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Phase Diagrams of Low-Melting Nematogenic Esters

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Phase Diagrams of Low-Melting Nematogenic Esters

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Binary, ternary and quaternary phase diagrams of six nematogenic esters were determined. In binary systems eutectic mixtures are usually formed but in one case a molecule-compound and in another a solid solution was formed. Except for these latter cases, both the experimentally determined and the thermodynamically calculated liquidus curves were in good agreement with each other. The quaternary mixture with negative dielectric anisotropy was found to have a melting point of +3°C.

1 INTRODUCTION

The appearance of low-melting nematogenic phenyl esters of aromatic carbonic acids promises some success in efforts to produce liquid crystal displays of good quality and durability. The substances—in contrast to the earlier used Schiff-bases—seem to be stable against electrochemical influences, and at the same time they do not exhibit the yellow colours of the similar chemically stable nematogenic azoxybenzene derivatives.[1]

Steinsträsser has found four compounds among the great number of phenyl benzoates to be the most suitable for producing display bases[2] (see Table I, compounds I-II-III-IV). Compounds V-VI were prepared by Ritvay-Emandity.[6]

According to Steinsträsser, the quaternary mixture of compounds I-IV possessing negative dielectric anisotropy, have a nematic temperature range between −20 and +52°C, but there are no data in the literature apart from Steinsträsser's incomplete allusions to the optimum concentration of the mixture.

The present paper is concerned with the solid to nematic and the nematic to isotropic phase transitions of the binary and ternary systems of compounds IV-V-VI, and of the binary, ternary and quaternary systems of compounds I-II-III-IV.

TABLE I

No.	Compounds	Nematic range °C
I.	*p*-*n*-hexyloxyphenyl-*p*'-butyryloxybenzoate	52–87
II.	*p*-methoxyphenyl-*p*-butyryloxybenzoate	78–84
III.	*p*-*n*-butylphenyl-*p*'-*n*-hexyloxybenzoate	47–49
IV.	*p*-*n*-hexyloxyphenyl-*p*'-*n*-butylbenzoate	29–46
V.	*p*-*n*-butylphenyl-*p*'-anisoyloxy-2-methylbenzoate	83–163
VI.	*p*-*n*-butylphenyl-*p*'-*n*-butyl-benzoyloxy-2-methylbenzoate	59–117

2 EXPERIMENTAL

The materials were prepared by classical organic chemistry methods, and were purified by vacuum distillation and multiple recrystallisation from methanol.

The transition temperatures were determined by thermo-optical apparatus.[3] The measurements were carried out at a heating rate of 0.5–1°C/min enabling the transition temperatures to be determined with an accuracy of ±0.3°C. The samples, which melted below room temperature, were quickly cooled in liquid nitrogen and were then kept at 10–15°C lower than the expected melting point until the formation of small crystallites, after which the melting temperatures were measured.

The enthalpy of fusion of the compounds were determined with a "Perkin–Elmer DSC-2" differential calorimeter. The weight of each sample was about 3 mg, and the heating rate was 10°C/min.

The experimental data concerning the system IV-V-VI are given in Figure 1, while Figures 2–4 represent the phase diagrams of the system I-II-III-IV.

The eutectic concentrations and transition temperatures of the examined two- and multicomponent systems together with the transition temperatures of the pure components are summarised in Tables II and III.

Table IV shows the enthalpy of fusion of the examined compounds.

3 DISCUSSION

General remarks

In the *binary phase-diagrams* the liquid curves have one minimum in every case. Although the measuring method used did not enable us to accurately determine the solidus lines it was nevertheless established, that the solidus

