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Studies on mixed mesomorphism: Determination of latent transition temperature (LTT) by extrapolation

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Abstract. A nonmesogenic component of a binary system mixed with a liquid-crystal component must have the latent ability to exhibit mesomorphism. But this cannot normally be observed because the transition temperature from the amorphous liquid to the mesophase lies below the normal melting point. This latent transition temperature of nonliquid crystal substances are determined by the extrapolation method. Binary systems consisting of structurally similar components, viz. *p*-methoxyphenyl-*p'*-methoxycinnamate (A) (117·0–141·5°C) as liquid crystal component and other a nonliquid-crystal component (B) (Schiff's base), are studied. Extrapolation of the transition curves yield the latent transition temperature of the nonliquid-crystal component. The values of LTT for different Schiff's bases are in fair agreement with literature values. The transition temperatures of the binary systems as well as the constituent components were observed.

Keywords. Liquid crystal; mesogen; mixed mesomorphism; monotropy; anisotropy.

1. Introduction

The liquid-crystal state is accepted as an intermediate state of existence, hence, some nonmesogenic substances must have the potential to exhibit mesomorphic behaviour. But the mesophase does not appear because the temperature of the transition from an amorphous liquid to the mesophase lies below the normal melting point. Such substances in their binary mixtures with a liquid-crystal substance or even a nonliquid-crystal substance can give rise to "mixed liquid crystal" formation over a range of temperature and composition. The range of composition over which liquid crystallinity is observed depends upon the degree of similarity of the molecules of the nonliquid-crystal and liquid-crystal substances in shape, size, polarity of the end groups and polarizability.

It has been possible to predict a temperature known as the "latent transition temperature" (LTT) for nonmesogenic components with a latent ability to exhibit mesomorphism on the basis of extrapolation of the mesomorphic-isotropic (or vice versa) transition curve. In all such cases the transition points might lie below its melting point. Naturally, a search for their virtual transition temperature thus acquires importance.

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2. Experimental

2.1 *Preparation*

Trans-p-methoxyphenyl-*p'*-methoxycinnamate (A) (Dave 1980) was synthesised by reacting *p*-methoxycinnamoyl chloride with *p*-hydroxyanisole and the product isolated, purified and recrystallised from alcohol.

Schiff's bases were prepared by refluxing equimolar proportions of the appropriate purified aldehydes and amines in alcohol on a waterbath till the reaction was complete. The products were purified and recrystallised from suitable solvents.

2.2 *Method of study*

The transition temperatures of the binary mixtures as well as the pure substances were observed with the help of a Kofler heating stage under a polarising microscope.

3. Results and discussion

Twelve binary systems are studied in the present investigations as recorded in table 1.

Bogojawlensky and Winogradow (1907, 1908) and Walter (1925) studied binary systems and determined the LTT of nonmesogenic substances. However, Dave and Dewar (1954, 1955) ruled out any possibility of reliable extrapolation as they obtained different values for the LTT of the same nonmesogen with different liquid-crystal components. A few years later Dave and Lohar (1959, 1960, 1962) reported binary systems which yielded reliable values of LTT by the extrapolation method. Dewar and Goldberg (1970) reported in their study of binary mixtures that reliable extrapolation is possible, as they obtained similar values of LTT for the same substance with different liquid-crystal components. Dave and Lohar (1966, 1967) supported the reliability of the extrapolation method by studying several binary systems. In the present investigation, the binary systems listed in table 1 consist of components (A)

Table 1. Component (A), *trans-p*-methoxyphenyl-*p'*-methoxy cinnamate (117–141·5°C), mixed with component (B), Schiff's base.

Schiff's base	X	Y	Melting point (°C)
1	$-OCH_3$	$-OCH_3$	147·0
2	$-OCH_3$	$-CH_3$	92·0
3	$-CH_3$	$-OC_2H_5$	108·5
4	$-Cl$	$-OC_2H_5$	121·5
5	$-Cl$	$-OCH_3$	123·5
6	$-N(CH_3)_2$	$-OCH_3$	140·0
7	$-Cl$	$-Cl$	112·0
8	$-N(CH_3)_2$	$-Cl$	152·0
9	$-OCH_3$	$-Cl$	93·0
10	$-OCH_3$	$-Br$	120·0
11	$-N(CH_3)_2$	$-CH_3$	121·0
12	$-CH_3$	$-OCH_3$	88·0

and (B), which are structurally similar, elongated and lath-like in shape. The extent of the composition range over which the liquid crystal mesophase is observed depends upon the degree of similarity of the molecules of the components A and B in shape, size, polarity of the end groups and polarizability. Solute molecules are structurally compatible and are conducive to mesophase formation. Therefore, mixed liquid crystals are formed over a wider composition range, either enantiotropically and/or monotropically, in the phase diagrams.

The eutectic points in the phase diagrams for systems 1, 2, 3, 4, 5, 6 (set 1) meet melting point curves to the left of the respective eutectic points while those for systems 7, 8, 9, 10, 11, 12 (set 2) meet the melting point curves to the right of the respective eutectic points. Therefore, eutectic points of systems belonging to set 1 are in equilibrium with the nematic liquid phase while eutectic points of systems belonging to set 2 are in equilibrium with the isotropic liquid.

