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Calculation and Experimental Verification of Eutectic Systems with Nematic Phases

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On the basis of the thermodynamics of ideal systems it is possible to calculate the melting curves of binary eutectic systems.

We compare calculated and experimental curves for 15 binary systems with 4,4′-di-*n*-alkoxybenzenes as components. Because of the occurrence of mixed solid crystals there are usually noticeable differences between calculated and experimental values in systems with neighbouring members of the homologous series. In most other cases the agreement between theory and experiment is good.

A simple method for the theoretical estimation of eutectic points of multicomponent systems is described and proved.

INTRODUCTION

For many practical purposes low melting liquid crystals are needed.[1] Although there are some pure substances with melting points in the range of ambient temperatures, in most cases lower melting mixtures of two or more components are used. The melting point depression is especially high if the mixture is a eutectic one.

It is no problem to examine experimentally the diagram of state of a binary system and to find out the eutectic point with respect to its concentration and temperature. In the case of ternary systems this is possible also, but only with a much greater expense of work. In systems with four or more components it is not possible with a reasonable expense of work to establish eutectic points. In these cases usually mixtures with arbitrary but not optium concentration are applied.

It has long been known to be possible to calculate melting curves of binary systems, but we know of no such published calculations for systems with liquid crystalline phases[14].

In the next section of this paper we give the thermodynamic basis and the assumptions needed for the calculation. In the Section 3 we deal with experimental investigations undertaken with the purpose of proving the validity of these suppositions.

The results of these investigations are discussed in connection with some opinions found in the recent literature.

THERMODYNAMIC BASIS

Binary system

In a simple eutectic (Figure 1) the homogenous melt coexists with one crystallized component along the melting curves T_{01} E and T_{02}. It is possible to calculate on a thermodynamic basis these melting curves under the following assumptions:

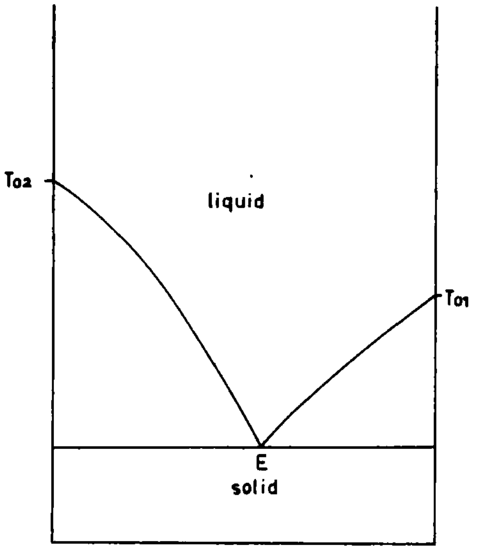


FIGURE 1 Diagram of state of a simple eutectic system.

1) The two components crystallize in pure form and do not form mixed crystals; thermodynamically this means the activity coefficient of the crystalline phase equals one.

2) The liquid phase is an ideal mixed phase; this means in the liquid phase the activity coefficients of the components equal one.

3) The differences of the heat capacities of the pure components in the molten and crystallized form are small. This is equivalent to the assumption of temperature-independent melting enthalpies.

It is worth pointing out that assumptions 1 and 2 are, to a certain extent, incompatible. The more similar molecules are, the more likely they are to form both ideal solutions and mixed crystals.

If these conditions are valid the upper melting temperature T_i (temperature at which the pure component i melts in the mixture) can be calculated with the following Eq. (12):

$$T_i = \frac{\Delta H_{oi}}{\dfrac{\Delta H_{oi}}{T_{oi}} - R \ln x_i} \tag{1}$$

where

ΔH_{oi} = molar heat of fusion of the component i
T_{oi} = melting point of the pure component i
R = gas constant
x_i = mole fraction of the component i

If there is a transition in the solid state of the pure compound i Eq. (1) is valid only in the region

$T_{oi}^{tr} < T < T_{oi}$ (T_{oi}^{tr} = Temperature of transition in the solid state).

In the region $T < T_{oi}^{tr}$ *Eq.* (1) has to be replaced by Eq. (2) which can be derived similar as Eq. (1):

$$T_i = \frac{\Delta H_{oi} + \Delta H_{oi}^{tr}}{\dfrac{\Delta H_{oi}}{T_{oi}} + \dfrac{\Delta H_{oi}^{tr}}{T_{oi}^{tr}} - R \ln x_i} \tag{2}$$

where ΔH_{oi}^{tr} = molar heat of transition.

Multi-component system

With Eq. (1) it is possible to calculate a universal melting curve for each component without consideration of the special kind of the second component; of course, the above 3 assumptions must be in force. This universal curve is also valid in the case of systems with 3 or more components, because the diveration of Eq. (1) requires no supposition that the system must have only two components. In a two-component system we find the eutectic point without difficulty by the intersection point of the two melting curves of the components. In a system with more components we have the additional condition at the eutectic point:

$$T_1 = T_2 = T_3 = \ldots \tag{3}$$

Practical determination of eutectic points

We can find the eutectic point at the intersection point of the melting curves of the components.