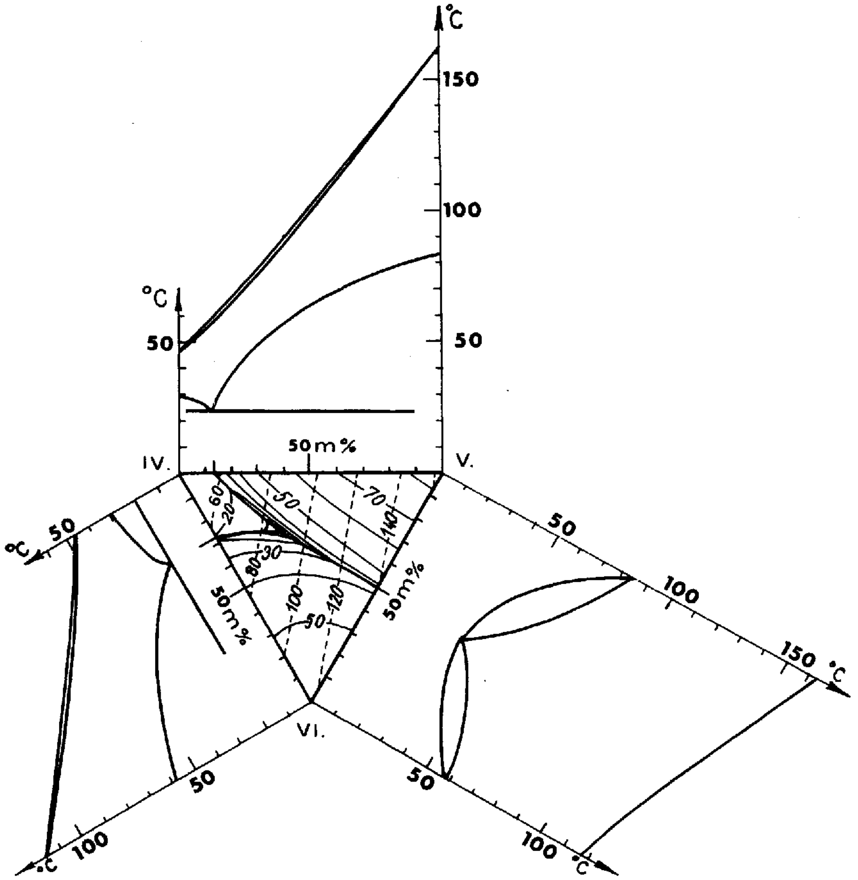

FIGURE 1 The phase diagrams of the system IV-V-VI. In the ternary diagram, the continuous curves are freezing isotherms, and the dotted curves are clearing isotherms.

lines are generally isotherms, according to the formation of a eutectic mixture. The system V-VI is an exception (Figure 1), as the shape of the solidus line indicates the possibility of the formation of uninterrupted mixed crystal series. This observation is in accordance with the experiments of Demus *et. al.*,[4] who found that such a considerable solid phase solubility does exist in the case of homologus compounds with nearly the same molecular length. It is noteworthy that the solid phase solubility of the isomeric compounds III and IV is very low, in spite of having the same molecular length. This is due to the opposite orientation of the central carboxylic groups in the two kinds of molecules (Figure 2).

TABLE II

Characteristic data of the system IV-V-VI (Figure 1)

Mole fraction			°C	
IV	V	VI	Melting point	Clearing point
—	1	—	83	163
—	—	1	58	117
1	—	—	29	46
—	0.50	0.50	38	138
0.72	—	0.28	20	62
0.87	0.13	—	24	57
0.48	0.26	0.26	9	85

TABLE III

Characteristic data of the system I-II-III-IV (Figures 2–4)

Mole fraction				°C	
I	II	III	IV	Melting point	Clearing point
1	—	—	—	52	87
—	1	—	—	78	84
—	—	1	—	47	49
—	—	—	1	29	46
0.56	0.44	—	—	34	84
0.67[a]	0.33[a]	—	—	25[a]	82[a]
—	0.26	0.74	—	39	52
—	—	0.33	0.67	9	47
—	—	0.33[a]	0.67[a]	0[a]	42[a]
—	0.14	—	0.86	23	47
0.24	—	—	0.76	26	53
0.50	—	0.50	—	26	64
0.40	0.18	0.42	—	18	60
—	0.09	0.30	0.61	6	47
0.19	0.17	—	0.64	19	57
0.03	—	0.32	0.65	8	47
0.03	0.09	0.29	0.59	3	47
no concentration data were given				−22[a]	52[a]

[a] Steinsträsser's data

TABLE IV

Enthalpy of fusion of the examined compounds

	V	VI	I	II	III	IV
cal/mole	5980	5210	4820	5935	5115	4250

TABLE V

Calculated and observed eutectic temperatures of multicomponent systems

	Eutectic temperature °C	
Eutectic	calculated	observed
IV-V	24	24
V-VI	44	38
IV-VI	18	20
IV-V-VI	13	9
I-II	39	34
II-III	36	39
III-IV	12	9
II-IV	23	23
I-IV	14	26
I-III	26	26
I-II-III	18	18
II-III-IV	6	6
I-II-IV	9	19
I-III-IV	2	8
I-II-III-IV	−2	3

The anomaly in the phase diagram of system I-IV (Figure 2) is probably caused by the formation of a molecular compound containing the two components in a ratio of 1:4.

