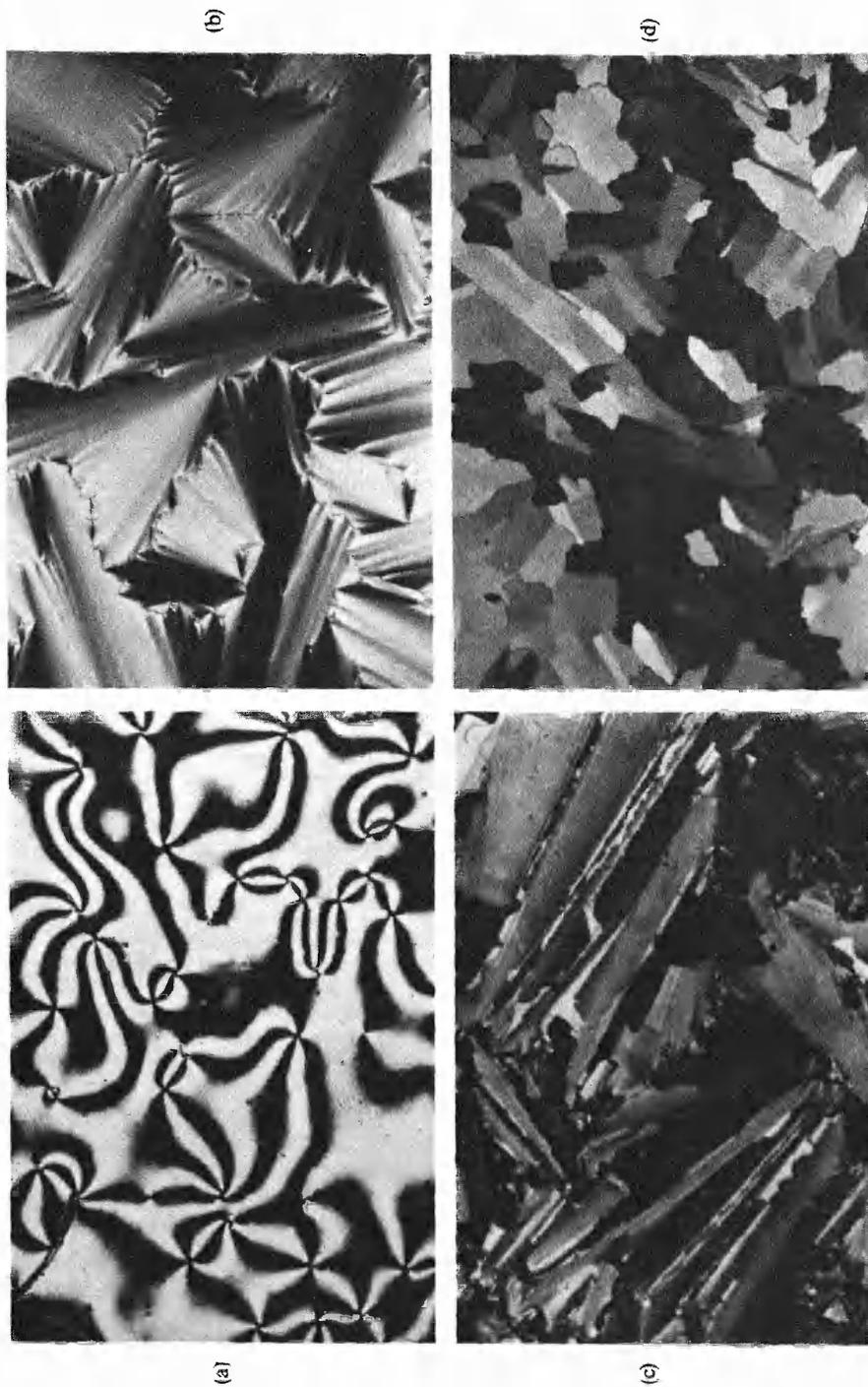


Figure 2. Textures of liquid crystals : (a) nematic Schlieren texture ; (b) fan-shaped texture of smectic A ; (c) broken fan-shaped texture of smectic C ; (d) mosaic texture of smectic E ; all crossed polarizers $\times 120$.

**POLYMORPHISM, STRUCTURE, MISCIBILITY.
A SYSTEM OF LIQUID CRYSTALS**

The occurrence of liquid crystals in various polymorphic forms has been ascertained in more than 5000 organic compounds⁵. The observation of the textures⁶, mentioned above, gives evidence of the number of liquid-crystalline modifications (degree of polymorphism) and the transition temperatures and provides a first indication of the kind of the modifications.

It has been shown that an investigation of the behaviour of binary systems with components forming liquid-crystalline modifications leads to a classification of the liquid-crystalline states⁶. The key to such a classification is the following empirical rule of selective complete miscibility. 'All liquid-crystalline modifications which exhibit complete miscibility in binary systems, without contradiction, can be marked with the same symbol'. 'Without contradiction' means that modifications which have the same symbol in no case exhibit complete miscibility with modifications of another symbol.

This principle may be explained by using the diagrams in *Figure 3*: In *Figure 3a* component I has one liquid-crystalline modification. It may be

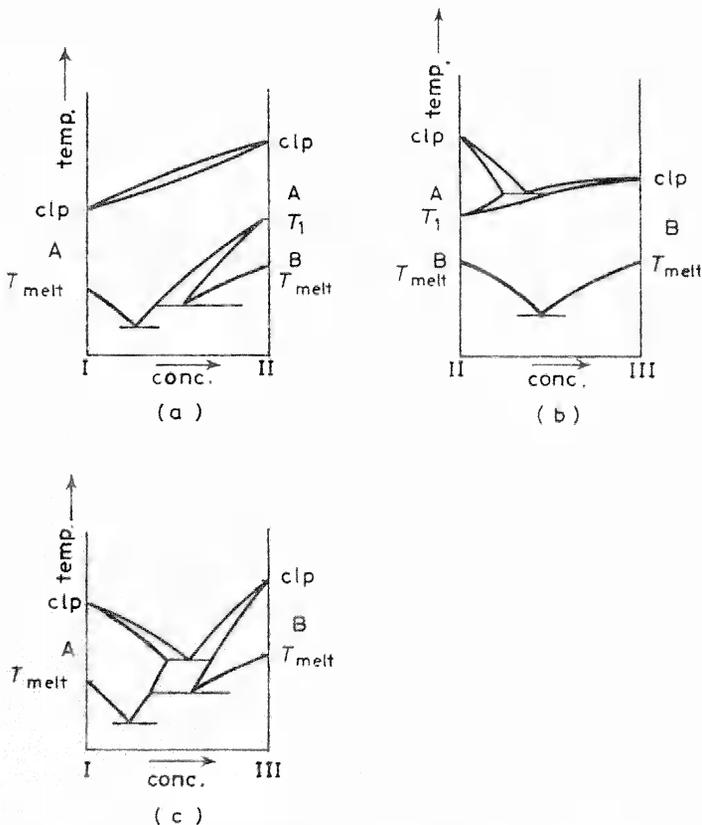


Figure 3. The method of marking liquid-crystalline phases (clp = clearing point; T_1 , T_{melt} = transition or melting temperature).

