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A. V. Ivashenko [a] , V. V. Titov [a] & E. I. Kovshev [a]
[a] Organic Intermediaries and Dyes Institute, B. Sadovaya, 1-4, Moscow, K-1, U.S.S.R.
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Liquid Crystalline Compounds

III On Applicability of Schröder–Van Laar Equations to Liquid Crystals Mixtures

A. V. IVASHCHENKO, V. V. TITOV and E. I. KOVSHEV

Organic Intermediaries and Dyes Institute, B. Sadovaya, 1-4, Moscow K-1, U.S.S.R.

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The phase diagrams for the mixtures of *p*-cyanophenyl-*p*-alkylbenzoates and *p*-alkoxycarbonyloxyphenyl *p*-butyloxybenzoates were investigated. The Schröder–Van Laar equation was found inapplicable for calculations of composition, eutectic-mixture melting points and crystalline-nematic transition heats of these compounds.

INTRODUCTION

Investigations on phase transition temperatures in binary and multicomponent liquid crystalline systems (LCS) are essential for the manufacture of materials with a broad mesomorphic range.

Recently an ideal solution Eq. (1) of Le Chatelier,[1] Schröder[2] and Van Laar[3] was proposed to calculate the binary LCS composition and their melting points.[4, 5]

$$\ln X_a = \frac{\Delta H_a}{R} x\left(\frac{1}{T} - \frac{1}{T_a}\right) \tag{1}$$

where ΔH_a and T_a are the melting heat and the melting point of the pure component A, T is the melting point of the eutectic mixture containing X_a moles of A, and R is the gas constant.

For calculations of eutectics of n-component mixtures[4–6] the system of n equations (2) was solved

$$\begin{aligned} \ln X_1 &= \frac{\Delta H_1}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \\ \ln X_2 &= \frac{\Delta H_2}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right) \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \ln(1 - X_1 - X_2 - \cdots - X_{n-1}) &= \frac{\Delta H_n}{R}\left(\frac{1}{T} - \frac{1}{T_n}\right) \end{aligned} \tag{2}$$

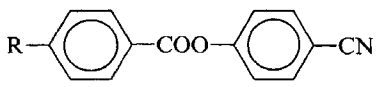
on the condition that

$$\sum_{i=A}^{n} X_i = 1.$$

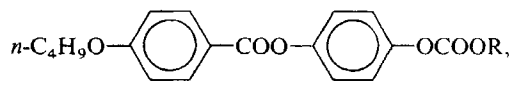
An excellent agreement of calculated and measured data was achieved in all the cases mentioned.

We have attempted to use the Schröder–Van Laar equation for a determination of eutectic mixtures in *p*-cyanophenyl-*p*-*n*-alkylbenzoates systems and for the calculation of melting heats from experimentally determined eutectic mixture parameters.

The compounds studied were: *p*-cyanophenyl-*p*-*n*-butyl- (I), *p*-*n*-hexyl- (II) and *p*-*n*-heptylbenzoate (III); *p*-*n*-hexyloxy- (IV), *p*-*n*-heptyloxy- (V) and *p*-*n*-octyloxycarbonyloxyphenyl-*p*-*n*-butyloxybenzoate (VI):



I–III



IV–VI

where R = n-C_4H_9 (I), n-C_6H_{13} (II and IV), n-C_7H_{15} (III and V), n-C_8H_{17} (VI).

EXPERIMENTAL

Phase transition temperatures were measured by means of DTA technique and by Mettler FP-5 + FP-51 apparatus with a GA 10 recorder. Composition and eutectic melting points were calculated with the help of MIR-1 computer. Melting heats of I–III compounds were determined using an adiabatic calorimeter.

RESULTS AND DISCUSSION

It follows from melt diagrams the IV–V binary system does not form an eutectic, while other LCS form eutectics with ratios of components 1.25 : 1, 1 : 1 or 1 : 2. Some systems (Figure 1*b*, *c* and 2*a*) have bended liquidus curves.

