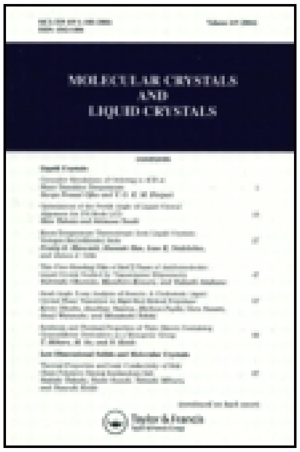


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Comparison of Methods for Determining the Eutectic Compositions of Ternary Liquid - Crystalline Mixtures

J. Szulc [a] , Z. Witkiewicz [a] & R. Dąbrowski [a]

[a] Institute of Chemistry, Military Technical Academy, 01 489 Warsaw, Poland

Version of record first published: 20 Apr 2011.

To cite this article: J. Szulc , Z. Witkiewicz & R. Dąbrowski (1984): Comparison of Methods for Determining the Eutectic Compositions of Ternary Liquid - Crystalline Mixtures, Molecular Crystals and Liquid Crystals, 109:2-4, 125-142

To link to this article: http://dx.doi.org/10.1080/00268948408078701

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 125–142
0026-8941/84/1094-0125/$18.50/0

Comparison of Methods for Determining the Eutectic Compositions of Ternary Liquid – Crystalline Mixtures

J. SZULC, Z. WITKIEWICZ and R. DĄBROWSKI
Institute of Chemistry, Military Technical Academy, 01 489 Warsaw, Poland

(*Received May 27, 1983; in final form December 29, 1983*)

Three methods of determining the eutectic compositions of ternary liquid crystal mixtures used as stationary phases in gas chromatography were compared. The method involving the heats of melting of the pure components of the mixtures and CSL equation, the method involving substitution of heats of melting of the components determined in binary mixtures into the CSL equation and a new, own method in which the eutectic composition of the mixture was determined by high-performance liquid chromatography.

INTRODUCTION

The determination of the eutectic composition of multicomponent mixtures is a significant scientific and technological problem. It has gained particular importance in connection with the search for new liquid-crystalline compositions used in information display devices.[1] Those compositions should reveal a wide mesophase range and a low melting point. This is why the mixtures of eutectic composition and the methods of their synthesis attract so much interest.

Liquid Crystals reveal advantageous properties as stationary phases in gas chromatography[2-6] where beside single compounds also mixtures of liquid crystals are used. The latter usually reveal greater selectivity and lower viscosity than the individual components of the mixture. The mixed liquid–crystalline stationary phase should reveal wide mesophase ranges as well as low melting points and low vapour pressures. These conditions are fulfilled by eutectic mixtures composed of compounds with high molecular weights.

In the recent years works have been carried out[7-10] devoted to the search for fairly simple methods that would allow determining the composition of eutectic mixtures with the use of small amounts of the components. The already known simple methods (computational ones) give proper results if the system fulfils the simplifying assumptions. The experimental methods giving results of some value are time-consuming and often require the use of large amounts of the substances. The methods of preparation of multicomponent eutectics have been reviewed in Ref. 11.

The determination of the composition of an eutectic, fairly simple in the case of binary mixtures, becomes complicated and very time-consuming for ternary and multicomponent mixtures. For the prediction of the eutectic composition of such mixtures use is made of the Le Chatelier, Schroder and Van Laar (CSL) equation.[12-14]

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

where: ΔH_i and T_i are the latent heat of melting and the melting point of the pure component i, x_i is the mole fraction of component i, T the melting point of the mixture, and R the gas constant. The composition of the eutectic mixture is found by substituting in that equation the values of the melting heats and melting temperatures of the components, as measured, e.g., with a scanning calorimeter.

The aim of the present work was to compare the methods of determining the eutectic compositions of ternary liquid crystal mixtures used as stationary phases in gas chromatography. The method involving the heats of melting of the pure components of the mixtures and the CSL equation, the method involving substitution of heats of melting of the components determined in binary mixtures into the CSL equation, and a new method in which the eutectic composition of the mixture was determined directly by high-performance liquid chromatography.

EXPERIMENTAL

Mixtures consisting of nematic liquid crystals (the smectic phase appears only in compound B_2 in the vicinity of the melting point) were tested. The methods of synthesizing and purifying those compounds are described in Refs. 15–17, and their phase transition temperatures are summarized in Table I.†

Method of determining the eutectic composition involving the use of the CSL equation and the melting enthalpies of the pure components

The melting enthalpies of the mixture components were measured with the Du Pont 910 scanning calorimeter. Aluminium trioxide was used as reference system. The masses of the tested samples were close to 10 mg. The weighing was carried out on an analytical balance with an accuracy up to 0.02 mg. The measurements were made during heating, the heating rate being 1 K/min in the phase transition region. Three measurements were made for each sample in nitrogen under isobaric conditions. The curves obtained were integrated graphically and converted to energy.

