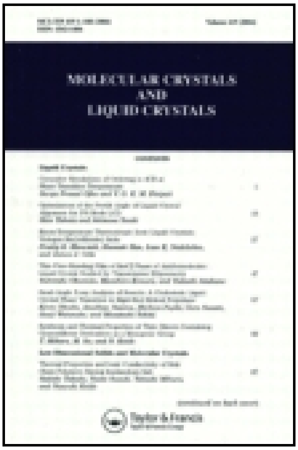

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Experimental Methods for Determining the Eutectic Composition of a Multi-Component Liquid Crystal Mixture

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Experimental Methods for Determining the Eutectic Composition of a Multi-Component Liquid Crystal Mixture

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Experimental techniques are described for determining the eutectic composition of multicomponent mixtures of nematic liquid crystals. These techniques were applied to the formulation of nematic esters, when the idealized eutectic composition calculated by the Schroeder-Van Laar relationship did not give a good melting point minimum for the mixture. One experimental procedure was based on the assumption that the composition of the initial nematic melt from a frozen, crystallized mixture is closer to a true eutectic than is the calculated value from which the frozen mixture was formulated. Another experimental procedure was based on the assumption that a new eutectic could be obtained by adding small amounts of a new component to an existing multi-component eutectic mixture, using the a plot of the melting point versus the percentage of the new component added to determine a new eutectic mixture corresponding to a new melting point minimum. High performance liquid chromatography was used to estimate the purity of each component, and to analyze quantitatively the component composition of each melt. The calibration plots for each liquid crystal component, as well as the chromatographic analysis of the mixtures are shown.

Keywords: eutetic nematic mixtures, liquid chromatography, Schroeder-Van Laar equation, phenylbenzoates, experimental methods

1. INTRODUCTION

Nearly all practical applications of liquid crystals require electro-optical and physical properties which can be obtained only by formulating multi-component mixtures of liquid crystal components. The Schroeder-Van Laar equation has been used for many years to calculate idealized eutectic mixtures,[1,2] and in our laboratories we have applied it extensively to the formulation of multi-component mixtures of various types of nematic ester liquid crystals.[3–5] This calculation assumes that each component in a mixture essentially acts as a completely non-interacting impurity in lowering the melting point of each other component. By using special selection rules for the combination of liquid crystal components,[5–7] it is possible to obtain many mixtures in which the observed melting point is close to the calculated eutectic value. However, in many other cases the components selected do not from an idealized mixture, so that the liquid crystal mixture has a considerably higher melting point than that of the calculated eutectic mixture. In this paper, we present details of two experimental methods which we used to determine eutectic compositions which had improved properties compared to those of the calculated mixtures.[8]

2. EXPERIMENTAL

The ester liquid crystal components used in these studies were synthesized and purified by standard methods, as previously described.[3–6] Their purity was confirmed by differential scanning calorimetry (DSC) and by HPLC (high performance liquid chromatography), which typically showed impurity levels of less than about 0.2%. The DSC equipment used was a Mettler TA2000B thermal analysis system. The HPLC equipment used was a Waters Associates Model ALC-202/401 with a microporasil column, using dual 254 nm absorbance detectors. Impurity amounts were determined from the sum of all of the chromatographic peaks which were observed besides the main component peak, arbitrarily assigning all of the peaks the same sensitivity as that of the main component. Low temperature melting point ranges were determined by cooling the samples in tubes for an extended period at a low temperature, typically at −40 or −17°C, transferring the tubes into a controlled isopropanol bath initially at −20°C, and observing the temperature at which melting began, as well as the temperature at which all the crystals melted as the bath was slowly warmed.[6] Samples for HPLC analysis of the first melt from a slowly warmed frozen liquid crystal mixture were obtained by separating the sample by cold centrifugation when the melt initially appeared, and then removing the melt with a syringe needle.