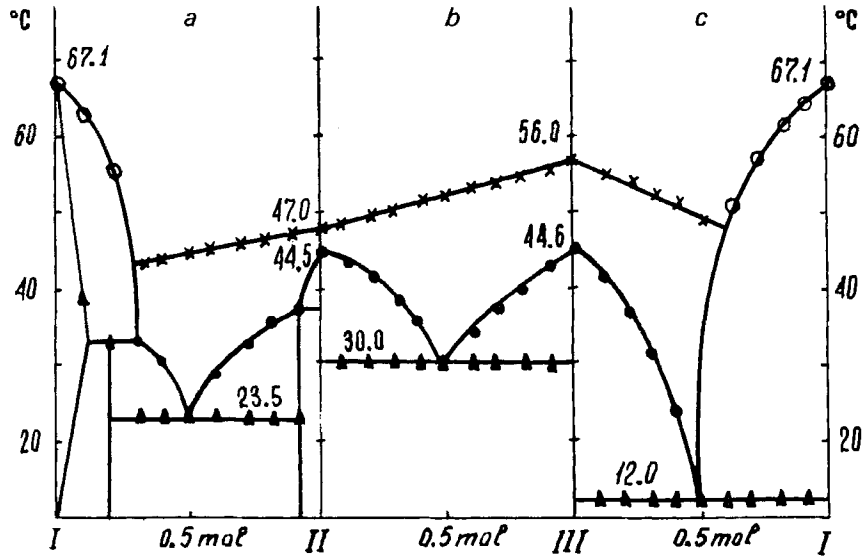


FIGURE 1*a–c* Phase diagrams of binary mixtures I–II, II–III, III–I.

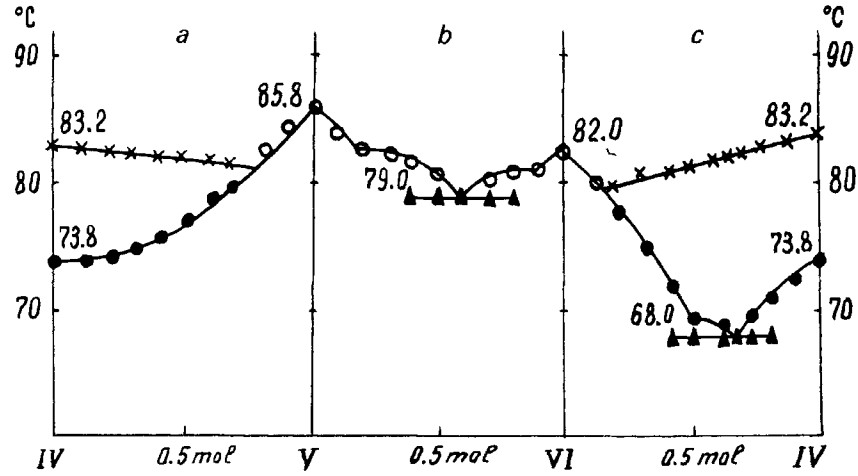


FIGURE 2*a–c* Phase diagrams of binary mixtures IV–V, V–VI, VI–IV.

Similar diagrams with bended liquidus curves have been recently described for other systems.[7] The reason is apparently the formation of systems which melt incongruously.

We have calculated melting heats of components I–VI by use of the Schröder–Van Laar equations and the experimentally found eutectic points of binary systems (Table I).

Melting heats calculated from different diagrams differ considerably both one from another and as compared with found values (for I–III). Experimentally measured melting points of binary systems are also considerably different from calculated data (Table II). Moreover, on the diagrams of ternary systems I–II–III and IV–V–VI (Figures 3, 4), besides the points of complete transition into the nematic phase (16° and 73°), there are peaks (2.7° and 68°) corresponding to eutectic melting points of these mixtures. This fact also confirms a difference between calculated and found eutectic melting points.

Thus, the Schröder–Van Laar equation is not applicable for eutectic-mixture calculations in the *p*-cyanophenyl-*p*-alkylbenzoates and *p*-alkozycarbonyloxyphenyl-*p*-butyloxybenzoates series. These compounds seem to form solutions differing sharply from ideal ones.