Similarly shaped liquidus surface with a single minimum characterise the solid-nematic phase transitions of the examined *three-component systems* (Figures 1 and 3), but the systems containing both the I and IV materials show the influence of the local maximum melting point.

It is interesting that the melting liquidus surface penetrates the clearing temperature surface in the ternary phase diagrams of compounds II-III-IV so that the three enantiotropic liquid crystals form monotropic mixtures in a certain concentration range (Figure 5).

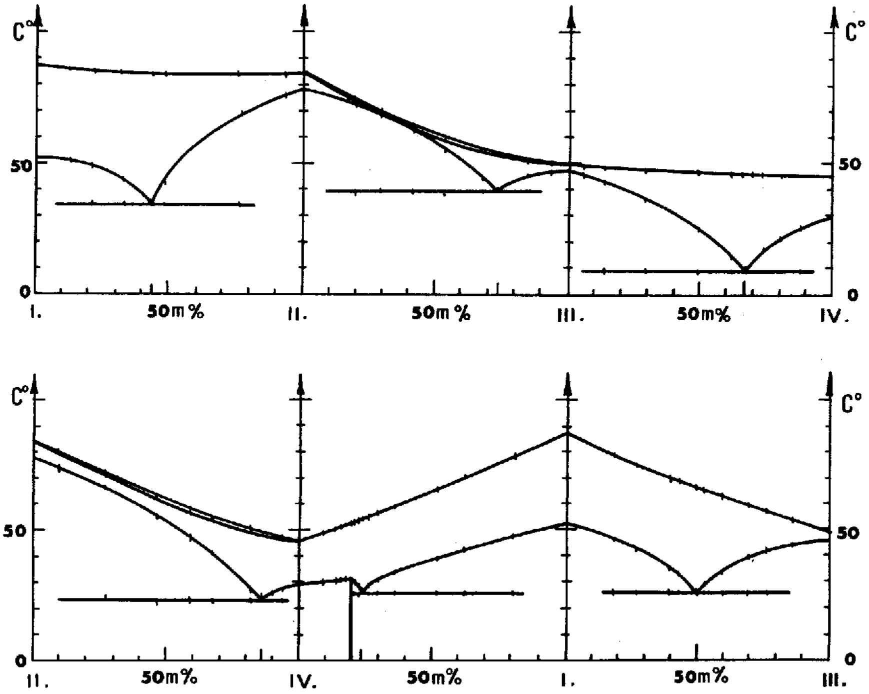

FIGURE 2 The binary phase diagrams of the system I-II-III-IV.

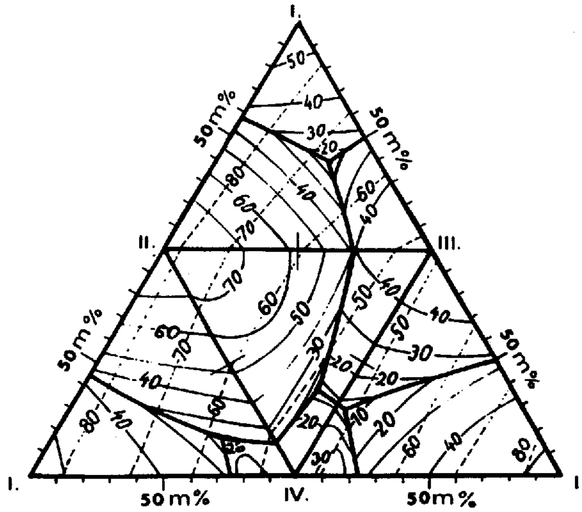

FIGURE 3 The ternary phase diagrams of the system I-II-III-IV. Continuous and dotted curves are freezing and clearing isotherms respectively.