For binary systems we determine the eutectic points in the following way: we draw the melting curves (T_i versus x_i) of the components on transparent film. Then we put the two curves toghether in such a manner that the temperature scales correspond to each other (Figure 2, full lines). By translation of the two films parallel to the x_i-axes we find an intersection point of the two curves and can read x_1 and x_2. If the sum of x_1 and x_2 does not equal one, it is necessary to shift the curves till this is the case (Figure 2, dotted lines). Then we can read the temperature and the composition of the intersection point of the two curves which in this state is corresponding to the eutectic point of the binary system. Without difficulty this procedure can be extended to systems with three or more components. In this case the films have to be shifted parallel to the x_i-axes till $\Sigma x_i = 1$.

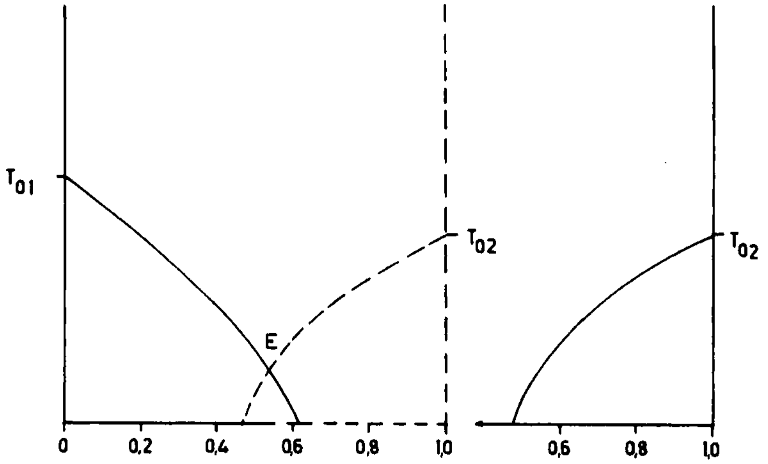


FIGURE 2 Illustration of the graphical method of evaluating binary eutectics.

It is also possible to find the eutectic point of a binary system by calculation: We taken an arbitrary value for T_i and calculate x_1 and x_2 for the two components by use of Eq. (1). If

$$x_1 + x_2 > 1$$

the chosen temperature T_i is higher than the eutectic one, if

$$x_1 + x_2 < 1$$

the chosen temperature T_i is lower than the eutectic one. In both cases we adjust the temperatures – if necessary, in several steps – till $x_1 + x_2 = 1$. Then T_i corresponds to the eutectic temperature. Also this procedure can be extended to systems with 3 or more components, if the adjustment of T_i is done till $\Sigma x_i = 1$.

This method is a valuable help for the estimation of the eutectic points, especially in the case of multicomponent systems. But for the practical use of the method it is necessary to test it experimentally with the purpose to find out in which cases we can expect the thermodynamic suppositions to be valid. We shall do this in Section 4.

Non-ideal system

If we take substances with chemically similar molecules, for instance members of a homologous series with not too different molecular lengths, we can hope that the mixed liquid phase is nearly ideal, so that assumption 2 is valid. In the case of non-ideal systems Eq. (1) has to be replaced by Eq. (4):

$$T_i = \frac{\Delta H_{oi}}{\frac{\Delta H_{oi}}{T_{oi}} - R \ln x_i - R \ln f_i} \tag{4}$$

f_i = activity coefficient
With the expression of Porter[3] we can read:

$$R \ln f_i = \frac{4(1 - x_i)^2 \, G^E_{0,5}}{T} \tag{5}$$

where $G^E_{0,5}$ = excess free energy at the mole fraction 0.5. In systems formed by components of one homolous series in most cases $|G^E_{0,5}| > 200$ J/mole.[4]
With the typical values $T_{oi} = 400°\text{K}$
$\Delta H_{oi} = 20\,000$ J/mole
$x_i = 0.5$
we find

$$R \ln f_i \approx 0.5$$

$T_i = 357{,}6°K$ for ideal systems
$T_i = 354{,}4°K$ for real systems
It is to be seen that the maximum deviation caused by the non-ideality of this system is to be expected not greater than ca. 3°

Test of third assumption

In some cases the heat capacities of the liquid crystalline substances have been measured in the region of the melting points[2] and the difference of the heat capacities above and below the melting point is small enough to influence only unimportantly the calculated melting curves. Thus assumption 3 is valid.

Test of first assumption

It seems of greater interest to test the first assumption: the forming of solid crystals by each pure compound. If the molecules of the components are very similar we can expect the existence of an uninterrupted series of mixed crystals in the solid state or at least regions of mixed crystals at the boundaries of the phase diagram. If the components are different but not neighbouring members of a homologous series the occurrence of eutectic systems without mixed solid crystals can be realized.

With the purpose of determining those cases for which the first assumption of the calculation is valid we have investigated 15 systems with components of one homologous series.