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given the designation A. Component II has two liquid-crystalline modifications. Because of its complete miscibility with the mesophase A of component I the liquid-crystalline high-temperature form is also given the designation A. The low-temperature form is given the new designation B. Now consider a component III which has only one liquid-crystalline modification. Miscibility of this modification with the low-temperature form of component II (*Figure 3b*) demands that the mesophase of substance III be denoted B. This designation is free of contradiction only if no complete miscibility is found between the modifications A and B, respectively, of the components I and III (*Figure 3c*).

A great number of liquid-crystalline modifications have been classified in the above manner, leading to eight types of liquid-crystalline states. Besides the nematic modification (*N*) seven types of smectic states are known at present which are conventionally designated *A, B, C, ... G*. Observed combinations of the various liquid-crystalline types are summarized in *Table 2*, where the modifications are listed from left to right in the sequence in which they form at decreasing temperature from the isotropic state. There are a great number of variants of polymorphism; predominantly the modifications are nematic states. Among the smectic states the *A, C, B* and *E* modifications are common, whereas the *D, F* and *G* modifications have been observed rarely. An analysis of *Table 2* yields a sequence rule which describes the appearance of modifications with decreasing temperature. The variants listed in *Table 2* (the rarely observed variants with modification *D, F* and *G* at first are not included) can be derived from the following variant of polymorphism

$$NACBE \quad (1)$$

They all omit one or more of the modifications in this variant but a change in the sequence has never been observed. *N* modifications appear always as

Table 2. System of liquid-crystalline modifications (variants of polymorphism)

Degree of polymorphism	Variants of polymorphism	Degree of polymorphism	Variants of polymorphism
Monomorphism (M)		Trimorphism (Tri)	
M ₁	N	Tri ₁	NAB
M ₂	A	Tri ₂	NAC
M ₃	C	Tri ₃	NCB
M ₄	E	Tri ₄	ABE
		Tri ₅	ACB
Dimorphism (D)		Tri ₆	ADC
D ₁	NA	Tri ₇	ACG
D ₂	NB		
D ₃	NC	Tetramorphism (Tet)	
D ₄	AB	Tet ₁	NACB
D ₅	AC	Tet ₂	ACFG
D ₆	AE		
D ₇	DC		
D ₈	CB		
D ₉	BE		

high-temperature forms; smectic *A* modifications are always high-temperature forms with respect to all other smectic modifications; the *C* modifications with respect to types *B* and *E*; and *B* modifications with respect to type *E*. The *D* modifications have been found in two neighbouring members of a homologous series only as high-temperature forms with respect to *C* modifications and as low-temperature forms towards *A* modifications. The *F* and *G* modifications are low-temperature forms with respect to *A* and *C* types. Concerning their arrangement with respect to types *B* and *E* a definite statement cannot yet be made.

This empirical classification of liquid crystals on the basis of the thermodynamic principle of complete miscibility can be compared with the results of structural investigations, which, however, have been performed only with a few substances.

In no case have identical structures been found for modifications belonging to different types. Otherwise the results could be discussed in terms of the schematically simplified representation of *Figure 1*. All the nematic modifications are characterized by the existence of only one preferential direction (*Figure 1a*). In the *A* modifications the arrangement of layers corresponds to *Figure 1b*. The distribution of the separations between the molecular axes in the layers is irregular⁷⁻¹⁰. The inclination of the longitudinal axes of the molecules in *Figure 1a* towards the planes of the layers is a characteristic feature of the *C* modifications¹¹⁻¹⁶. For the *B* modifications two hexagonal arrangements have been found (*Figure 1c, d*)^{17, 18}. Preliminary investigations of *E* modifications⁷ indicate a packing geometry of the molecules in the layers different from that of the *A, C* and *B* modifications, with orthogonal or tilted positions of the longitudinal axes towards the planes of the layers.

The x-ray scattering by *D* modifications⁷ shows a cubic structure, in agreement with their optical isotropy. The scattering patterns of *F* and *G* modifications¹⁹ again indicate layer structures; the former appearing similar to those of the *C* modifications and the latter showing peculiarities which do not correspond to any one of the other modifications. In the case of optically active molecules the nematic states are replaced by a cholesterinic modification (*CH*), and the *C* modification also appears in a twisted form (*C**)²⁰ (*Figure 1e, f*). So far the following variants of polymorphism are known in substances with optically active molecules²¹⁻²³.



From the standpoint of miscibility these variants are identical with the variants M_1 , D_1 , D_3 and T_2 in *Table 2*, since complete miscibility between *CH* and *N* as well as *C* and *C** has always been observed. The classification of liquid crystals and the special phenomena of polymorphism shown in *Table 2* can be readily interpreted. The breakdown of crystalline order at the melting point involves a partial loss of long-range order. At the transition to the isotropic liquid state the residual long-range order disappears. As the nematic states exhibit a lower degree of order than the smectic states, the observed sequence *N, S* with decreasing temperature is easily understood; furthermore, for the sequence within the smectic modifications (*ACBE*) the degree of order also seems to be responsible.

The rarely occurring *D* modifications cannot at first be fitted into the

picture identifying the smectic type liquid crystals with systems having layer structures. However, cubic structures are known in lyotropic systems²⁴. Since relatively few investigations of the structure and properties of smectic liquid crystals have been carried out, the reasons for the occurrence of the various modifications are not fully understood. The wide variety of variants of polymorphism, as demonstrated in *Table 2* [i.e. the omission of modifications from the sequence (1)], indicates the variation of the intermolecular interactions from substance to substance. They determine the details of the stability criteria.

Another important question is: Why does the observation of complete miscibility lead to a system of liquid crystals? It is impossible to take the existence of complete miscibility as a comprehensive criterion for a system of classification, either in the isotropic liquid or in the solid state.