The determined molar melting enthalpies and temperatures were used for calculating the eutectic compositions of ternary mixtures. The calculations were carried out on a programmed Texas Instruments TI-57 calculator according to the scheme given in Ref. 18. In accordance with the results of calculations the components were weighed (the total weight of the sample being ca. 0.3 g), dissolved in chloroform and melted after evaporation of the solvent. Next the mixture was cooled to ambient temperature and again slightly heated to accelerate crystallization and prevent vitrification of the sample. A sample of the crystallized mixture was placed on the heated stage of a polarization microscope and its initial and final melting temperatures were measured.

Method of determining the ternary eutecting compositions on the base of the melting curves in binary systems

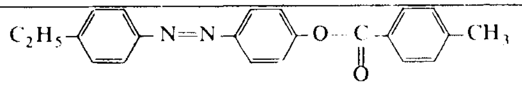
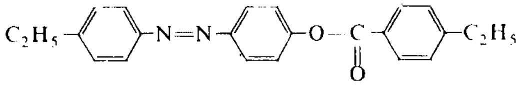
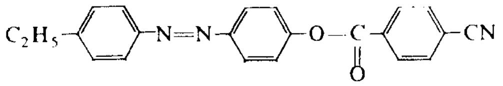
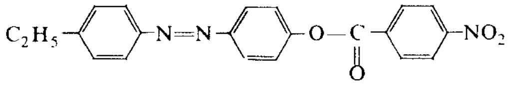
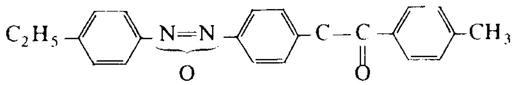
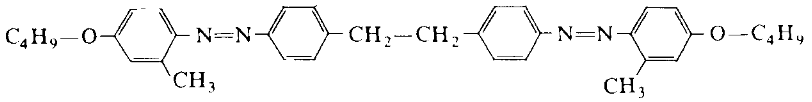
In the calculations of eutectic compositions use was made of the melting enthalpies found from the melting curves of the given component in binary systems. Those curves were determined basing on the final melting temperature of binary melts in which the given compound was in excess as compared to the eutectic composition.

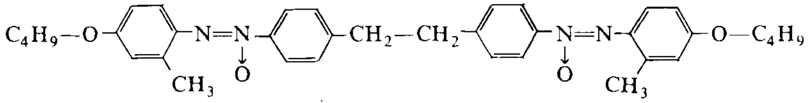
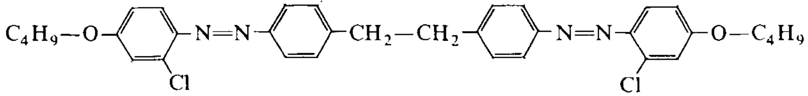
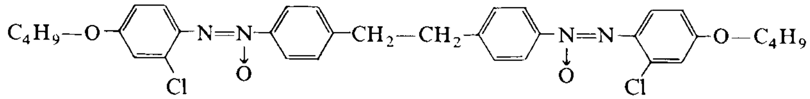
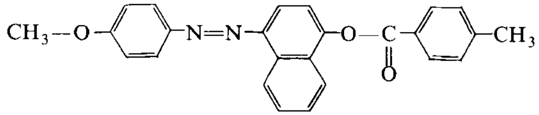
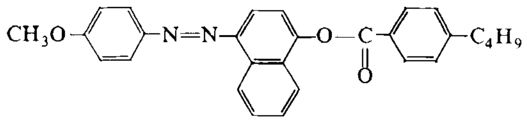
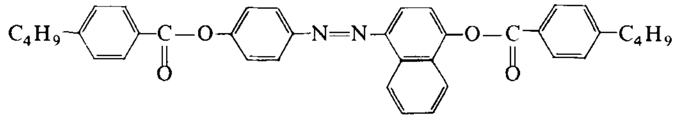
---

†The compounds are available on a commercial scale from ZOCh, Lublin, Mełgiewska 18, Poland.

TABLE I

Characteristic of investigated compounds

Notation 1	Formula 2	Temperature of: Melting (K) 3	 Clearing (K) 4
A_1		393	502
A_2		399	489
A_3		414	561
A_4		416	533
A_5		371	523
B_1		389 [392]	502

B_2		431	541
B_3		410	504
B_4		443	(540)
C_1		441	476
C_2		399	463
C_3		417	(566)

[ ] melting temperature of higher melting form
( ) clearing temperatures estimated from phase diagrams smectic in temperature range 431–441 K, above nematic.