EXPERIMENTAL

Materials

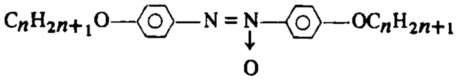
For the investigations we have chosen the first six members of the homologous series of the 4,4'-di-*n*-alkoxyazoxybenzenes. We have used the original substances described elsewhere by Arnold.[2] The transition temperatures and melting enthalpies of the substances measured by Arnold[2] are given in Table 1. The molecular lengths have been estimated with the help of "Stuart-Kalotten", which we have used in the most stretched form with respect to the alkyl chains.[13]

Method of investigation

We have investigated the diagrams of state by means of thermal microscopy in linearly polarized light. This method has been described elsewhere.[7]

TABLE I

4,4'-Di-*n*-alkoxyazoxybenzenes



$C_nH_{2n+1}O-C_6H_4-N(\rightarrow O)=N-C_6H_4-OC_nH_{2n+1}$

Number of carbon atoms n	$T_{C/N}$ [°C]	$\Delta H_{C/N}$ [J/mole]	$T_{N/I}$ [°C]	Molecule length Å
1	118,2	29570	135,3	18,3
2	136,6	26870	167,5	20,3
3	115,5	26900	123,6	23,3
4	102,0	20940	136,7	26,3
5	75,5	14590	123,2	29,3
6	81,3	41390	129,1	32,3

Results

We have studied in a systematic manner binary combinations of each compound with all other substances used in this investigation. The results are given in Figures 3–17.

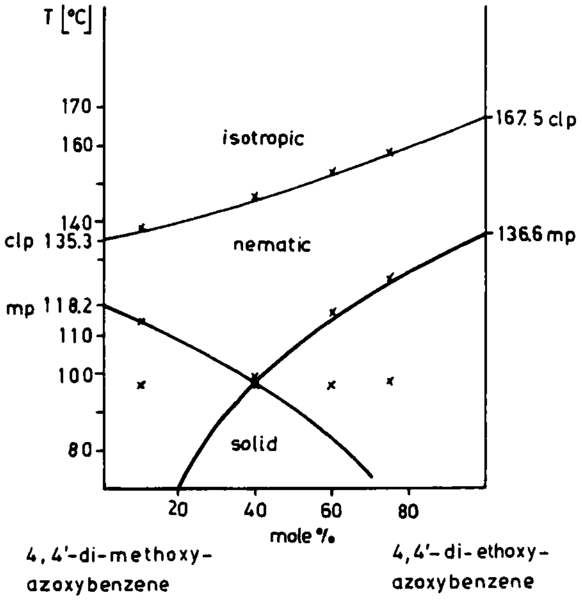


FIGURE 3 Diagram of state of the binary system (after Arnold[5] and Prins[6]).

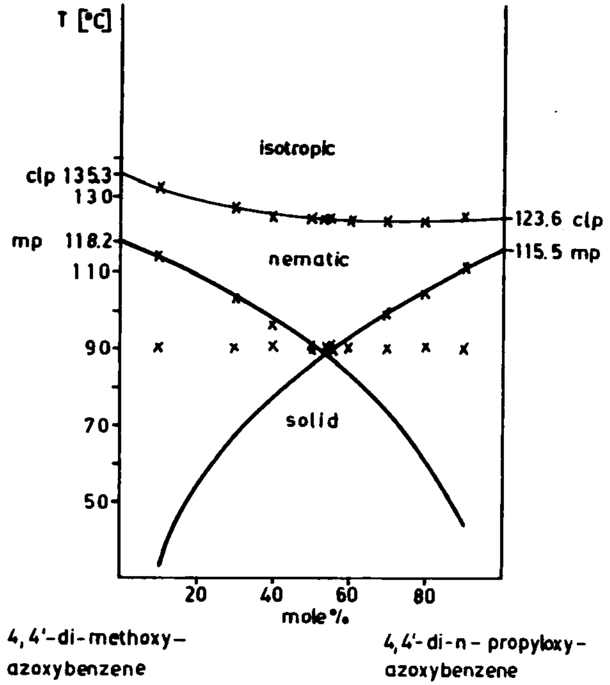


FIGURE 4 Diagram of state of the binary system.

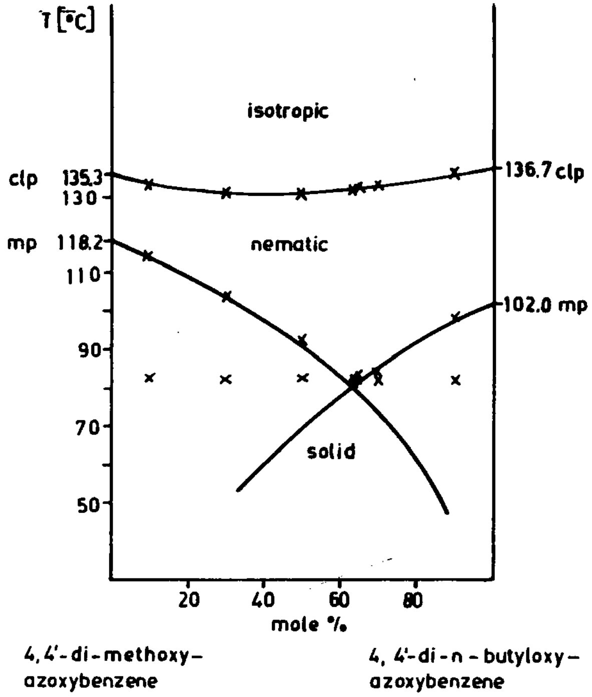


FIGURE 5 Diagram of state of the binary system.