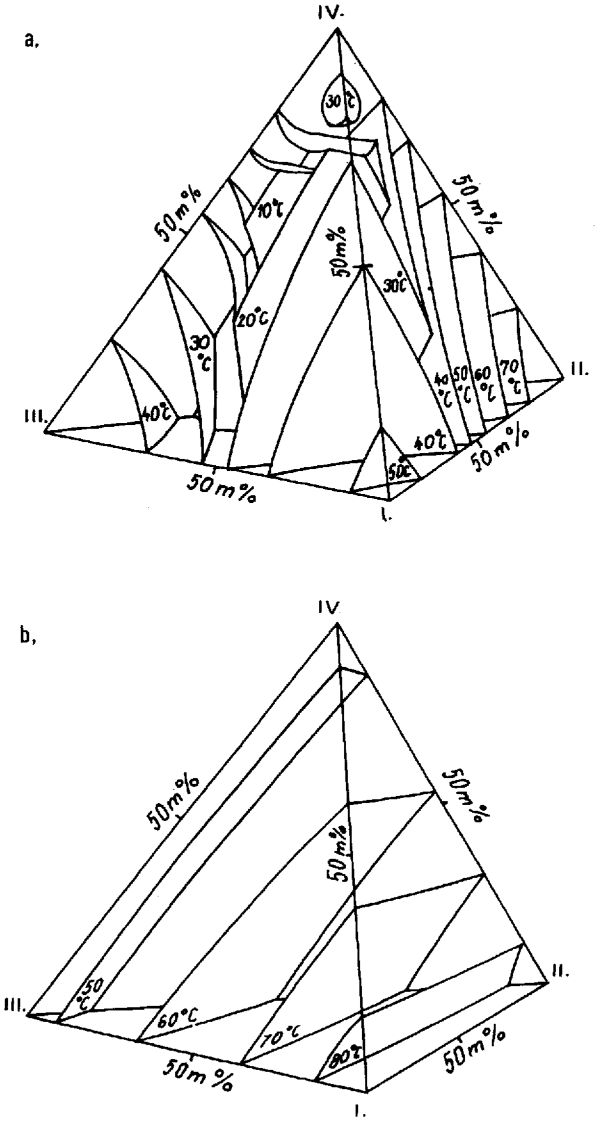

FIGURE 4 The quaternary phase diagram of the system I-II-III-IV represented with isothermal-surfaces
(a) melting liquidus function
(b) clearing temperature function

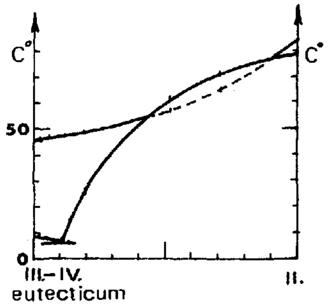

FIGURE 5 Monotropic mixture of three enantiatropic components.

The melting liquidus function and the clearing temperature function of the I-II-III-IV *quaternary system* are represented with isothermal-surfaces in Figures 4a and 4b, respectively. The separated 30°C isothermal surface surrounds the 31°C melting point of the molecule compound of substances I and IV. With regard to quaternary system, we have found very considerable and—from the aspect of the technical application—essential deviations from Steinsträsser's eutectic data (Table III). In that the melting points are higher in our experiments, it is assumed that Steinsträsser's materials were less pure, or that the considerable super-cooling effects of the nematic mixtures influenced his experimental data.

Thermodynamics

The liquidus curves of the individual components are compared in Figure 6. These curves were determined experimentally in different binary and ternary systems, and calculated on thermodynamical considerations using the equation:

$$\ln x_i = \frac{\Delta H_i}{R}\left(\frac{1}{T_i} - \frac{1}{T}\right) \tag{3.1}$$

where x_i is the mole-fraction of component "i" in the mixture
T the freezing point of the mixture
T_i the melting point of the pure component "i"
ΔH_i the enthalpy of fusion of the component "i"
R is the gas constant.

To formulate the equation it was assumed that the solubility of the component is negligible in the solid phase, the nematic phase is an ideal mixture, and the melting heat is independent of the melting temperature of the mixture.