3. RESULTS AND DISCUSSION

Our studies began with a 9-component liquid crystal mixture containing the components listed in Figure 1, which also shows the abbreviation codes used for these structures and their nematic ranges as determined by DSC. A typical DSC plot showing the melting point and clearpoint of 6O-O1 is shown in Figure 2. Each liquid crystal was purified to yield minimal impurities, as indicated by the typical HPLC curves in Figure 3 for 2O-[C]3, which showed about 0.05% impurities. The Schroeder-Van Laar equation was used to calculate a eutectic mixture from these nine components. The composition of this calculated mixture, which is named HRL-256N1, is shown in the first weight percent column of Table I. When the Schroeder-Van Laar equation is satisfied for each component, the mixture will be a eutectic mixture if ideal interaction (non-interaction) occurs. The calculated melting point of this mixture was 0°C. However, the actual melting of HRL-256N1 had a range of 8 to 20°C, showing that it was not a particularly good eutectic mixture.

The Schroeder-Van Laar relationship, Equation 1, is used to estimate the crystal to nematic melting point and the mole fraction of the components in an ideal eutectic mixture:

$$T_i = \frac{\Delta H_f}{(\Delta H_f/T_M) - R \ln x_i}. \tag{1}$$

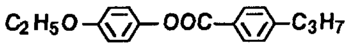
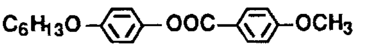
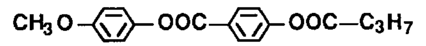
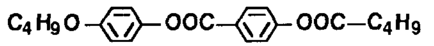
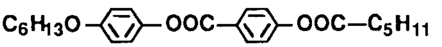
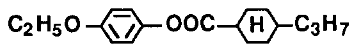
STRUCTURE	CODE	NEMATIC RANGE (°C)	
		mp	clpt
	20-3	74.5	65.2
	20-5	62.8	63.3
	60-01	55.0	77.4
	10S5	63.8	72.0
	10S06	65.0	100.0
	10-00C3	81.1	84.4
	40-00C4	67.2	84.0
	60-00C5	50.7	86.0
	20-[C]3	48.1	79.0

FIGURE 1 Structures, code, and nematic range of liquid crystals used in nine-component mixtures.

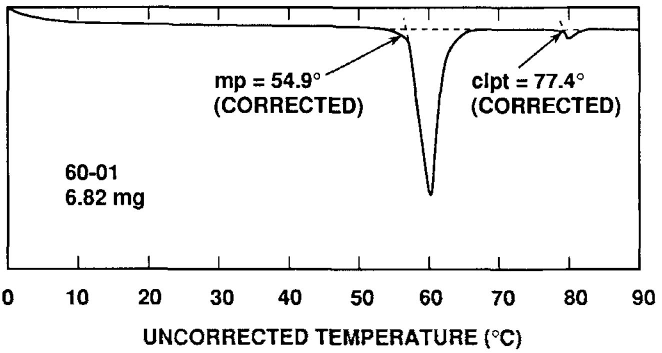


FIGURE 2 DSC of *p*-hexoxyphenyl *p*-methoxybenzoate.

where: T_i = the upper end of the melting range with the i component in the mixture, ΔH_f = the molar hear of fusion of the pure compound i, T_M = the melting point of the pure compound, x_i = the mole fraction of component i in the mixture, and R = the gas constant.