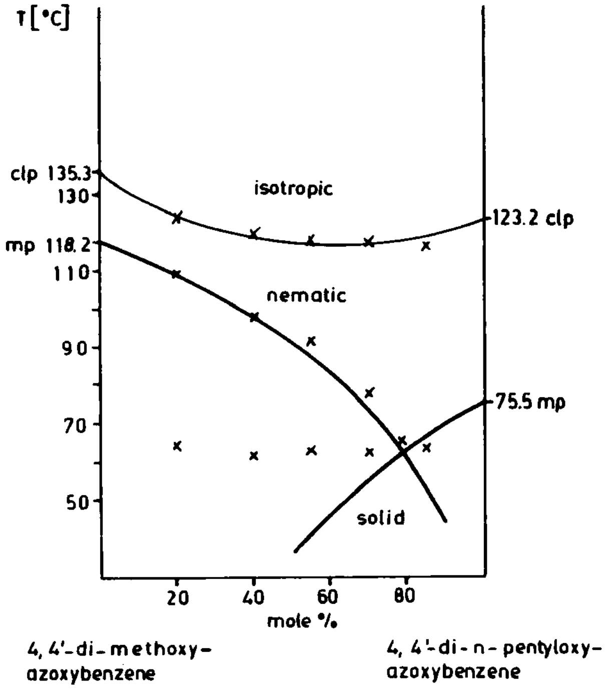


FIGURE 6 Diagram of state of the binary system.

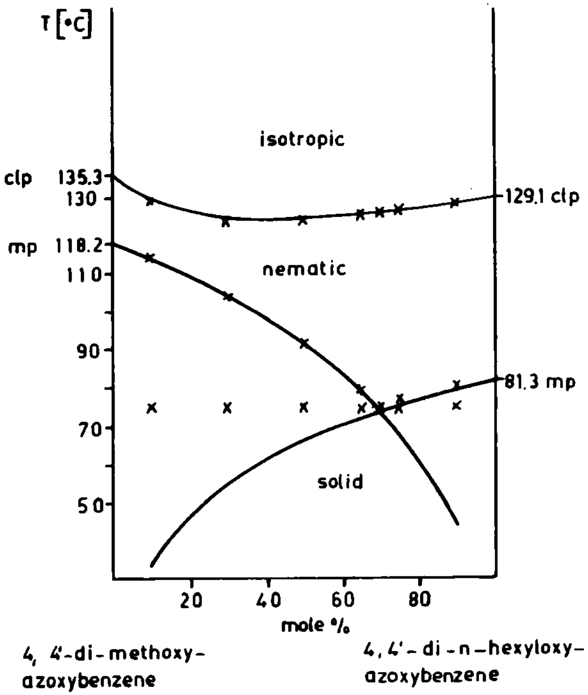


FIGURE 7 Diagram of state of the binary system.

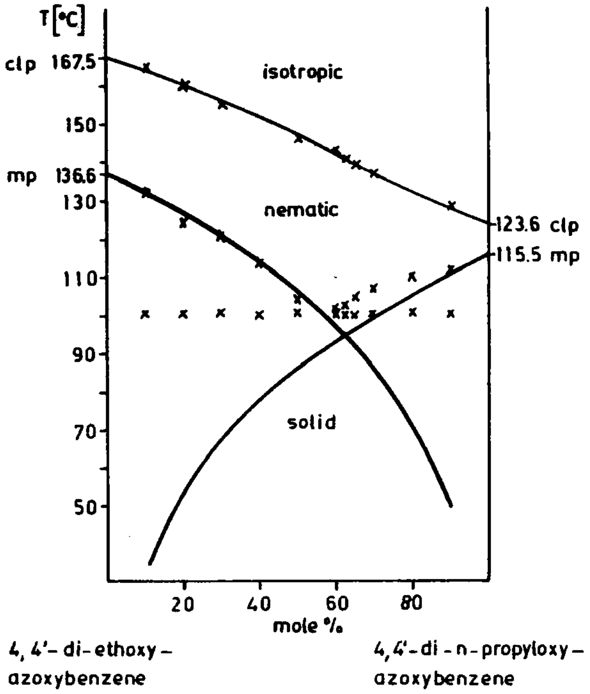


FIGURE 8 Diagram of state of the binary system.