The binary mixtures were prepared by weighing out their components in changing proportions on the average by 10 wt. %. The mass of the samples varied from 30 to 40 mg. The samples were melted and mixed. When there was a risk that the mixing might be insufficient, the mixture was dissolved in a volatile solvent, which was next evaporated. Samples liable to supercooling were slightly heated after cooling to prevent their vitrification. The phase transition temperatures of the mixtures obtained in this way were measured thermooptically by heating them in the region of the phase transitions at a rate of 0.5 K/min. When measuring the melting temperatures only one microscopic slide was used; when a cover glass was placed on the small quantity of the mixture its homogeneity was affected and the molten eutectic flowed to the sides leaving melted crystals of the component present in excess. In the described way the final melting temperature of the sample was determined.

After preliminary plotting the phase diagram basing on the measured final melting temperature of the mixtures, complementary mixtures were prepared so as to have at least four experimental points on each branch of the phase diagram. Then the dependence of the final melting temperature reciprocal of the component being in excess with respect to the eutectic composition was plotted as a function of the natural logarithm of the mole fraction of the given component in the mesomorphic solution. When it was found that the dependence is linear, what proved that a eutectic is present in the system, the directional coefficient and the free term in the equation below were calculated by the least squares method: $1/T = -R/\Delta H_i \ln x_i + 1/T_i$. Then the values of the melting enthalpy ΔH_i of the component i and of its final melting temperature T_i were found. The standard deviation of the melting enthalpy calculated from the standard deviation of the directional coefficient was contained in the range of 0.2–0.9 kJ/mole. The correlation coefficient was not lower than 0.99.

We referred to the calculated melting enthalpy as apparent since it includes the effects related to the existence of solid solutions and to the non-ideal character of the mesomorphic solution.

In the tested mixtures we obtained after melting a nematic phase even in the case of those including compound B_2 which is a smectic.

In order to avoid thermal decomposition, the clearing temperatures were measured by placing the sample on the microscopic stage (heated to a temperature close to the expected clearing temperature) between two microscopic slides. The clearing temperature was assumed as the point at which the mesophase appeared on cooling and disappeared on heating.

The eutectic composition of the ternary mixture was determined from equation (1) making use of the apparent melting enthalpies and melting temperatures of the components determined in the course of measurement carried out for three binary mixtures containing the given component. In some cases the values of the apparent melting enthalpy differed in two binary systems, whose components have been selected for obtaining the ternary eutectic. Then the mean apparent melting enthalpy of the given component from both binary systems was used in the calculations. The concentrations of the components in the ternary system were calculated and next apparent melting enthalpy was again determined for that system. For instance, the value of the apparent melting enthalpy of component A ($\Delta H_{A(ABC)}$) in the ABC ternary system was determined from proposed by us formula:

$$\Delta H_{A(ABC)} = \frac{x_B}{x_B + x_C} \Delta H_{A(AB)} + \frac{x_C}{x_B + x_C} \Delta H_{A(AC)}$$

where x_B and x_C are the mole fractions of compounds B and C, respectively, in the ternary system ABC, and $\Delta H_{A(AB)}$ and $\Delta H_{A(AC)}$ are the values of the apparent melting enthalpies of component A calculated from the eutectic curves for the binary AB and AC systems.

After evaluating the apparent melting enthalpy of the components we calculated again their concentrations in the ternary system. If the mole fractions calculated the first and second time differed by more than 1%, we calculated the apparent melting enthalpies again, substituting new calculated mole fractions into the formula.

Having calculated the eutectic compositions of the ternary mixtures we weighed out the required portions of their components and melted them. After crystallization we measured the melting temperatures and compared them with the calculated values.

Method of determining the eutectic compositions by liquid chromatography

The first step of the method consisted in preparing the ternary mixture of a composition not very distant from the eutectic one. For this purpose it was assumed that the molar melting heats of the components are equal and amount to 30 kJ/mole. Next we calculated, using the CSL equation, the concentrations of the components in the mixture. The assumed value of the molar melting heat has only a minor effect on the result obtained.

Portions of the components were weighed out in accordance with the results of calculations (totalling ca. 0.3 g), melted and mixed. Next the mixture was cooled to ambient temperature and then slightly heated.

The temperature corresponding to the beginning of melting of the mixture was measured thermooptically. At that temperature the eutectic was melted out from the greater part of the weighed out mixture. The remaining portion was used for determining the correction coefficients in chromatographic analysis. The melting out was carried out in a glass funnel with a G 3 fritted glass bottom connected to a vacuum flask (see Figure 1).