In the isotropic liquid state the existence of complete miscibility is a widely occurring feature, so that only a few conclusions on structural or intermolecular details can be drawn from this fact. Here only the investigation of the mixed phases themselves can be the starting point for further work. On the other hand, in the solid state, miscibility is very often limited even in components of equal structure. Small differences in the values of the parameters of intermolecular interaction, such as different size of the molecules, may prevent complete miscibility so that it can scarcely be used as a classifying feature. In liquid crystals, however, the conditions are less restrictive so that the phenomenon of complete miscibility is apparently representative of a relation between equal or similar classes of structures. This can be seen from *Table 3*. The complete miscibility found between modifications of different

Table 3. Relations of miscibility between the members of a homologous series

2	3	2	8	4	8	4	10	7	12	8	9	8	10	8	12	11	12
is—	is																
sd	sd																

members of 4,4'-di-n-alkoxyazoxybenzenes²⁵ is marked by lines. In the columns the components are indicated by the number of carbons in the side chain. As one can see, complete miscibility is observed between the isotropic, nematic and smectic states, irrespective of differences in size. In the solid state it can be observed only in combinations whose components differ by no more than two carbon atoms.

TOPOLOGY OF PHASE DIAGRAMS. LIQUID-CRYSTALLINE MIXED PHASES

The topology of heterogeneous equilibria in binary systems with liquid crystals is determined primarily by the degree of polymorphism of the

components and by the kind of the variants of polymorphism. At present little but isobaric T - X diagrams are known.

The simplest situation arises in the case of complete miscibility between modifications of the same type. In *Figure 4* three binary combinations are selected which exhibit the variants

$$\begin{pmatrix} A & A \\ C & C \\ B & B \end{pmatrix} \quad \begin{pmatrix} A & N \\ C & A \\ B & B \end{pmatrix} \quad \begin{pmatrix} A \\ C & C \\ B \end{pmatrix}$$

In *Figure 4a* three regions of homogeneous miscibility between equal liquid-crystalline types are to be seen. Note the change in this simple type of diagram if component II is replaced by a substance III which exhibits no modification C but a modification N instead (*Figure 4b*), or by a substance IV with modification C only (*Figure 4c*). Moreover, the procedure of denoting liquid-crystalline modifications by complete mixed crystal formation, as outlined above, is again illustrated. Starting from component I with the variant of polymorphism ACB we obtain the designation of the liquid-crystalline modifications of the three components II, III and IV.

The sequence of modifications usually ends at the freezing point of a

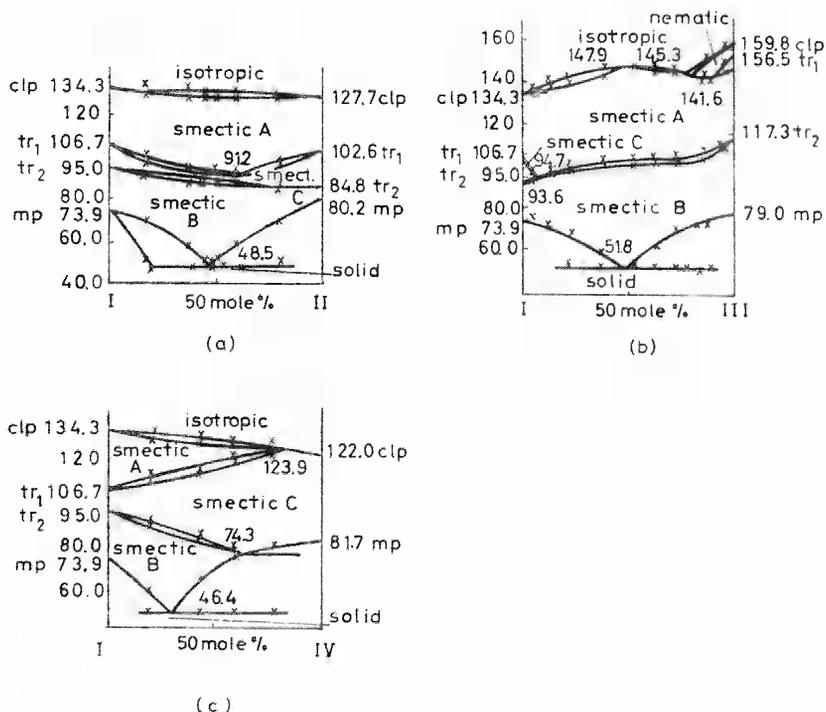


Figure 4. Phase diagrams of three binary systems²⁶, some *n*-alkyl-4-*n*-alkoxybenzylidene-4-aminocinnamates (I, II, III) and substance IV; I = $\text{CH}_3 \cdot [\text{CH}_2]_{11} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2 \cdot [\text{CH}_2]_4 \cdot \text{CH}_3$; II = $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2 \cdot [\text{CH}_2]_4 \cdot \text{CH}_3$; III = $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$; IV = 4,4'-di-*n*-dodecyloxyazobenzene.

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substance. However, if one succeeds in avoiding solidification, liquid-crystalline modifications which are unstable with respect to the solid state, often designated as monotropic states, can be observed. In *Figure 4c* the transition curve of *B* and *C* mixtures can be extrapolated into the region where the solid phases prevail and a transition temperature is found of about 65°C for a phase transition smectic *B*-smectic *C* of component IV. Considering the transition temperature in connection with the variants of polymorphism in the series of alkoxyazoxybenzenes (*Figure 10g*), stable *B*-*C* transitions are observed for 16 and 18 carbon atoms in the side chain. From the dependence of the transition temperature on decreasing number of carbon atoms a transition temperature of about 70°C is estimated for IV.

Extrapolations of this kind are permissible only if the diagrams have a simple form and if further supporting arguments are available. This is emphasized by the following diagram (*Figure 5*). Here the existence of *A* and

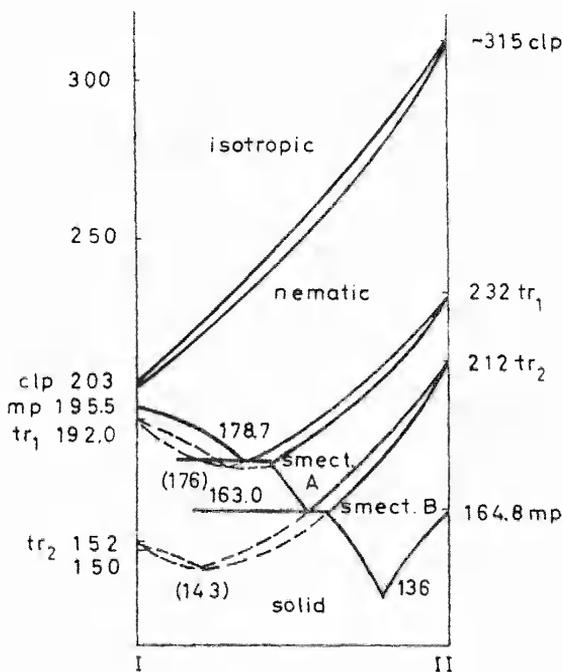


Figure 5. Phase diagram of the system I = $C_6H_5 \cdot CO \cdot O \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot CO \cdot CH_3$, II = $CH_3O \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot C_6H_4 \cdot CO \cdot CH_3$ (Ref. 27).