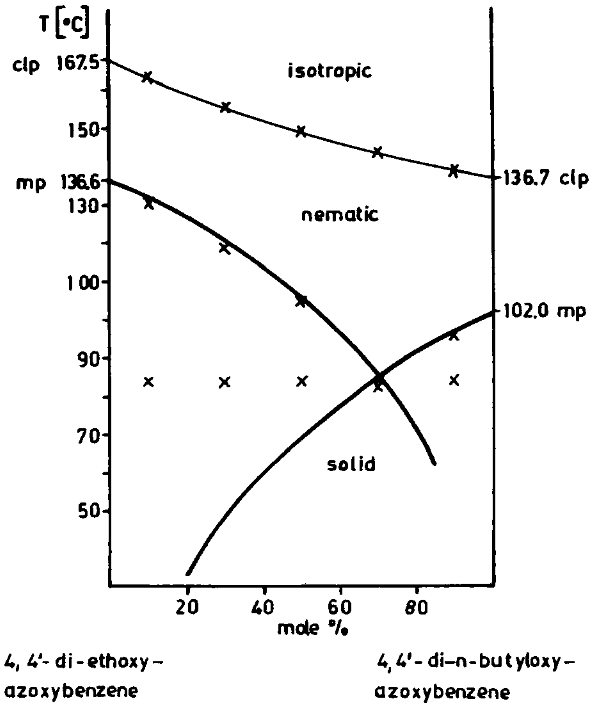


FIGURE 9 Diagram of state of the binary system.

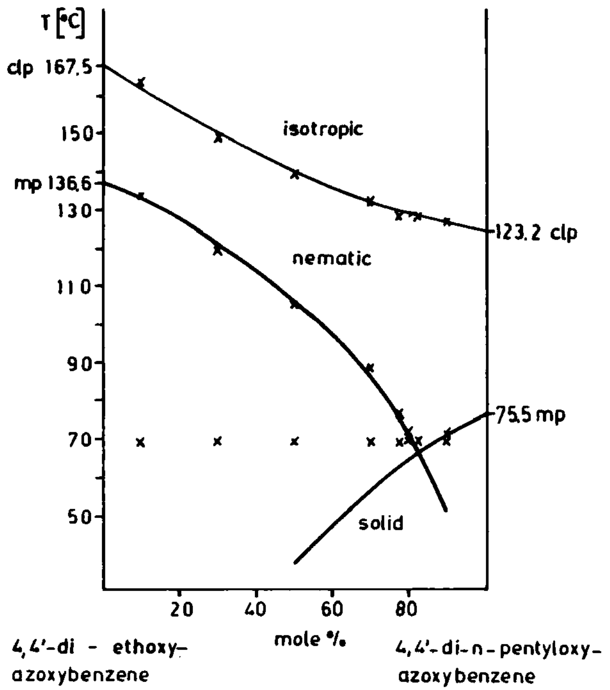


FIGURE 10 Diagram of state of the binary system.

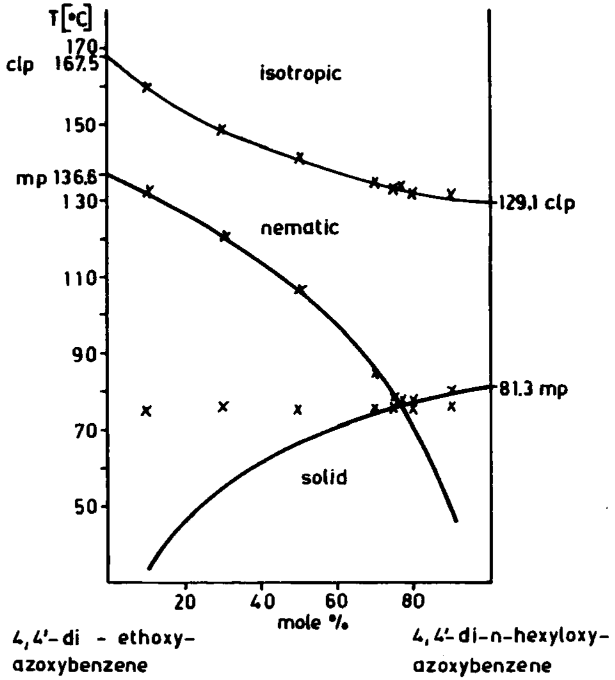


FIGURE 11 Diagram of state of the binary system.

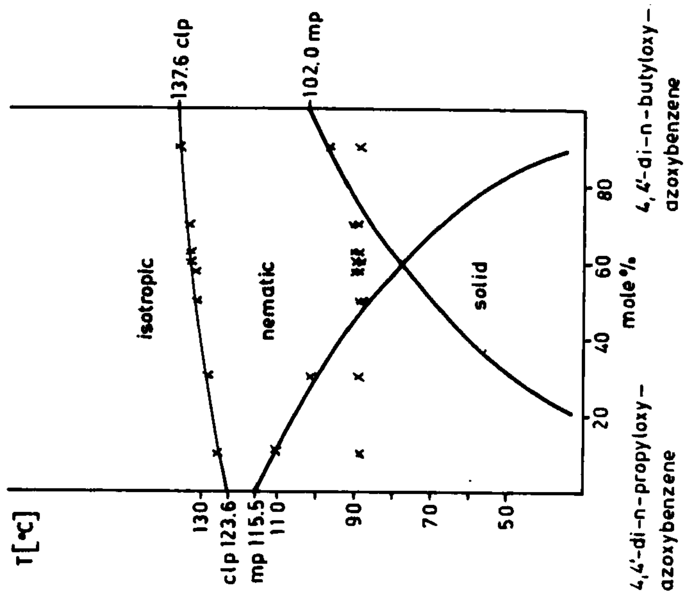


FIGURE 12 Diagram of state of the binary system.