In all the twelve binary systems studied, the isotropic liquid could be supercooled to the mesophase and, hence, extrapolation is easily achieved. The values of LTT determined by the extrapolation method (table 2) for *p*-anisal-*p'*-anisidien, *p*-anisal-*p'*-toluidine, *p*-chlorobenzal-*p'*-phenetidene, *p*-N,N-dimethylaminobenzal-*p'*-anisidine and *p*-tolual-*p'*-anisidine are concurrent and comparable with those from previous work (Lohar and Shah 1973) as these Schiff's bases possess sufficiently polar end groups. For Schiff's bases *p*-tolual-*p'*-phenetidine, *p*-chlorobenzal-*p'*-chloroaniline, *p*-N,N-dimethyl-aminobenzal-*p'*-chloroaniline and *p*-N,N-dimethylaminobenzal-*p'*-toluidine, the LTT are determined by the extrapolation method. In the case of *p*-anisal-*p'*-chloroaniline, the transition curve is deviating within 90 to 100 mole % of mesomorphic component. The deviation observed may be attributed to the formation of a molecular complex compound between the constituent components. However, a metastable monotropic phase is observed within sufficient ranges of temperature and composition prior to the formation of the complex compound, leading to smooth extrapolation of the transition line. Hence LTT of this Schiff's

Table 2. Comparative values of LTT.

	LTT of Schiff's base (°C)				
No.*	a	b	c	d	e
1	100·5	103·5	101·0	104·0	101·0
2	40·0	39·0	39·0	39·0	40·0
3	90·0	—	—	—	—
4	86·0	87·0	90·0	—	86·5
5	73·0	—	—	—	—
6	50·0	52·3	52·0	—	61·5
7	75·0	—	—	—	—
8	52·5	—	—	—	—
9	42·0	—	—	—	—
10	82·0	—	—	—	—
11	46·5	—	—,	—	32·0
12	55·0	—	51·8	—	—

*Schiff's bases as in table 1

References: a – present study: b – Lohar and Shah (1973); c – Patel (1979); d – Yadwadkar (1983); e – Mashru (1981)

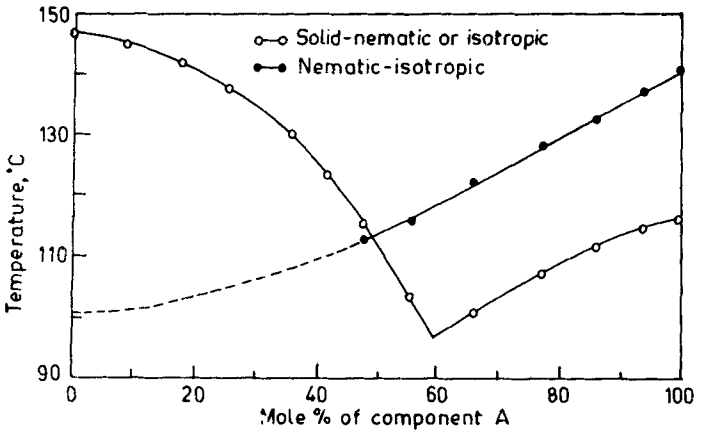

Figure 1. Phase diagram of the system *trans*-*p*-methoxyphenyl-*p'*-methoxycinnamate and *p*-anisal-*p'*-anisidine.

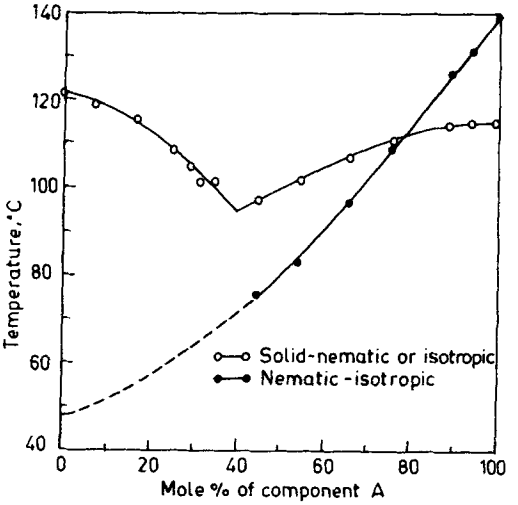

Figure 2. Phase diagram of the system *trans*-*p*-methoxyphenyl-*p'*-methoxycinnamate and *p*-N,N-dimethylaminobenzal-*p*-toluidine.