We decided to try an experimental procedure to obtain a better eutectic for HRL-256N1, based on the assumption that the composition of the initial nematic melt from a frozen, crystallized mixture would be closer to a true eutectic than the calculated value from which the frozen mixture was formulated. This method consisted of the following steps: thoroughly crystallizing the calculated mixture at a low temperature, partially melting it and separating this melt from the crystals,

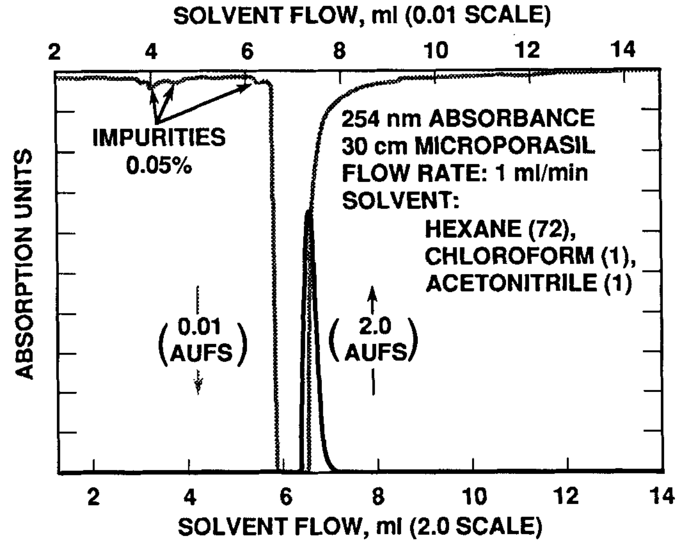


FIGURE 3 HPLC analysis of 2O-[C]3, showing two sensitivity scales of 2.0 and 0.01 absorption units full scale.

Table 1. Revised Nine-Component Eutectic Mixture

Component	Impurity Level	Calc. Wt. %	HPLC Analysis Initial Wt.%	HPLC Analysis 3rd Melt Wt.%
2O - 3	0.19	6.96	6.9	7.3
2O - 5	0.04	8.22	7.9	8.3
6O - O1	0.10	14.50	15.4	15.4
1O S 5	0.01	14.98	14.0	15.5
1O S O6	0.17	10.41	10.8	11.3
1O - OOC3	0.04	3.89	4.5	4.5
4O -OOC4	0.02	5.59	5.5	6.3
6O - OOC5	0.02	20.96	21.9	17.2
2O - [C]3	0.05	14.49	14.4	14.4
Total Wt.%	0.06	100.00	101.3	100.2
HRL Mixture No.	--------	256N1	256N1	256N4
mp Range, °C	--------	-0.2° (Calc.)	8° to 20° (Obs.)	6° to 13° (Obs.)
Clpt., °C	--------	78.9° (Calc.)	77° (Obs.)	76° (Obs.)

analyzing the composition of the melt, and then reiterating this procedure with a second melt from the crystallized first melt, etc. High performance liquid chromatography[9] was used to estimate the purity of each component, and to analyze quantitatively the component composition of each melt. The calibration plots for each liquid crystal component are shown in Figures 4 and 5, using two different solvent systems in the volume ratios indicated. The HPLC analyses of the complete mixture, under the two sets of conditions (as used in the calibrations of each component) which give good separation for each peak, are shown in Figures 6 and 7. The results of this analysis as applied to the initial HRL-256N1 composition is shown in the second weight percent column of Table I. After thoroughly freezing this mixture, some of the first melt was separated. This melt was refrozen, and some of its first melt was separated. This was repeated again, and then the separated melt portion was reanalyzed and found to have the composition shown in the third weight percent column in Table I. A mixture was made up with this revised composition, called HRL-256N4, and was found to have a melting point range of 6 to 13°C. This illustrates that the revised composition is a better eutectic mixture,