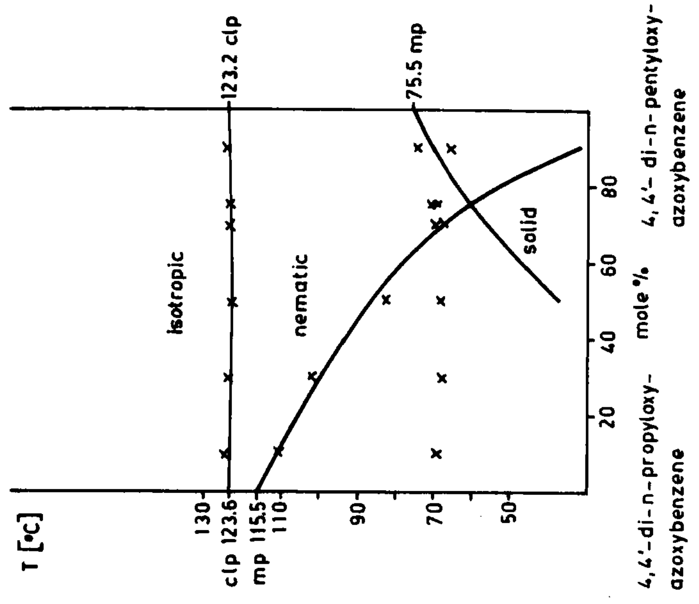


FIGURE 13 Diagram of state of the binary system.

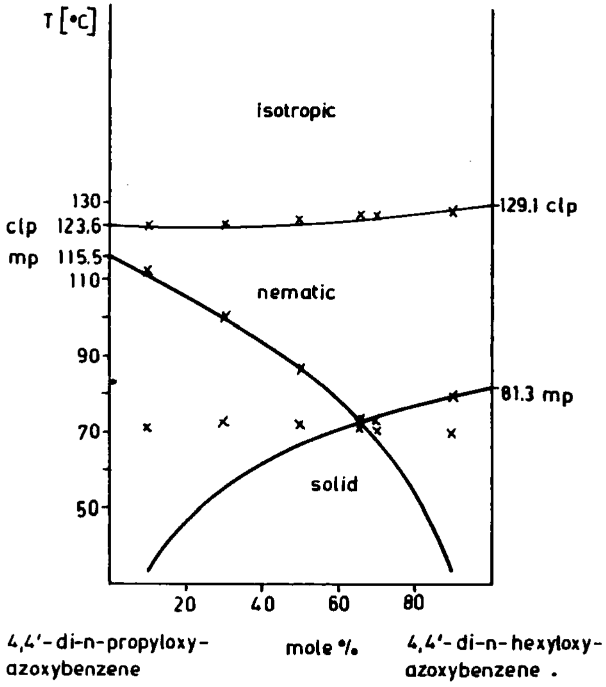


FIGURE 14 Diagram of state of the binary system.

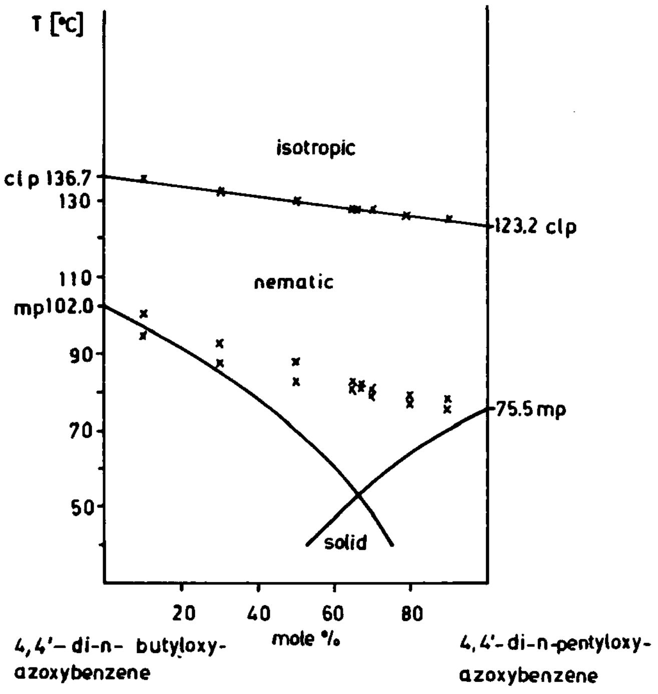


FIGURE 15 Diagram of state of the binary system.