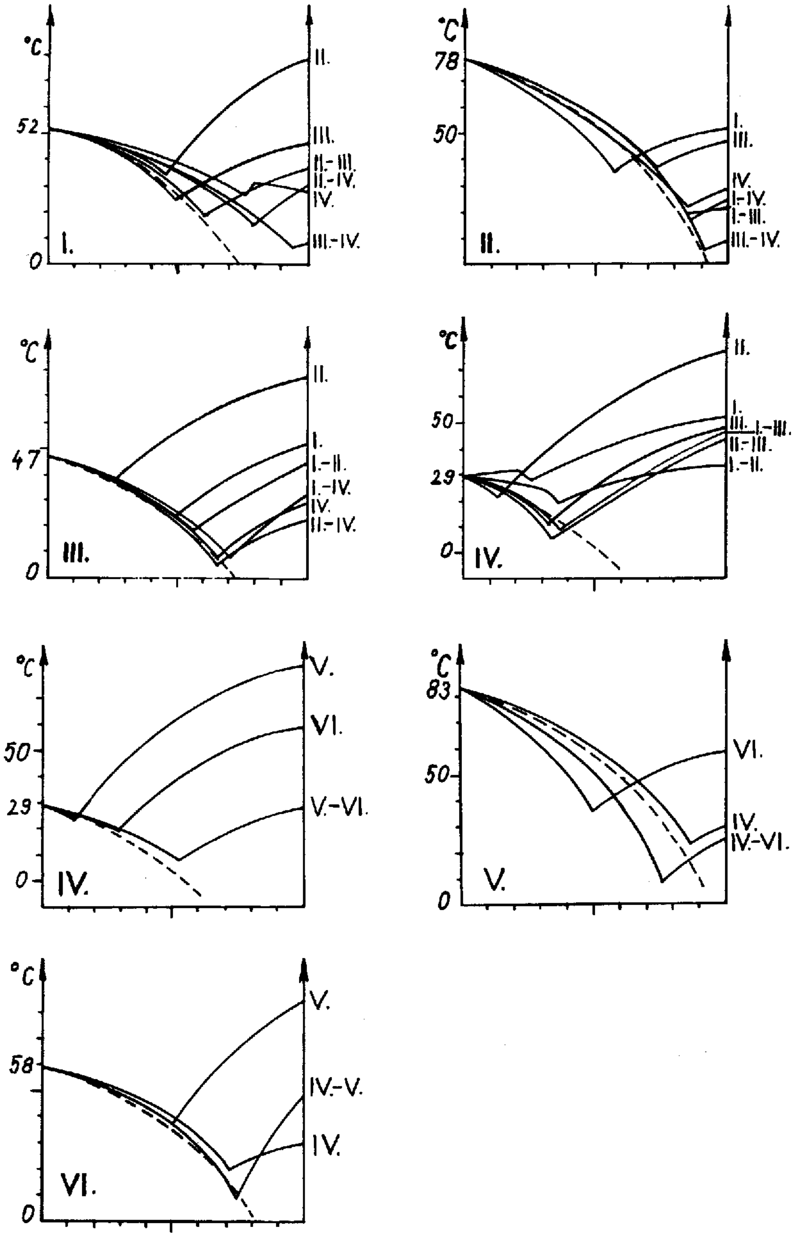

FIGURE 6 Comparison of the different liquidus curves of the individual components. Continuous curves are experimentally determined in two and three-component systems, and dotted curves are calculated with the equation 3.1.

Solving the equation 3.1 simultaneously for the multicomponent systems,[4] we calculated the eutectic temperatures, which are compared with the observed values in Table V.

Hsu *et al.*,[5] and Demus *et al.*,[4] also compared their experimental results using equation 3.1, and each of them established that the eutectic data of the azoxybenzene type nematogens may be estimated by the application of equation 3.1, if the solubility of the components was negligible. Our experimental results suggest that this estimation is generally applicable in the case of nematogenic phenyl benzoates, too. It can be seen that only in those cases, where the phase diagrams indicate considerable solid solubility (system V-VI, Figure 1) or non-ideal behaviour of the nematic mixture (system I-IV, Figure 2) is there a great difference between the experimental and calculated curves.

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