The melting out was carried out in an air thermostat with temperature control within ±1 K. Before the melting out procedure was started the sample was heat-conditioned for 2 hours at a temperature by 2 K lower than the initial melting temperature. Samples prepared the previous day were heat-conditioned for 15 min. The conditioning had for aim ensuring thermodynamic equilibrium of the system. After heat-conditioning the temperature of the thermostat was raised by

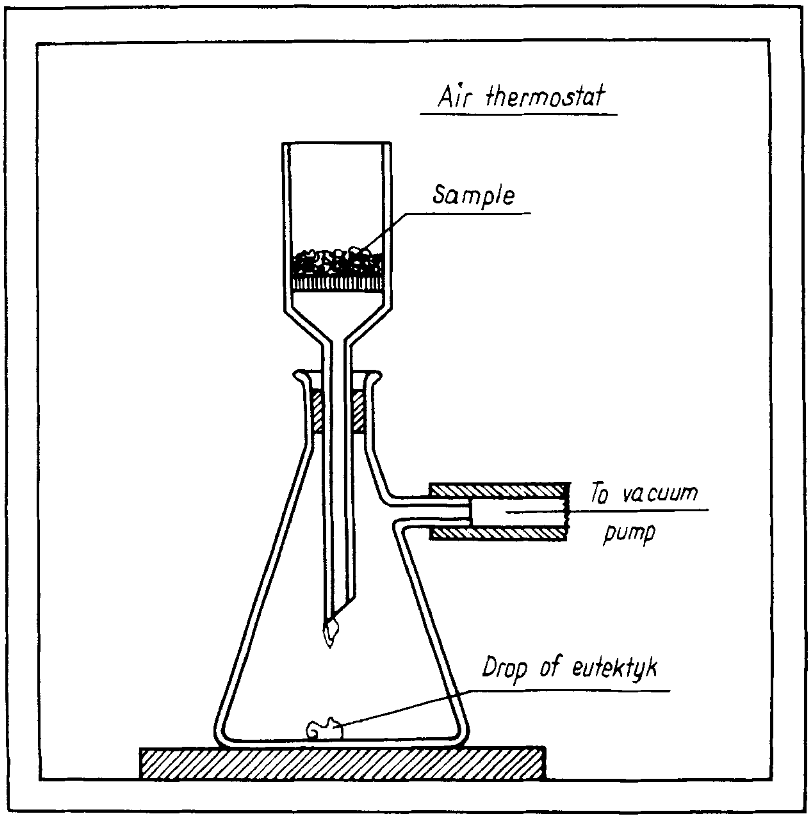


FIGURE 1

about 2 K and after 10 min the vacuum pump connected to the suction flask was put in operation. When the melting out was concluded the obtained drop of the eutectic was cooled and then heated in order to make it crystallize then the melting temperature of the mixture was measured. If the melting took place in the range of 3 K it was assumed that the melting out of the eutectic has been properly carried out. The melted out eutectic was next dissolved in chloroform so as to obtain a solution containing 3 mg of the mixture in 1 cm^3. The part of the mixture designed for determination of the correction coefficients was dissolved in a similar manner.

The components of the eutectic mixture and of the mixture of calculated composition were separated twice by high-performance liquid chromatography. A Pay Unicam liquid chromatograph was used with a LC-UV detector operating at wave length 270 nm. The column was 100 mm long and had 4 mm I.D. It was filled with silica gel Si 60 of 5 μm particle size. n-Hexane with an addition of chloroform (0.25–0.75%) was used as the eluent. The flow rate of the eluent was 1 cm^3/min. 10^{-3} cm^3 of the solution were introduced into the column. Example of chromatogram is given in Figure 2.

The surface areas of the peaks were measured by means of a planimeter and the calculations of the quantities of the components were found by the internal normalization method. The correction coefficients were calculated from the formula:

$$f_i = \frac{a_s w_i}{a_i w_s}$$

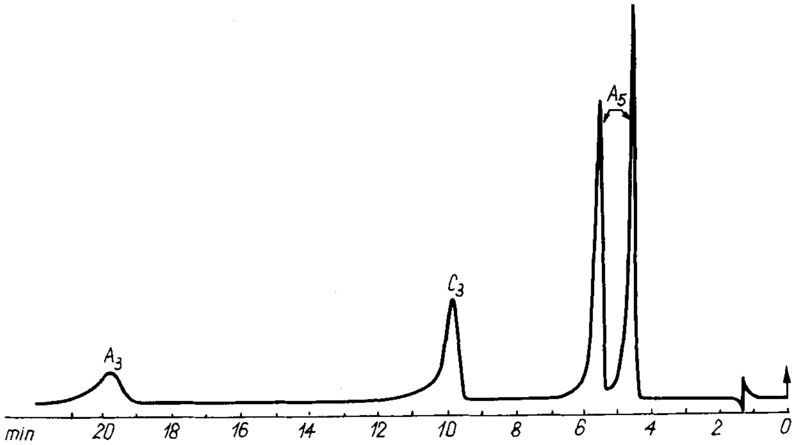


FIGURE 2

and the weight fractions of the eutectic components were found from the formula:

$$w_i = \frac{f_i a_i}{a_s + \Sigma f_i a_i}$$

where: a_s and a_i are the fractions of the surface area of the peak of the standard and that of one of the remaining components, respectively, in the total surface area of the peaks; w_s and w_i are weight fractions of the internal standard and one of the remaining components, respectively. The arithmetic mean values of the fractions giving the contribution of the peak surface area of each component to the total surface area of the peaks determined from four chromatograms were substituted into the second of these formulae.