B modifications of component I is expected from the course of the stable equilibria. Indeed, they can be observed as unstable modifications but because of the minima in the transition curves between phases *A* and *N*, and between *A* and *B* an extrapolation from the stable part of the diagram would not yield the correct transition temperatures.

The importance of observations in the unstable region is demonstrated

in Figure 6. Here one succeeds in proving the existence of complete miscibility between the *E* modification of I and the low-temperature form of II, whereby the latter is shown to be an *E* modification.

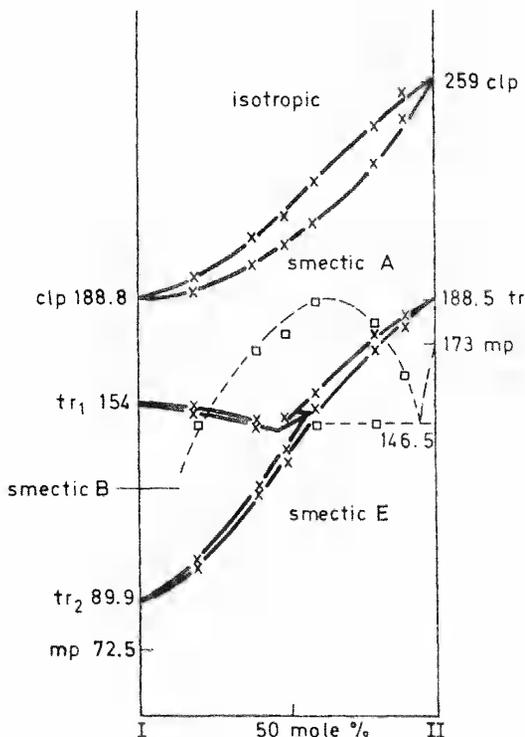


Figure 6. Phase diagram of I = $C_6H_5 \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot O \cdot [CH_2]_9 \cdot CH_3$ and II = diethyl-*p*-terphenyl-4,4'-dicarboxylate;----- stable curves of the solid state²⁸.

The transition curves between two liquid-crystalline mixed phases may exhibit all the generally known features of heterogeneous equilibria, such as the formation of extrema (Figure 5). The topology of the diagram shown in Figure 7, with the extremely pronounced maximum in the transition curves between *A* and *N*, and solid and *A*, indicates the formation of a compound.

A special feature in the topology of such diagrams occurs when intermediate mixed phases are formed (Figure 8). The initial designation of such a phase is signalled by the observation of its texture (see above). In this connection it must be added that the textures of all mixed phases show the same features as those of the modifications of the components from which they have been formed.

An attempt to identify intermediate mixed phases by miscibility can be made by the investigation of suitable sections in a three-component system. A third component is selected of the type postulated and mixtures of fixed concentration in the range of the intermediate mixed phase are added. In

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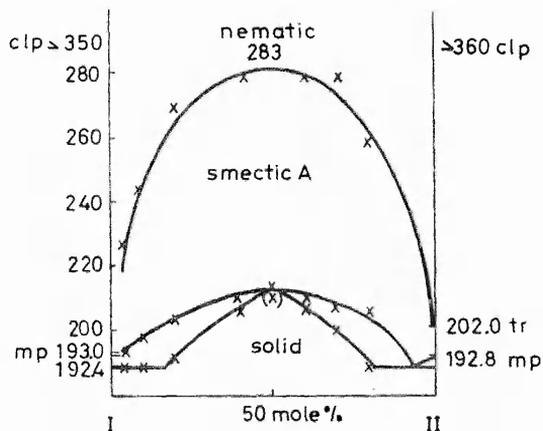


Figure 7. Phase diagram of I = $\text{CH}_3\text{-R-CH}_3$ and II = Cl-R-Cl ; R = $\cdot\text{C}_6\text{H}_4\cdot\text{N}$; $\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{N}$; $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}$; $\text{C}_6\text{H}_4\cdot\text{N}$.

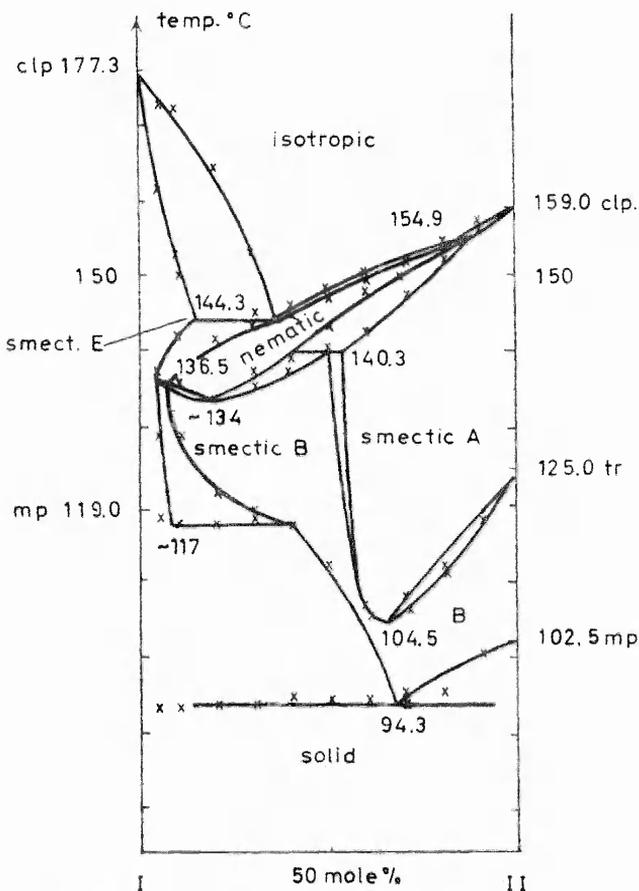


Figure 8. Phase diagram with intermediate nematic phase³⁰: I = 4-n-propyloxy-4'-n-propanoyl-biphenyl, II = $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_{11}\cdot\text{CH}_3$.

this way one may find a complete series of mixed phases between the intermediate mixed phase and one modification of the third component, and thus achieve an unambiguous designation^{29, 31}.

In most cases the intermediate mixed phases can be interpreted as stabilized regions of phases which originate from unstable modifications of the pure components (see *Figure 10f*). Such intermediate mixed phases are called stabilized mixed phases. Of course, an intermediate mixed phase can occur as a stabilized mixed phase also in systems where only one or even no component exhibits stable liquid-crystalline modifications²⁹.

Whenever these heterogeneous equilibria occur within a region which is unstable with respect to the solid, there is (as demonstrated above) a chance of finding these transitions when an appropriate method for suppressing solidification of the substance is applied. On the other hand it seems that no remarkable undercooling of transitions between liquid crystals occurs.