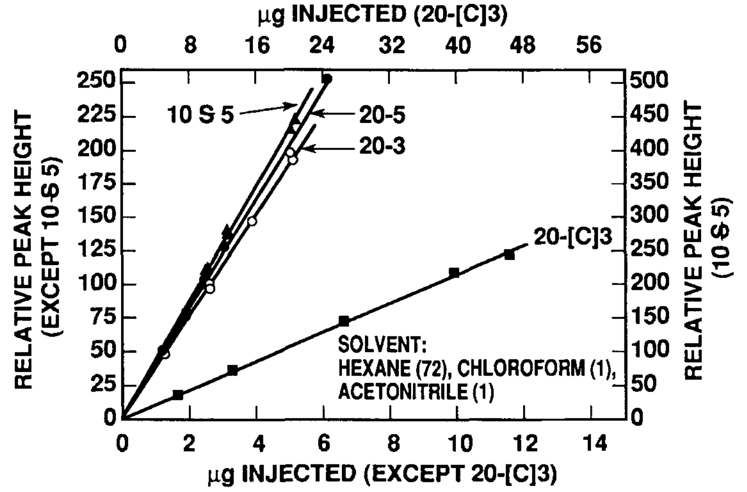


FIGURE 4 HPLC calibration of liquid crystal components, using hexane, chloroform, and acetonitrile in 72:1:1 ratio.

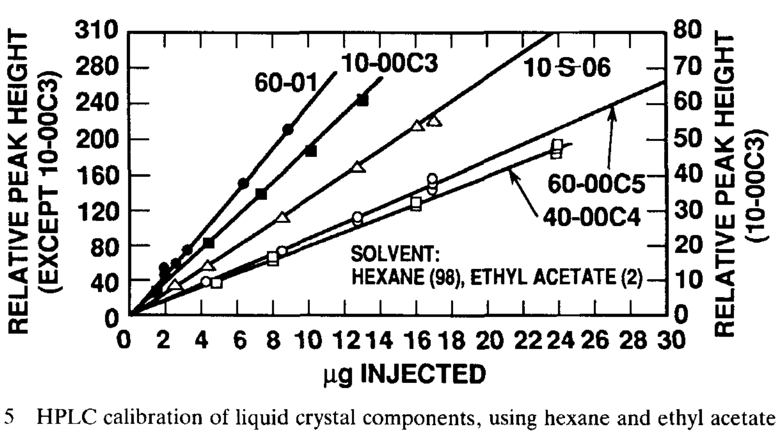


FIGURE 5 HPLC calibration of liquid crystal components, using hexane and ethyl acetate in a 98:2 ratio.

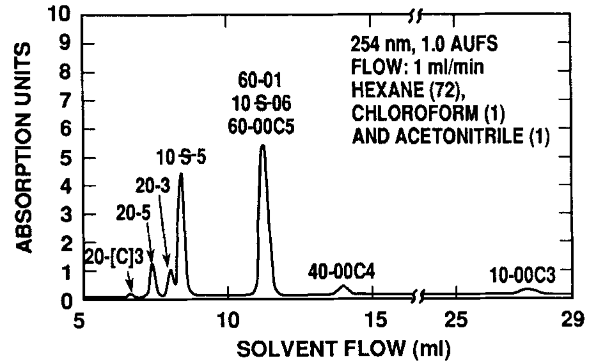


FIGURE 6 HPLC analysis of HRL-256N1 mixture, using hexane, chloroform, and acetonitrile in 72:1:1 ratio.

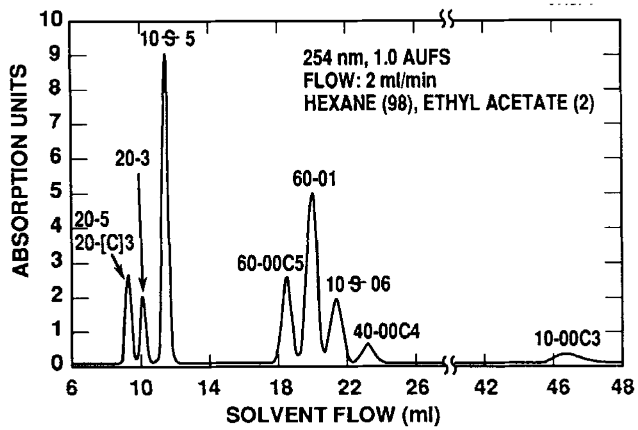


FIGURE 7 HPLC analysis of HRL-256N1 mixture, using hexane and ethyl acetate in a 98:2 ratio.

completely melting to the nematic state 7°C lower than that of the initial composition. As shown in Table I, the main difference in their compositions is the smaller amount of 6O-OOC5 in the experimental eutectic as compared to the calculated mixture.