RESULTS AND DISCUSSION

In the first method the compositions of the ternary eutectics were calculated making use of the melting enthalpies of the particular components, upon which melts of those compositions were prepared. The melting temperatures of 40 mixtures containing compound A_1 as one of the components have been tested thermooptically. In all cases the measured temperatures were higher than the calculated ones. The presence of an eutectic system was ascertained only in seven cases: $A_1B_2C_3$, $A_1B_2C_1$, $A_1B_3C_1$, $A_1B_4C_1$, $A_1B_3C_3$, $A_1B_4C_3$ and $A_1C_1C_3$. In those systems the temperatures at which the liquid appeared were also by at least 5 K higher than the calculated melting temperatures, and the melting (to the disappearance of the last crystal) proceeded in the range of 4 to 10 K.

In order to find why the first method did not give good results, the greater part of the binary systems composed of the tested compounds were studied. They are summarized in Table II, classified into groups according to the obtained type of the phase diagram. For systems with one eutectic point the apparent melting enthalpy of the components was calculated in the binary systems. The results are summarized in Table III. It was found that the apparent melting enthalpies of a given component differ in different binary systems, sometimes even significantly, and they are usually greater than the melting enthalpy of a pure component. It is very probable that those differences between the apparent and real melting enthalpies are due to that the eutectics are composed of saturated solutions and not of the pure components. The solubility of a given compound in other compounds may vary, and therefore the value of the apparent melting enthalpy depends on the kind of the other component. This hypothesis is supported by the fact that the systems containing compound C_3 reveal small differences between the real and apparent melting enthalpies of the components. In the cases of systems with compound C_3 probably small mutual solubility of the components take place, what is due to that the molecules of compound C_3 differ largely in shape from the molecules of the other compounds. It is believed that the values of the apparent enthalpies are in the cases tested in the present work only little affected by the unideal state of the mesophase. Only in the case of systems with compound A_4 the effect of specific interactions in the region of the mesophase is very distinct and therefore the apparent melting enthalpies of the particular components in the systems $A_4 + A_5$, $A_4 + B_1$, $A_4 + B_2$, $A_4 + B_3$, $A_4 + B_4$ and $A_4 + C_1$ are smaller than those of the pure components.

The observations made during the determination of the phase diagrams have allowed us to detect a certain regularity. The compounds whose molecules differ in shape (e.g. length) but not as regards

TABLE II

Two components systems investigated thermooptically

Systems with			
continuous solutions with a minimum on the melting curve	intermolecular compound melting		one eutectic
	congruently	incongruently	
$A_2 + A_5$, $A_1 + A_5$, $A_1 + A_2$	$A_1 + A_3$, $A_2 + A_3$, $A_1 + A_4$	$A_5 + B_3$, $A_1 + C_2$, $A_5 + C_2$	$A_1 + B_2$, $A_1 + B_3$, $A_1 + B_4$, $A_1 + C_1$, $A_1 + C_3$, $A_2 + A_4$, $A_2 + B_2$, $A_2 + B_3$, $A_2 + B_4$, $A_2 + C_1$, $A_2 + C_2$, $A_2 + C_3$, $A_3 + A_4$, $A_3 + A_5$, $A_3 + B_1$, $A_3 + B_2$, $A_3 + B_3$, $A_3 + B_4$, $A_3 + C_1$, $A_3 + C_2$, $A_3 + C_3$, $A_4 + A_5$, $A_4 + B_1$, $A_4 + B_2$, $A_4 + B_3$, $A_4 + B_4$, $A_4 + C_1$, $A_4 + C_2$, $A_4 + C_3$, $A_5 + B_2$, $A_5 + C_3$, $B_1 + B_2$, $B_1 + C_2$, $B_1 + C_3$, $B_2 + B_3$, $B_2 + C_1$, $B_2 + C_2$, $B_2 + C_3$, $B_3 + C_1$, $B_3 + C_2$, $B_3 + C_3$, $B_4 + C_1$, $B_4 + C_2$, $B_4 + C_3$, $C_1 + C_3$, $C_2 + C_3$