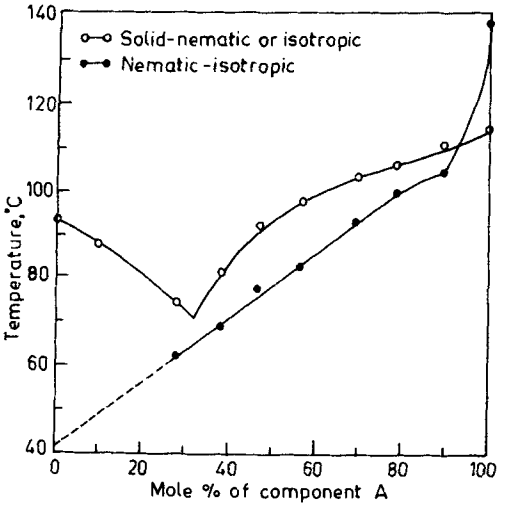

Figure 3. Phase diagram of the system *trans*-*p*-methoxyphenyl-*p'*-methoxycinnamate and *p*-anisal-*p'*-chloroaniline.

Table 3. Transition temperatures of binary systems:solid nematic/isotropic.

	Mole % of component (A)												Eutectic point	
No.	0	10	20	30	40	50	60	70	80	90	95	100	Mol %	Temp. (°C)
1	147·0	145·0	140·75	135·0	126·0	113·0	97·5	103·75	109·5	114·25	116·0	117·0	59·5	97·0
2	92·0	87·25	82·25	77·5	72·5	83·25	93·25	102·0	109·0	115·0	116·5	117·0	40·0	72·5
3	108·5	106·5	112·5	98·0	93·0	97·75	103·5	109·0	113·5	115·5	117·0	117·0	47·0	89·0
4	121·5	118·5	113·25	107·25	99·0	89·25	93·25	102·75	108·5	114·0	116·0	117·0	53·0	86·0
5	123·5	119·25	115·5	110·25	103·75	95·75	97·75	104·5	109·75	114·0	115·5	117·0	53·5	92·75
6	140·0	135·75	130·5	125·0	118·75	111·5	103·5	103·25	109·0	113·5	115·25	117·0	64·0	100·0
7	112·0	107·0	101·0	94·5	91·0	99·25	99·5	104·0	108·0	112·5	114·75	117·0	36·75	89·0
8	152·0	146·25	140·0	133·0	125·25	116·5	106·75	106·75	110·25	114·0	115·5	117·0	63·25	103·0
9	93·0	87·0	80·75	72·5	85·5	95·0	101·5	106·0	109·0	112·5	114·25	117·0	31·0	71·75
10	120·0	155·25	110·0	105·25	100·25	98·0	102·0	105·5	109·5	113·25	115·25	117·0	47·5	96·5
11	121·0	118·5	112·5	104·5	95·25	100·25	105·25	109·5	113·25	116·0	116·75	117·0	40·5	94·75
12	88·0	85·25	77·25	75·25	84·5	92·5	99·5	105·0	110·0	113·5	115·25	117·0	28·0	73·5

Table 4. Transition temperatures of binary systems:nematic-isotropic.

	Mole % of component (A)												Triple point	
No.	0	10	20	30	40	50	60	70	80	90	95	100	Mol %	Temp. (°C)
1	—	—	—	—	(110·0)	114·0	119·0	124·5	130·25	135·75	139·0	141·5	49·5	114·0
2	—	—	(66·5)	(76·5)	86·25	95·5	104·5	113·5	123·0	132·0	136·5	141·5	30·25	77·0
3	—	—	—	(92·75)	95·5	98·75	103·25	111·0	121·5	133·0	138·0	141·5	37·0	94·5
4	—	—	(99·5)	(102·0)	103·25	107·0	111·0	116·5	124·0	133·25	138·0	141·5	33·75	102·5
5	—	—	—	—	(91·25)	97·5	105·0	113·0	111·5	131·5	136·25	141·5	48·75	96·75
6	—	—	—	—	—	(96·6)	105·0	114·25	123·5	133·0	137·5	141·5	59·25	104·25
7	—	—	—	—	—	—	(94·75)	102·0	113·0	127·5	134·5	141·5	74·0	106·0
8	—	—	—	—	—	(87·25)	(97·0)	105·75	116·5	128·5	134·75	141·5	71·0	106·5
9	—	—	—	(65·0)	(72·5)	(80·5)	(88·0)	(95·5)	(103·0)	(110·0)	119·0	141·5	92·0	113·0
10	—	—	—	—	—	(95·0)	(101·5)	111·0	121·25	131·5	136·5	141·5	60·25	101·5
11	—	—	—	—	—	(80·25)	(90·75)	(102·75)	116·0	129·0	135·25	141·5	77·5	112·5
12	—	—	—	(73·0)	(80·75)	(89·25)	(98·5)	(107·75)	118·5	130·5	136·5	141·5	64·0	102·0

Parentheses indicate monotropy.

base is reliable. The values of LTT determined from the phase diagrams of some binary systems (figures 1 to 3) are reported in table 2 and compared with previous work. The transition points derived from the phase diagrams of the binary systems are shown in tables 3 and 4.

Thus extrapolation could be quite dependable when the nonmesomorphic substances are structurally similar to mesomorphic substances and possess sufficiently polar terminal groups. Of course, for greater dependability of the extrapolation method, the eutectic points in such binary systems should preferably be in equilibrium with the anisotropic liquids and the terminal groups of the non-mesomorphs should be sufficiently polar. The evidence obtained by the present investigation places the extrapolation hypothesis on a sound footing.

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