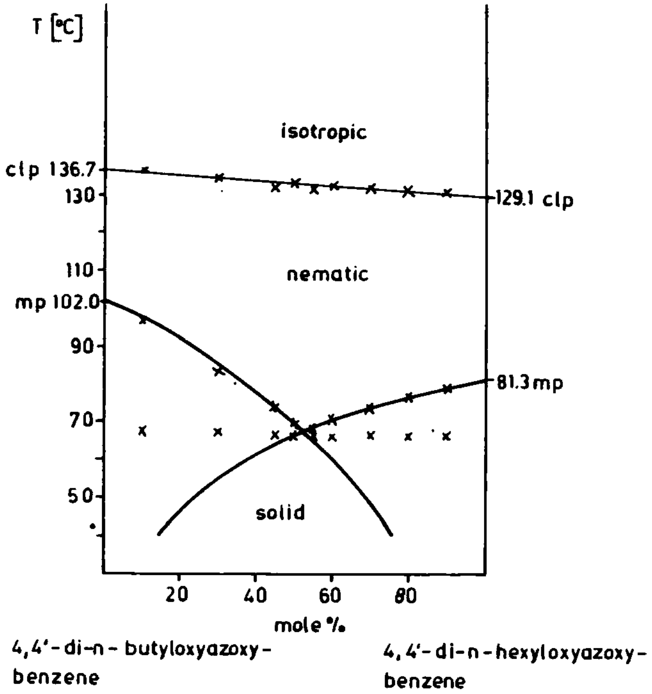


FIGURE 16 Diagram of state of the binary system.

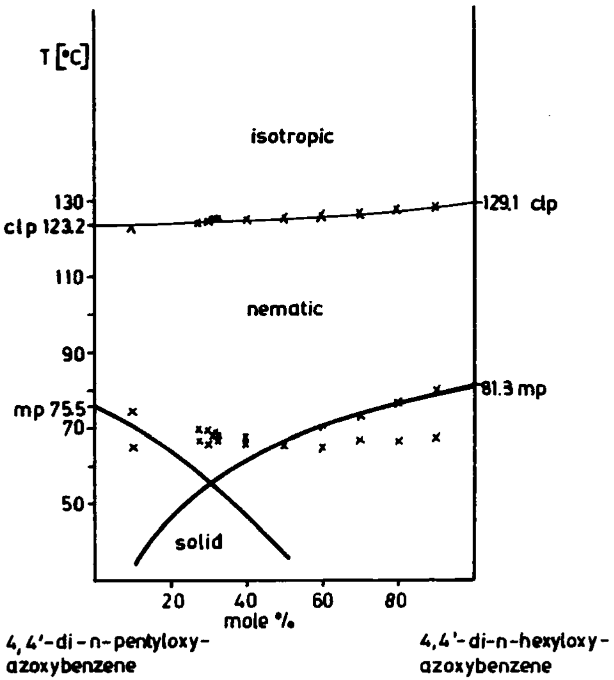


FIGURE 17 Diagram of state of the binary system.

DISCUSSION

Binary systems[14]

In Table 2 it is so to be seen that in many cases the investigated systems show good agreement of the experimental values of the eutectic points with the theoretical ones. If the ratio of the molecular length is equal or less than ca. 0.80, the investigated systems show the occurence of eutectics without remarkable forming of mixed crystals in the edge regions of the diagrams of state. In these cases the agreement of the experimental values with the theoretical ones is good. For this reason we can also assume that the thermodynamic assumptions 2 and 3 of the calculation are sufficiently fulfilled: the systems seem to be only weakly non-ideal and the differences of the heat capacities of the nematic and the crystalline solid phases are sufficiently small.

With the exception of the system C_1/C_2, in all systems with neighbouring members of the homologous series we find, to a greater or lesser extent, differences of the experimental values from the theoretical curves. It is to be assumed that in these cases the forming of mixed crystals takes place. This is very clearly seen in the system C_4/C_5, where the experimental values indicate the occurrence of an uninterrupted series of mixed crystals in the solid state. In the system C_2/C_3, C_3/C_4, C_3/C_5 and C_5/C_6 mixed crystals possibly may occur

TABLE II

Comparison of experimental and theoretical values of binary eutectics formed by alkoxyazoxybenzenes