TABLE III

Comparison of apparent and real melting enthalpies

component second first[a]	A_1	A_2	A_3	A_4	A_5	B_1	B_2	B_3	B_4	C_1	C_2	C_3	real melting enthalpies
A_1							32.0	29.9	31.5	28.7		26.2	25.1
A_2			31.1	28.3		24.5	27.1	27.7	26.1	34.0	26.8	25.0	22.2
A_3				34.0	22.1	24.1	23.4	28.6	24.4	25.3	24.5	20.6	20.0
A_4		38.5	55.7		33.0	36.1	30.5	32.0	32.2	33.2	34.6	35.3	34.3
A_5			32.5	63.8			58.2					28.2	22.4
			50.9	37.3			50.2				61.1	58.2	50.9
B_1[b]		57.8									57.9	65.9	
B_2	48.7	51.8	49.2	46.4	53.4	62.1		63.5		52.5	55.5	62.0	42.9
B_3	59.0	57.5	59.3	45.5			58.4			66.0	60.0	55.3	46.4
B_4	57.1	60.7	53.1	48.2	52.7					54.5	58.8	60.6	46.5
C_1	42.7	46.0	41.3	36.0			42.9	42.7	38.0			40.0	36.4
C_2		38.2	38.4	35.7		45.4	40.6	45.0	40.8			36.6	33.5
C_3	36.5	40.0	47.7	34.8	36.5	38.2	36.1	42.1	44.1	38.2	39.2		32.3

[a] melting enthalpies of the first components (kJ/mole) are shown.
[b] values on the top refer to higher melting form.

polarity, what means that they do not have different terminal functional groups nor other fragments that might react specifically, dissolve well in the mesophase but are insoluble or poorly soluble in the solid.

If the molecules of the compounds included in the binary system differ but slightly as regards their structure, then they reveal a tendency to form continuous solutions. In the systems tested we chiefly have continuous solutions with a minimum on the melting temperature curve. If the molecules of the components contain terminal groups that differ as regards their chemical character, then they may yield intermolecular compounds in the solid phase.

The calculated apparent melting enthalpies served for computing the composition of 49 ternary systems. The compositions and clearing points as well as the melting temperatures of 42 ternary eutectic systems are summarized in Table IV. The agreement of the computed and experimental temperatures is good. The melting of the mixtures prepared on the basis of calculations takes place in the range of 2 to 5 K what can be considered as a good result if we take into account the fact that the pure compounds melt in the range of 2 to 3 K. Only seven systems: $A_1A_4B_3$, $A_2B_2C_3$, $A_3A_4C_1$, $A_3C_2C_3$, $A_3A_5C_3$, $A_4B_2C_1$ and $A_2B_2C_3$ melted in a wider temperature range.

TABLE IV

Characteristic of ternary eutectic systems computed by second method

No	Components	Mole fractions	Calculated temperatures of:		Measured temperatures of:	
			Melting K	Clearing K	Melting K	Clearing K
1	2	3	4	5	6	7
1.	A_1	0.671	377.5	509	379	508
	B_2	0.120				
	B_3	0.209				
2.	A_1	0.712	378.7	507	379	505
	B_2	0.147				
	C_1	0.141				
3.	A_1	0.625	371.9	531	371	527
	B_2	0.096				
	C_3	0.279				
4.	A_1	0.668	375.7	499	375	499
	B_3	0.200				
	C_1	0.132				
5.	A_1	0.755	381.0	503	380	498
	B_4	0.081				
	C_1	0.164				
6.	A_1	0.590	369.6	524	370	522
	B_3	0.158				
	C_3	0.252				
7.	A_1	0.653	373.7	530	372	528
	B_4	0.054				
	C_3	0.293				
8.	A_1	0.615	371.3	523	374	522
	C_1	0.116				
	C_3	0.269				
9.	A_2	0.562	375.1	512	375	513
	A_4	0.313				
	B_2	0.125				
10.	A_2	0.569	377.7	509	377	511
	A_4	0.333				
	B_4	0.071				
11.	A_2	0.547	375.7	501	376	504
	A_4	0.314				
	C_1	0.139				
12.	A_2	0.440	364.2	488	364	489
	A_4	0.221				
	C_2	0.339				
13.	A_2	0.499	368.6	525	368	528
	A_4	0.254				
	C_3	0.247				
14.	A_2	0.632	378.7	502	378	499
	B_2	0.119				
	B_3	0.249				
15.	A_2	0.685	383.3	489	392	494
	B_2	0.161				
	C_1	0.154				

TABLE IV(*Continued*)