Another experimental procedure for determining an improved eutectic mixtures was based on the assumption that a new eutectic could be obtained by optimizing a small amount of another component added to an existing multi-component eutectic mixture. We chose to use *p*-*n*-butoxyphenyl *p*-*n*-pentoxybenzoate (4O-O5) as another component added to HRL-256N4. Our 4O-O5 had a nematic range of 70.8°C (mp) to 83.6°C (clpt.), and an impurity level of 0.05%. In this method, a phase diagram type of plot was made of the melting point range versus the percentage of the new component added to a eutectic mixture to determine the appropriate percentage to use for a melting point minimum corresponding to a new eutectic mixture. We applied this to the new mixture HRL-256N4, by adding various amounts of the liquid crystal component 4O-O5 and measuring the melting point range for each addition. The results are shown in Figure 8, which shows a very

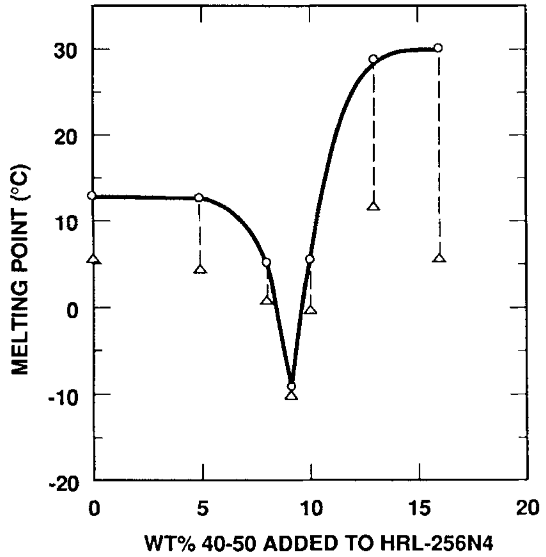


FIGURE 8 Determination of the amount of 4O-O5 for the 10-component eutectic HRL-256N5.

Table 2. Revised Ten-Component Eutectic Mixture

Component	Calc. Wt. %	Experimental Eutectic, Wt.%
2O - 3	5.22	6.61
2O - 5	6.29	7.52
4O - O5	12.19	9.00
6O - O1	13.21	14.00
1O S 5	13.82	14.12
1O S O6	9.42	10.25
1O - OOC3	3.49	4.10
4O -OOC4	4.95	5.70
6O - OOC5	19.10	15.61
2O - [C]3	12.32	13.09
Total Wt.%	100.00	100.00

HRL Mixture No.	256N3	256N5
mp Range, °C	-2.2° (Calc.)	---------
	6° to 19° (Obs.)	-10° to -9° (Obs.)
Clpt., °C	79.8° (Calc.)	---------
	77 to 78° (Obs.)	77.4° (Obs.)

good minimum melting point of −10°C with 9% of 4O-O5 added to HRL-256N4. This new mixture, called HRL-256N5, also had a much more narrow melting point range than HRL-256N1 or HRL-256N4. Thus, this simple procedure resulted in a 10-component mixture with considerably improved eutectic properties over that of the 9-component mixture. Table II shows the overall composition and observed nematic range of HRL-256N5, as compared to the calculated eutectic (HRL-256N3) for the same ten components. The biggest differences in their compositions are the lesser amount of 4O-O5 and 6O-OOC5 present in HRL-256N5 than in HRL-256N3. Their observed clearpoints are approximately equal, but the experimental eutectic mixture has a melting point that is 20°C lower than that observed for the calculated mixture.

Acknowledgment

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