System	Ratio of the molecule length	Eutectic point				Agreement	
		Experimental		Theoretical			
		T [°C]	X_2	T [°C]	X_2	Good	Not good
C_1/C_2	0,90	97	0,39	97	0,40	x	
C_1/C_3	0,78	90	0,53	89	0,54	x	
C_1/C_4	0,70	82	0,64	81	0,64	x	
C_1/C_5	0,63	63	0,79	63	0,79	x	
C_1/C_6	0,57	75	0,70	74	0,70	x	
C_2/C_3	0,87	101	0,55	95	0,62		x
C_2/C_4	0,77	83	0,71	85	0,71	x	
C_2/C_5	0,69	68	0,83	66	0,83	x	
C_2/C_6	0,63	75	0,77	75	0,77	x	
C_3/C_4	0,89	88	0,55	78	0,59		x
C_3/C_5	0,78	68	0,62	60	0,76		x
C_3/C_6	0,72	71	0,66	72	0,66	x	
C_4/C_5	0,90	–	–	53	0,67		x
C_4/C_6	0,81	66	0,52	67	0,52	x	
C_5/C_6	0,90	65	0,45	55	0,30		x

near the edge of the diagrams of state. It is improbable that the differences of the experiments from the theory in these cases are due to non-ideal behaviour of the components: systems of neighbouring members of a homologous series should be more nearly ideal in the liquid crystalline state than systems with more different substances. The validity of the third thermodynamic assumption should be nearly the same as in the other cases, as we can see in the work of Arnold.[2]

The behaviour of the systems with the higher members of the homologous series is understandable from consideration of the occurrence of mixed crystals in connection with the ratios of the molecule lengths. If this ratio is 0.80 or less, usually eutectics occur without formation of mixed crystals. Asbach and Kilian[8] have investigated binary and ternary systems of *n*-paraffins. In aggreement with our results they have found that there are eutectics if the lengths of the molecules are sufficiently different.

Let us consider separately the system C_1/C_2. The ratio of the molecule length is 0.80, but no mixed crystals in the solid state occur. The agreement between experiment and theory is very good. Often we find in homologous series that the first one or two members have special properties and do not show the normal trend of the higher homologues. This is the case for the melting and clearing points of the di-*n*-alkoxyazoxybenzenes. There are great differences between the respective values for C_1 and C_2, which point to great differences in the intermolecular energies. It is possible that for this reason the formation of mixed crystals does not occur, in spite of the similar molecular lengths of the two components.

Multi-component systems

It is of great interest to investigate the possibility of evaluating eutectics of multicomponent systems. This is most likely to agree with experiment if the evaluated eutectics of all binary systems of the components show good agreement with experiment. We have selected C_1, C_2, C_4 and C_6 as components . All binary systems which can be formed by these components show eutectics which can be evaluated with good agreement. In Table 3 we have listed the results of the theoretical and experimental estimation of both a ternary and a quarternary eutectic mixture. The agreement between experiment and theory is good.

Pohl and Steinsträsser's work

Pohl and Steinsträsser[9] claim to have established the hypothesis of the existence of nematic secondary structures in eutectic systems. They prove their hypothesis with the assumption that the existence of secondary structures is an explanation for:

1) the existence or nonexistence of eutectic systems;

2) the constancy of the eutectic composition with nearly 65% of the lower melting component;

3) the great existence range of eutectic mixtures of 4,4′-substituted benzylidene-anilines.

We feel that these conclusions are questionable for the following reasons:

1) The existence or nonexistence of eutectic systems is a question of the miscibility of the components in the solid state.

2) The eutectic composition is not constant in general, as is to be seen also in some examples given by Pohl and Steinsträsser.[9] But on the basis of the thermodynamic theory we can understand that a composition of 65% of the lower melting component is a not improbable value.

3) The enlargement of the existence range of eutectic nematic mixtures,is, as we know from the thermodynamics, essentially a question of the molar heat of fusion. In some 4,4′-disubstituted benzylideneanilines we have found indeed unusual low molar heats of fusion[10] and therefore extremely low melting eutectics are to be expected. Fishel and Hsu[11] have recently published some eutectics of this kind.

Thus, although we do not know if a nematic secondary structure is really possible, we are convinced that the arguments of Pohl and Steinsträsser for its existence are not valid.

In some cases low melting eutectics are not stable, because most substances exhibit also instable lower melting solid phases, which may occur in eutectic systems. We have found mixtures which have been formed by melting of the instable solid phases of the components, and remained in the nematic state some months or nearly one year, till they crystallized in the higher melting stable solid phases.

TABLE III

Eutectics of Multicomponent Systems Formed by Alkoxyazoxybenzenes

Components	X_i	Theoretical	Eutectic Point [°C] Experimental
C_1	0,27		
C_2	0,21	70	70
C_4	0,52		
C_1	0,17		
C_2	0,13	55	55
C_4	0,37		
C_6	0,33		

Acknowledgement

We are indebted to Mrs. S. Fiedler who has proved the practical possibility of calculating eutectics of multicomponent systems, and to Prof. Sackmann for his interest in this work.

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14. Note added in proof: The systems Figures 3, 4, 5, 7 have been recently experimentally investigated and calculated by E. C. H. Hsu and J. F. Johnson, *Mol. Cryst. Liq. Cryst.* **20**, 177 (1973) with only little deviations to our results.
    Calculations of phase diagrams with liquid crystalline phases have been given by M. Domon and J. Billard, paper of the International Conference on Liquid Crystals Bangalore December 3-8, 1973; see also M. Domon, Thèse Paris: 1973.