No 1	Components 2	Mole fractions 3	Calculated temperatures of:		Measured temperatures of:	
			Melting K 4	Clearing K 5	Melting K 6	Clearing K 7
	A_2	0.522				
16.	B_2	0.083	369.3	484	370	480
	C_2	0.395				
	A_2	0.615				
17.	B_3	0.247	379.3	493	378	491
	C_1	0.138				
	A_2	0.495				
18.	B_3	0.142	368.0	482	368	479
	C_2	0.363				
	A_2	0.559				
19.	B_3	0.188	372.5	517	372	514
	C_3	0.253				
	A_3	0.498				
20.	A_4	0.317	382.9	547	383	547
	B_2	0.185				
	A_3	0.543				
21.	B_2	0.156	383.6	535	383	533
	B_3	0.301				
	A_3	0.601				
22.	B_2	0.198	386.4	539	387	540
	C_1	0.201				
	A_3	0.460				
23.	B_2	0.103	372.8	513	372	511
	C_2	0.437				
	A_3	0.577				
24.	B_2	0.137	380.6	558	385	
	C_3	0.286				
	A_3	0.531				
25.	B_3	0.288	383.4	542	384	525
	C_1	0.181				
	A_3	0.430				
26.	B_3	0.163	371.5	507	371	505
	C_2	0.407				
	A_3	0.516				
27.	B_3	0.227	377.4	545	377	548
	C_3	0.257				
	A_3	0.641				
28.	B_4	0.122	390.2	537	390	537
	C_1	0.237				
	A_3	0.476				
29.	B_4	0.056	374.7	510	376	505
	C_2	0.468				
	A_3	0.609				
30.	B_4	0.084	383.1	560	384	
	C_3	0.307				
	A_3	0.557				
31.	C_1	0.164	379.3	549	380	548
	C_3	0.279				

TABLE IV (*Continued*)

			Calculated temperatures of:		Measured temperatures of:	
No 1	Components 2	Mole fractions 3	Melting K 4	Clearing K 5	Melting K 6	Clearing K 7
32.	A_4	0.460	383.6	521	387	525
	B_2	0.161				
	B_3	0.379				
33.	A_4	0.360	376.7	489	376	500
	B_2	0.126				
	C_2	0.514				
34.	A_4	0.442	383.1	510	388	515
	B_3	0.355				
	C_1	0.203				
35.	A_4	0.331	373.6	494	376	495
	B_3	0.223				
	C_2	0.446				
36.	A_4	0.375	377.9	535	381	536
	B_3	0.292				
	C_3	0.333				
37.	A_4	0.512	391.9	519	392	517
	B_4	0.162				
	C_1	0.286				
38.	A_4	0.373	378.4	495	378	497
	B_4	0.081				
	C_2	0.546				
39.	A_4	0.454	385.5	551	386	
	B_4	0.113				
	C_3	0.433				
40.	B_2	0.223	395.3	508	395	509
	B_3	0.516				
	C_1	0.261				
41.	B_2	0.150	389.0	536	389	531
	B_3	0.414				
	C_3	0.436				
42.	B_2	0.201	393.7	543	394	547
	C_1	0.261				
	C_3	0.528				

Thermooptical testing of those systems has shown that in several cases the major part of the sample melts at one temperature, and only a small portion remains unmelted. This allowed us to believe that if the components were mixed in other proportions than those found in the calculations, the whole sample would melt at one temperature, lower than the melting points of the components. The chromatographic method was applied to find such compositions of those mixtures. In order to test the method, it was applied to determine the compositions of several known eutectic mixtures. The results are given in Table V. The mole fractions of mixtures 1, 3 and 6 calculated by the

TABLE V

Characteristic of ternary eutectic systems computed by chromatographic method

No	Components	Mole fractions	Melting temperatures (K)
1	A_2	0.56 ± 0.05	371–375
	A_4	0.30 ± 0.03	
	C_1	0.14 ± 0.03	
2	A_2	0.62 ± 0.04	372–375
	B_2	0.11 ± 0.03	
	C_3	0.27 ± 0.03	
3	A_3	0.50 ± 0.04	381–384
	A_4	0.30 ± 0.03	
	B_2	0.20 ± 0.03	
4	A_3	0.49 ± 0.03	379–383
	A_4	0.29 ± 0.03	
	C_1	0.22 ± 0.03	
5	A_3	0.21 ± 0.03	352–355
	A_5	0.65 ± 0.04	
	C_3	0.14 ± 0.02	
6	A_3	0.60 ± 0.03	381–387
	B_2	0.20 ± 0.02	
	C_1	0.20 ± 0.03	
7	A_4	0.49 ± 0.05	386–391
	B_2	0.24 ± 0.02	
	C_1	0.27 ± 0.03	

chromatographic method and found by the one making use of apparent melting enthalpies reveal good agreement, and all the mixtures of the composition determined chromatographically melt completely in the range of 5 K. This is a proof of the correctness of the method.

The clearing of the binary mixtures tested thermooptically occurred in a narrow temperature range (ca. 2 K). The temperatures of appearance and disappearance of the mesophase were the same within the limits of the experimental error. Therefore only one line was obtained in the plots which was common for the turbidity and clearing temperatures. In most cases that was a straight line connecting the clearing temperatures of the pure components. In some cases the line was slightly concave or convex. In several cases the departures from linearity were quite significant, e.g. for $A_4 + A_5$ and $A_3 + B_1$ systems. Those deviations were due to that the mesophase was not ideal. On the other hand small departures from linearity are due to the differences in the molecular clearing heats. It has been found that in such cases the linearity of the curve can be considerably improved by plotting it as a function of weight per cent instead of the molar fraction. For that purpose we used the calculated clearing temperatures of compounds decomposing before those temperatures are reached, making use of the clearing temperature versus weight per cent plot. Likewise, when calculating the clearing temperatures of eutectics, use was made of weight per cents advantage being taken of the principle of additivity. The clearing points calculated by this method as well as the measured clearing temperatures of ternary eutectics are presented in Table IV.