In mixtures of enantiomers of optically active compounds, which give rise to the formation of *CH* and *C** modifications, complete miscibility is found, with symmetrical *T-X* diagrams of the kind which is also known in the solid state (melting diagram). *Figure 9* shows two examples. In the equimolar

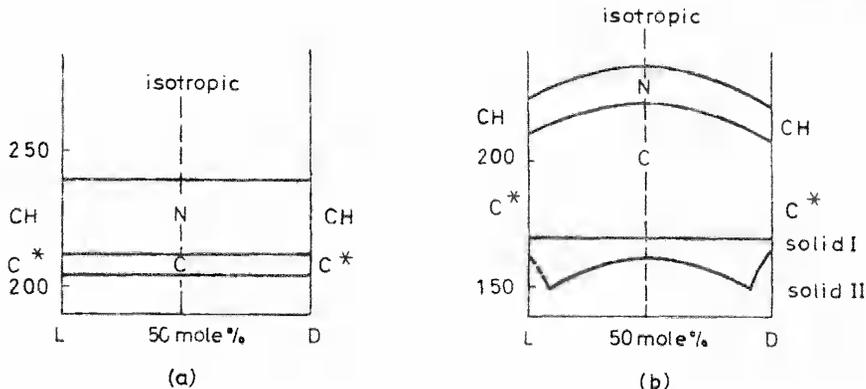


Figure 9. Phase diagram with enantiomers²²: (a) 3-Phenyl-2-alkylpropyloxy-4'-biphenyl-4-carboxylic acid; (b) (2-Methyl-hexyloxy)-4'-biphenyl-4-carboxylic acid.

mixtures full compensation occurs. These mixtures have the characteristics of nematic phases. This can also be understood on the basis of the structural concept (*Figure 1*). Moreover, complete miscibility can always be observed between *N* and *CH*, and between *C* and *C** modifications, where the mixed phases possess the character of *CH* and *C** modifications, respectively. With enantiomers of different substances, the concentration at which compensated mixed phases are formed becomes dependent on temperature.

The above considerations are concerned with the topology of the phase diagrams, taking into account the kind of variants of polymorphism, including transitions between modifications in the unstable region. It is of interest to consider this question on the basis of intermolecular parameters by studying the variation of the phase diagrams in a series of homologous chemical compounds.

To this end a series of binary systems is shown in *Figure 10*, representing a

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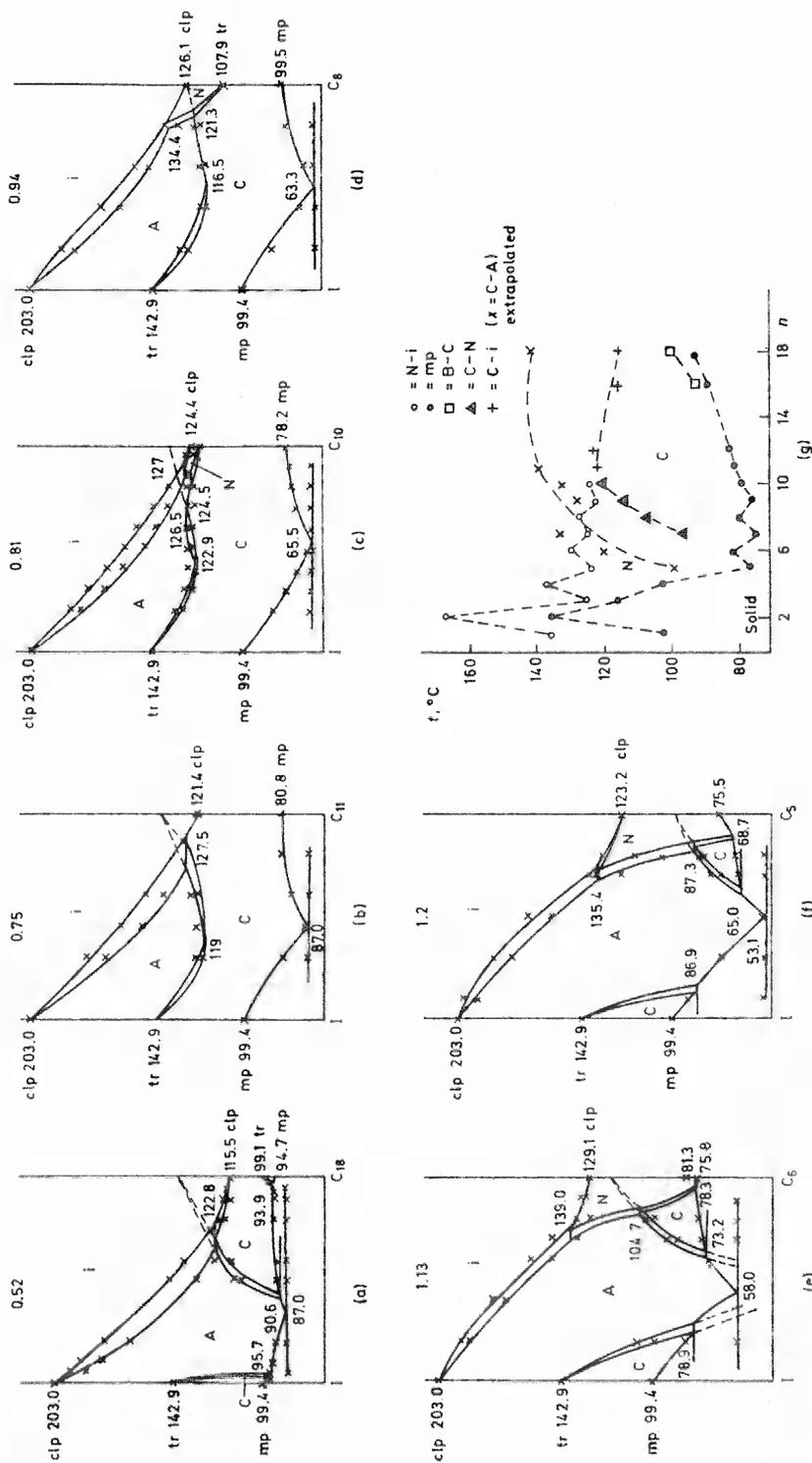


Figure 10. Phase diagrams of binary systems of di-n-amy-4,4'-azoxycinnamate (I) with homologues of the di-n-alkoxyazobenzene^{3,2}; (g) transition temperatures of the alkoxyazobenzene.

combination of one single compound, di-n-amyl-4,4'-azoxycinnamate (component I), with members of a homologous series of 4,4'-alkoxyazoxybenzenes. Component I has the variant of polymorphism AC. The transition temperatures of the homologues are plotted in *Figure 10g* as a function of the number of carbon atoms in the side chain. The lower members possess nematic modifications, the members from C₇ to C₁₀ nematic and smectic C modifications, and the compounds from C₁₆ to C₁₈ B and C modifications.