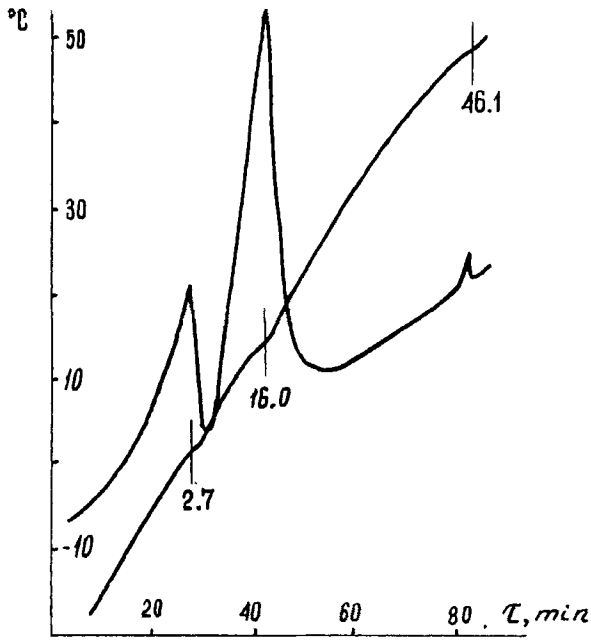


FIGURE 3 Triple mixtures thermogram of I–II–III.

TABLE I

Melting points and melting heats of LC components

Component	Transition temperature		Melting heat (joules per mole)	
	C—N	N—I	calculated (Fig.)	found
I	67.1	42.6	13,251 (1*a*)	37,200
			10,097 (1*c*)	
II	44.5	47.0	25,683 (1*a*)	40,000
			38,022 (1*b*)	
III	44.6	56.0	37,772 (1*b*)	39,500
			15,907 (1*c*)	
IV	73.8	83.2	78,720 (2*a*)	—
V	85.8	81.0	140,706 (2*b*)	—
VI	82.0	79.0	176,666 (2*b*)	—
			68,571 (2*c*)	

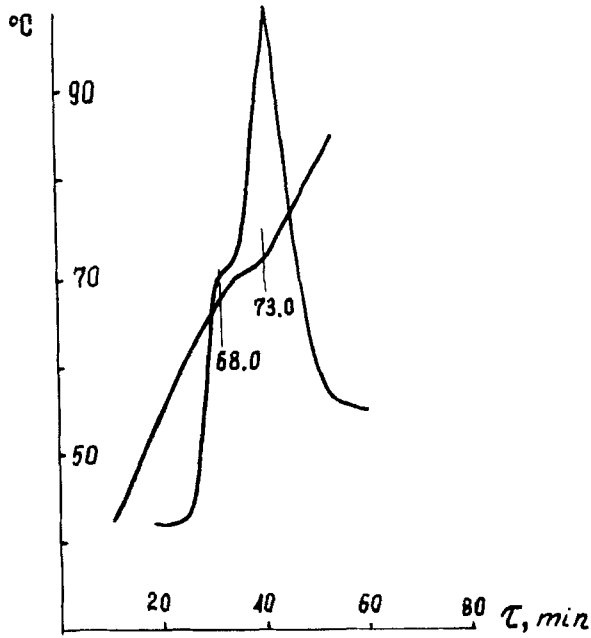


FIGURE 4 Triple mixture thermogram of IV–V–VI.

TABLE II

Phase transitions temperatures and eutectic mixtures compositions

Components molar part		Transition temperatures °C			
		calculated		found	
		C—N	N—I	C—N	C—I
I	0.30	38.2	45.6	29.4	43.2
II	0.70				
II	0.48	30.7	51.7	31.0	51.5
III	0.52				
III	0.72	37.1	52.0	56.0	52.0
I	0.28				
I	0.17				
II	0.40	27.1	52.7	33.0	46.0
III	0.43				
IV	0.43				
V	0.37	63.0	81.3	73.0	79.5
VI[a]	0.20				
IV	0.42				
V	0.32	61.6	81.3	71.3	79.5
VI[b]	0.26				

[a] Calculated value of $\Delta H = 176666$ J/mole was used
[b] Calculated value of $\Delta H = 68571$ J/mole was used.

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