When calculating the clearing temperatures it is not always advantageous to express concentrations in weight titer instead of molar titer. This is the case when the compositions of a mixture are given in molar titer but the clearing temperature plot is linear. Then expressing concentration in mole titer is evidently more convenient.

CONCLUSIONS

The lack of success in calculating multicomponent eutectics with the use of the CSL equation and the melting enthalpies of the components is due to that the tested systems containing compound A_1 do not fulfil the simplifying assumptions made when deriving the CSL equation. There are many compounds with which compound A_1 does not yield simple eutectics. In those cases when eutectics are obtained, many of them are composed of saturated solutions and not of the pure compounds.

The second method yielded better results, since the calculations were carried out only for those ternary systems whose three pairs of components gave eutectics. The occurrence of eutectics in binary systems allowed us to expect the same kind of interactions in the ternary systems. Furthermore the use of apparent melting enthalpies took largely into account the solubility of the components in the solid phase.

In spite of the fact that the experimental way of obtaining the eutectic by the chromatographic method seems difficult to use, sometimes it is worth the while because the chromatographic method gives good results irrespective of the character of interactions between the components. It allows the determination not only of the composition of a simple eutectic but also that of one of the eutectics combined with an intermolecular compound or the concentration of a mixture with the lowest melting temperature in the system in which the solid continuous solution occurs (with a minimum on the melting temperature curve). The consumption of the tested substance is small in the chromatographic method.

The chromatographic method as well as the one making use of the apparent melting enthalpies allow to determine the compositions of multicomponent eutectics without the need to carry out preliminary calorimetric measurements. Those methods have, however, certain limitations. Among them is the difficult determination of the composition of multicomponent mixtures which reveal a tendency to supercool. Thus the application of those methods to low-temperature liquid crystals is limited for technical reasons.

In the case of eutectics composed of compounds whose molecules differ in shape, the CSL method gives satisfactory results being at the same time simple. In other cases the results obtained by the CSL method are deceptive and the methods described by us give better results.

References

1. J. A. Castellano and K. J. Harrison, in The Physics and Chemistry of Liquid Crystal Devices, G. J. Sprokel (Ed.), Plenum Press, New York, 1980, 263.
2. H. Kelker and R. Hatz, Handbook of Liquid Crystals, Chemie Verlag, Weinheim, 1980.
3. G. Kraus and A. Winterfeld, *Wiss. Z. Univ. Halle*, **27**, No. 5, 83 (1978).
4. G. M. Janini, *Advan. Chromatogr.*, **17**, 231 (1979).
5. M. S. Vigdergauz, R. V. Vigalok and G. V. Dmitrieva, *Usp. Khim.*, **50**. 943 (1981).
6. Z. Witkiewicz, *J. Chromatogr.*, **251**, 311 (1982).
7. J. Malthete, M. Ledercq, J. Gabard, J. Billard and J. Jacques, *C. R. Acad Sci., ser. C*, **273**, 265 (1971).
8. D. Demus, Ch. Fietkau, R. Schubert and H. Kehlen, *Mol. Cryst. Liq. Cryst.*, **25**, 215 (1974).
9. V. A. Molochko, O. P. Chernova and G. M. Kurdumov, *Zh. Prikl. Khim.*, **1**, 45 (1977).
10. A. V. Ivashchenko and V. V. Titov, *Zh. Phys. Khim.*, **51**, 1581 (1977).
11. J. Szulc and Z. Witkiewicz, *Wiad. Chem.*, **36**, 31 (1982).
12. H. Le Chatelier, *C. R. Acad. Sci.*, **100**, 50 (1885).
13. I. Z. Schroder, *Z. Phys. Chem.*, **11**, 449 (1893).
14. J. J. van Laar, *Z. Phys. Chem.*, **63**, 216 (1908).
15. Z. Witkiewicz, M. Pietrzyk and R. Dąbrowski, *J. Chromatogr.*, **177**, 189 (1979).
16. A. Ziółek, R. Dąbrowski and Z. Witkiewicz, *Mol. Cryst. Liq. Cryst.*, to be published.
17. Z. Witkiewicz, J. Szulc, A. Ziółek, R. Dąbrowski and J. Dziaduszek, *J. Chromatogr.*, **246**, 37 (1982).
18. D. S. Hulme, E. P. Raynes and K. J. Harrison, *J. C. S. Chem. Comm.*, 98 (1974).