The ratio of the lengths of the molecules, component I/component C_n, can be taken as a parameter indicating the differences in the intermolecular interaction of the two components of this series. The length of the fully extended form of the molecules has been estimated from molecular models. In such a way, ratios ranging from 0.52 to 1.2 are obtained, and these ratios are indicated at the top of each diagram.

In the first diagram (*a*) one recognizes two areas of smectic C mixed phases which are separated from each other. Thus it would not be possible here to identify the two C modifications on the basis of the rule of selective complete miscibility. In diagrams (*b*) and (*c*), however, we find a region of uninterrupted miscibility. This behaviour in connection with the course of the transition temperatures (*Figure 10g*) shows that the phase regions in diagram (*a*) belong to the same type C. Observation of the texture and further investigations on miscibility with these components verify this assessment. The course of the transition curves between A and C shows that only at low temperatures would it be possible to decide whether the two regions C pass into each other in a homogeneous way (via a minimum in the transition curves) or via a heterogeneous area (gap in the range of miscibility).

In diagram (*b*) a minimum can be observed. The difference between the two diagrams (*a*) and (*b*) with respect to the C-A transition corresponds to a significant difference in the ratio of molecular lengths.

A slight difference in this ratio exists between systems (*b*) and (*c*). This can also be recognized by the slightly varying characteristic temperatures. In addition, there appears a small region of nematic mixed phases in diagram (*c*) due to the existence of a nematic modification of component C₁₀. The size of this area of nematic mixed phases at first increases only a little (diagram *d*). The temperature of the minimum, however, again begins to decrease: if the upper values of the ratio of length are approached, the C regions separate again (diagram *e*), and finally the azoxybenzene-rich C phase appears as an intermediate region, because in component C₅ the transition to the C modification would take place in the unstable region at too low a temperature so that it can no longer be observed.

In all diagrams an extrapolation of the transition curves C-A can be made towards the second component and thus one can arrive at a transition A-C for this component. This rough estimate has been plotted in *Figure 10g* together with the other transition temperatures in the homologous series. One recognizes that with increasing number of carbon atoms the extrapolated A-C transition temperature exhibits a weak increase and possibly passes through a maximum. Similar behaviour can be observed in another homologous series (cf. *Figure 14a*) in stable C-A transitions. Using the extrapolated transition temperatures, one notices that the transition curves

C-A show the widest deviation from those of ideal mixed crystals for low and high ratios of the lengths of the molecules, i.e. for strongly different interaction of the components. Thus, in principle there appears a possibility for a thermodynamic treatment of the topology of these diagrams. Comprehensive material on transition heats in such homologous series recently became available⁴² and this should lead to an analytical treatment.

The summary presented here on heterogeneous equilibria in binary systems containing liquid crystals should logically be followed by a representation of the thermodynamic behaviour of mixed phases of liquid-crystalline states. This, however, has been scarcely investigated. There are several reasons for this, e.g. the difficulty of preparing sufficiently large samples of these substances and the danger of thermal decomposition if the substances are kept for some time in the liquid-crystalline state.

A molecular field treatment of liquid-crystalline mixtures on the basis of the Maier-Saupe theory of nematics has also been applied for calculating simple phase diagrams (deviations from the ideal behaviour in *N-I* transition curves)³³.

Some thermodynamic data have been obtained via gas chromatography since liquid-crystalline phases have been used for separations for some time³⁴⁻³⁹. Nematic phases, but also a few smectic modifications, have been used as stationary phases and the solubility properties of various organic systems have been investigated. The thermodynamic quantity, which can be derived from the retention volume, is the solute activity coefficient at infinite dilution (f_2).

More comprehensive material has been gained from variants of higher degree of polymorphism⁴⁰. Figure 11 shows f_2 values of the solution of three alkanes and of *o*-, *m*- and *p*-dichlorobenzene in a smectic trimorphous substance of the variant ACB. From the f_2 values the solute partial molar excess enthalpies, excess entropies and excess Gibbs energies at infinite dilution can be obtained (\bar{H}_2^e , \bar{S}_2^e , \bar{G}_2^e). From these quantities the partial molar enthalpies and entropies of solution $\Delta\bar{H}_2^{\text{sol}}$, $\Delta\bar{S}_2^{\text{sol}}$ are obtained by making use of the evaporation enthalpies ΔH_{2v} . The partial molar Gibbs energy of solution $\Delta\bar{G}_2^{\text{sol}}$ yields

$$\Delta\bar{G}_2^{\text{sol}} = \Delta\bar{H}_2^{\text{sol}} - T\Delta\bar{S}_2^{\text{sol}} = \bar{G}_2^e \quad (2)$$

In Table 4 differences in the partial molar Gibbs energies of solution between two modifications at the transition temperature are given. These values give the range of values for twelve compounds (alkanes, *o*-, *m*- and *p*-substituted dimethyl- and dihalogenobenzenes) at the transitions *I-N*, *I-A*, *A-C*, *C-B*, *N-C* [e.g. $\bar{G}_2^e(I) - \bar{G}_2^e(N) = \Delta\Delta\bar{G}_2^{\text{sol}}(I-N)$]. These differences were obtained from three solvents exhibiting these transitions.

At first one recognizes the well-known fact that in the transition from the isotropic to the liquid-crystalline medium a decrease in solubility takes place. Corresponding to the higher degree of order of the *A* modifications the transition *I-N* shows smaller differences than *I-A*. *A* and *C* modifications differ only a little. The ranges *I-N* and *N-C* are distinctly smaller than *I-A*. According to the stepwise increase of order in the sequence *I-N-A* and the small differences between *A* and *C* the sums fall in the vicinity of the *I-A*

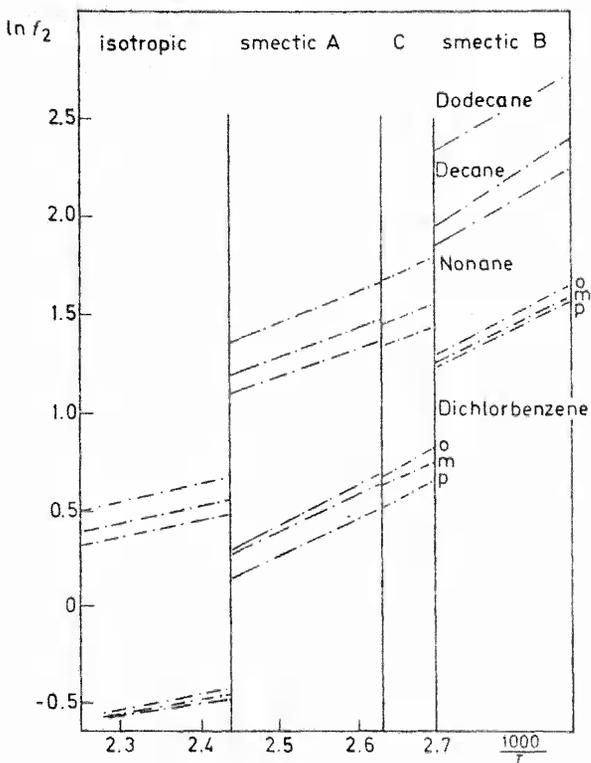


Figure 11. $\ln f_2$ versus $1/T$; solvent: 2-(4-n-hexyloxyphenyl)-5-(n-octyl)-pyrimidine⁴⁰.

range. Another strong decrease in solubility takes place in the transition to the still more ordered state B. Thus one can suppose that the range of variations reflects structural features of the liquid-crystalline modifications.

For a discussion of details within the range of values it is necessary to consider the solution entropies in terms of the translational, rotational and vibrational changes in the solution process³⁷.

Table 4. Range of values of differences in Gibbs free energy of solution, cal/mol

Type of polymorphism	Range
I-N	- 63 -174
I-A	-370 -624
A-C	+ 45 - 13
C-B	-309 -426
N-C	-146 -205

POLYMORPHISM IN LIQUID CRYSTALS
**CALORIC INVESTIGATIONS OF THE POLYMORPHISM
 OF LIQUID CRYSTALS**

The nature of the polymorphism of liquid crystals should be reflected in the properties of the various phases that have been determined up to now⁵. It is therefore important to investigate the temperature dependence of these properties and, in particular, the changes occurring at the phase transitions. Most frequent are caloric investigations which detect the variation of enthalpy. The methods of differential thermal analysis and scanning calorimetry are far more frequently used than adiabatic calorimeters.

An important question is whether characteristic effects can be detected for transitions involving modifications of the same type, which may be independent of the nature of the substance. Using the results of earlier investigations of this kind⁴¹, which have been supplemented by new measurements, the transition enthalpies of about 200 compounds have been obtained⁴². The results are summarized in *Figure 12*. The transition enthalpy ΔH of the C-A transitions is generally within a relatively small range of values of up to ca. 300 cal mol⁻¹. Most values are smaller than 100 cal mol⁻¹. Compared with the majority of the ΔH values of the transitions leading

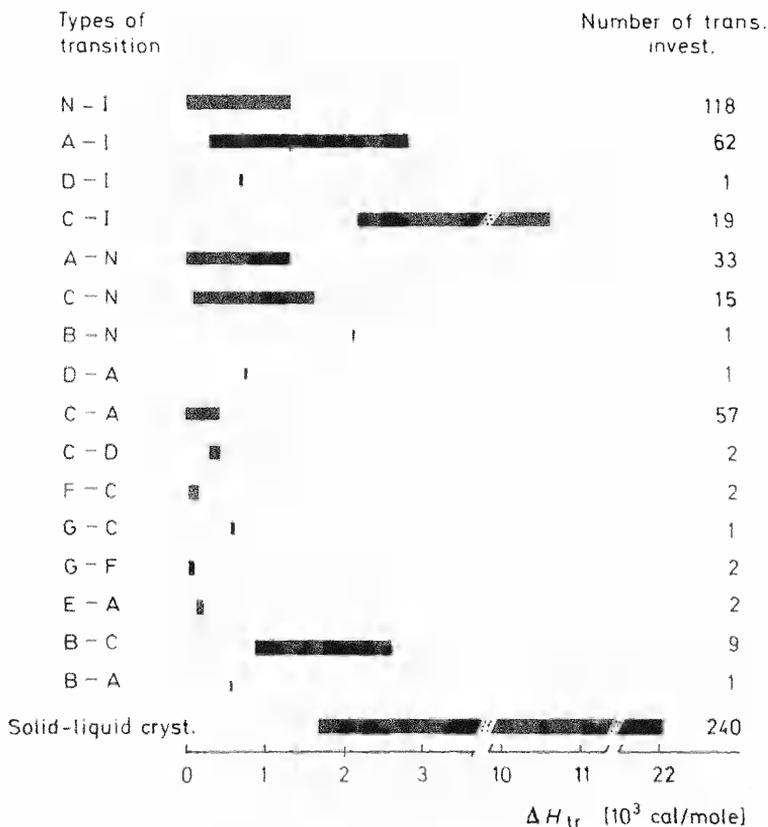


Figure 12. Partition of values of transition enthalpies on the types of transition⁴².

from a smectic to the isotropic state ($A-I$, $C-I$), the transition enthalpy $N-I$ is smaller. The transitions $A-N$ and $C-N$ show transition enthalpies which are smaller than those for the transitions $A-I$ and $C-I$, respectively. This is not unexpected in view of the decrease of order in the sequence smectic–nematic–isotropic.

A strongly specific behaviour appears in the transition enthalpy of the $A-I$ and $C-I$ transition and especially in the melting enthalpies; in the latter case, no distinction with respect to the type of liquid-crystalline modification to which the solid is melting can be found.

For the entropies of transition, results which are essentially similar to those shown in *Figure 12* are obtained.

The substance-specific variability of the transition behaviour of the liquid-crystalline modifications can best be discussed on the basis of homologous series. In this way it is possible to study the changes of the properties due to a successive alternation of molecular shape. In many relevant homologous series a given molecular skeleton is extended by an aliphatic chain (*Table 1*), and first the influence of the length of these chains will be discussed. The comparison of different homologous series will then show the influence of the fundamental skeleton.

Two points of view are needed. They concern the distribution of the variants of polymorphism in homologous series and the variation of transition properties for each group of transitions in the series with modifications of the same type. First, let us consider the transition temperatures^{2,5}. They usually show a regular trend; the frequently observed odd–even alternation forms part of this trend. Transition temperatures fitting into such trends indicate that the transitions are of the same type, as can be seen from *Figures 10g*, *13* and *14*. The degree of polymorphism in homologous series is generally subject to a regular trend. Frequently the lower members of a homologous series show only nematic phases (e.g. *Figure 10g*). Additional smectic modifications appear as low-temperature modifications in higher members, and further smectic low-temperature forms occur in even higher members of the homologous series. The nematic state often disappears in higher members and only smectic states prevail.

Regular trends are less frequently observed at the melting temperatures. Changes in the type of modification of the crystals might be responsible for this. The regular trends of the transition temperatures have some parallel in the behaviour of enthalpies and entropies of transition. The groups of transition types which appear in *Figure 13a* are also distinguished by their transition enthalpies and entropies. The $C-A$ transitions form a group, too. However, because of the small values ($\sim 20 \text{ cal mol}^{-1}$) they are not shown. Note that the $A-I$ transitions show strongly increasing values of ΔH and ΔS with increasing number of C atoms. In the quotient $\Delta H/\Delta S$ the values compensate in such a way that the transition temperature first falls slightly and finally remains nearly unchanged. However, in the case of the $A-I$ transitions in *Figure 14*, the decreasing transition temperatures correspond to decreasing values of the transition enthalpy and entropy, with the transition entropy decreasing less strongly than the enthalpy.

At this point we may discuss the influence of the molecular skeleton, which differs between the series of *Figures 13* and *14* only by two methyl

POLYMORPHISM IN LIQUID CRYSTALS

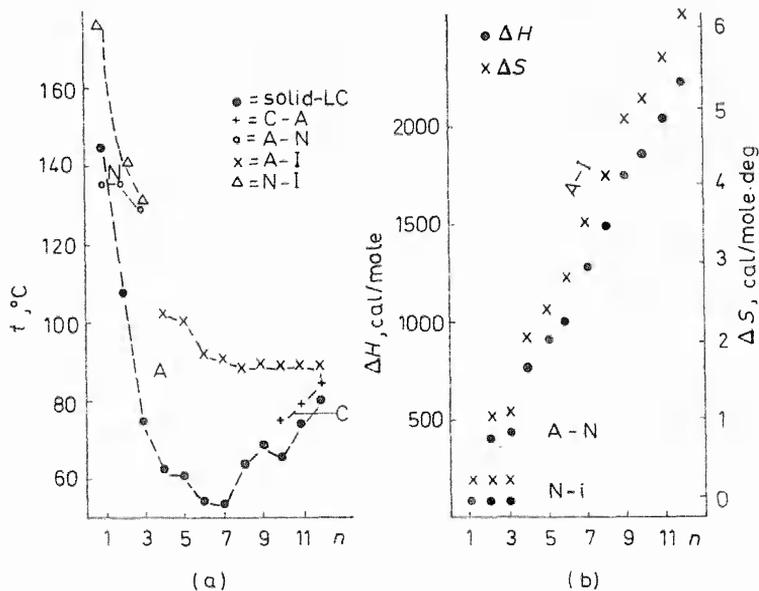


Figure 13. Transition temperatures and transition enthalpies (ΔH) and entropies (ΔS) in the homologous series of the di-n-alkyl-4,4'-azoxy- α -methylcinnamate⁴².

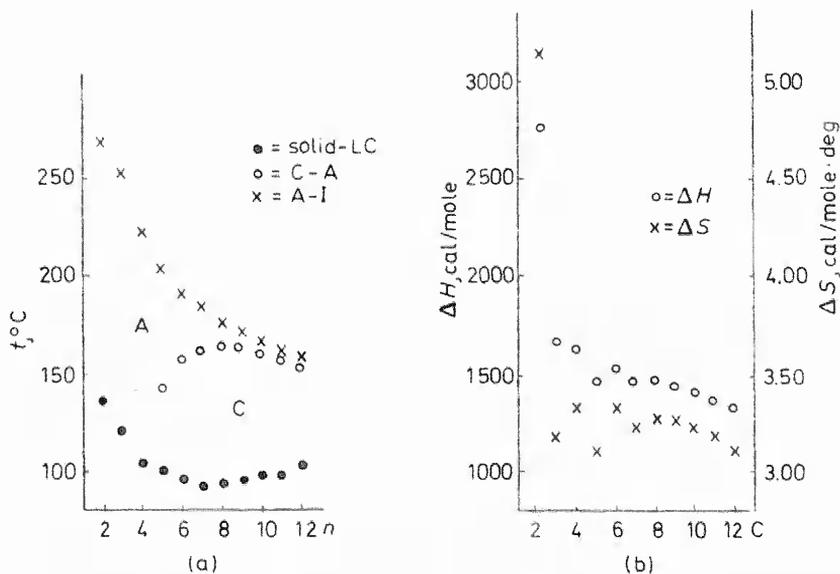


Figure 14. Transition temperatures and A-I transition enthalpies (ΔH) and entropies (ΔS) in the homologous series di-n-alkyl-4,4'-azoxycinnamate⁴².

groups. This methyl group will disturb the parallel arrangement of the molecular axes. Thus the stability of the *A* phases of these compounds should be less than in the non-methylized series. Accordingly, they have lower clearing points, and lower values of transition entropy and enthalpy. With increasing length of the aliphatic chains this behaviour is modified. Because of the higher clearing temperatures the mobility of the hydrocarbon chains of the non-methylized ester is greater than in the methylized ester. With increasing chain length this leads to an altogether less ordered arrangement; the opposite situation is observed in methylized compounds at low clearing temperatures. Here increasing length of the aliphatic chains leads to a somewhat higher degree of order. This might be a first crude explanation for the opposite trend of the ΔH and ΔS values in the two series. Discussions of this kind suggest the application of molecular-physical methods for investigating the subtleties of the transition processes.

Adiabatic calorimetry follows the transition processes in a more accurate way. In some cases pretransformation effects have been observed^{41,43}. Below the transition temperature the molar heat capacity increases strongly and above the transition temperature it decreases. One can suppose that all types of liquid-crystalline transitions show such effects. Their quantitative detection, however, depends on the magnitude of the transition enthalpies, and the purity of the material plays an important role^{41,43}.

SUMMARY AND CONCLUSION

In this review on thermodynamic aspects of the polymorphism of liquid crystals it has been shown that a classification of liquid crystals can be developed on the basis of miscibility criteria in binary systems. In this classification of all liquid-crystalline modifications which have been investigated up to now are classified as nematic and seven types of smectic modifications. Their appearance as a function of temperature is subject to a sequence rule. The structural investigations seem to confirm this classification of liquid crystals.

The topology of binary isobaric phase diagrams (*T-X*) is primarily determined by the variants of polymorphism, which result from the classification. In the interpretation of intermediate mixed phases the unstable modifications are of particular significance. Selecting suitable components the phase diagrams enable us to make some qualitative statements on molecular contributing factors.

The quantitative thermodynamic data on solutes in liquid-crystalline phases, which are obtained by gas-chromatography, reflect the degree of order of the liquid-crystalline modification.

The study of transition enthalpies and transition entropies shows characteristics of the corresponding liquid-crystalline modifications, but also a considerable substance-specific variability. The substance-specific variability in homologous series was discussed for selected examples.

Polymorphism of liquid crystals represents an opportunity for extending thermodynamic investigations to various mixed phases and their transition processes, and to make comparative studies by a proper variation of the individual chemical compounds.

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