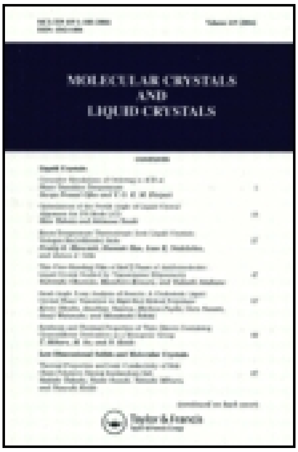

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Determination of Latent Transition Temperatures of Nonmesomorphs by Extrapolation Method in Binary Systems

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Eight binary systems consisting of mesomorphs and nonmesomorphs (A_1 or A_2, + B_1, B_2, … B_7, B_8) were studied with a view to determine the latent transition temperature (LTT) for the nonmesomorphic component (B) of a binary system by an extrapolation method. Encouraging results supporting earlier views and LTT values were obtained for seven binary systems. Instead of reporting a single value of LTT, the range of temperature or two or three values are reported herewith depending upon the possible paths of extrapolation. LTT reported earlier for nonmesomorphs lie within the range of temperature determined presently. Though the "group slope value" differs from the earlier reported value, the group efficiency order remains the same. Thus, the present investigation raises the credibility of an extrapolation method to determine LTT and group efficiency order for nematic mesophase. Component A_1 and A_2 are nematogenic, namely, p-(p′-n-propyloxy benzoyloxy) anisole (A_1) (90.0 to 116.0) and p-(p′-n-butyloxy benzoyloxy) anisole (A_2) (116.0 to 105.5). B_1 to B_8 are Schiff's bases. Transition and melting temperatures are observed through hot stage polarizing microscope for binary mixtures and pure components.

Keywords mixed mesomorphism, mixed melt, nematic, smectic, liquid crystal

1. Introduction

The melting point and transition points are depressed by mixing two like components of a binary system following a law of mixtures. Such binary systems are studied with a view to understand the effect of molecular structure on mesophase formation and to determine latent transition temperature (LTT) of nonmesomorph by extrapolation method for obtaining low temperature liquid crystal material applicable and useful for the devices to be operated at room temperature or desired temperature at economical cost.

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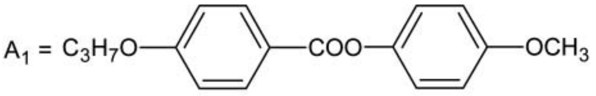
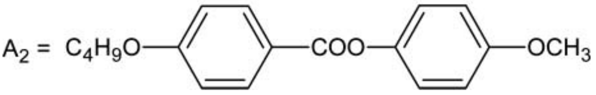
2. Experimental

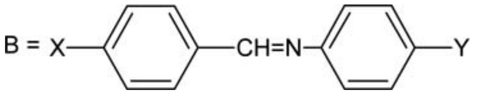
2.1 Synthesis of Component A_1 and A_2

Mesogenic components of a binary system, namely, p-(p′-n-propyloxy benzoyloxy) anisole (A_1) and p-(p′-n-butyloxy benzoyloxy) anisole (A_2), were synthesized and purified by the usual method [1].





2.2 Synthesis of Component B_1–B_8



Components B of the binary mixtures are Schiff's bases. Schiff's bases are prepared [3] by refluxing equimolar proportion of corresponding Aldehyde and aromatic amine in alcohol for about 1–2 hours. Products obtained were purified in alcohol until it gave constant melting point.

2.3 Preparation of Binary Mixtures and Method of Study

Binary mixtures of binary systems were prepared by usual established standard method [3].

3. Results and Discussion

Nonmesomorphic substances without passing through anisotropic state of existence have the potential to exhibit mesomorphic behavior. But mesophase does not appear because the transition temperature from amorphous liquid to mesophase lies below normal melting point. Such substances in their binary mixtures with mesomorphic or nonmesomophic substances can give rise to "mixed liquid crystal" formation over a range of composition and temperature. Thus search for virtual transition temperature is important.

More than eight binary systems were studied presently; among those, results of seven binary systems ($A_1 + B_1$, $A_1 + B_2$, $A_2 + B_3$, $A_2 + B_4$, $A_2 + B_5$, $A_2 + B_6$, and $A_2 + B_7$) are considered here for discussion.

Temperatures are plotted versus the mole percent of component A_1/A_2. Smooth curves are drawn through like and related points. Mesomorphic–isotropic (or vice versa) transition curve is extrapolated to zero mole percent of A_1/A_2 by selecting possible reliable paths of extrapolation. The transition temperatures of pure components and binary mixtures, as derived from phase diagrams, are recorded in Table 1. The representative phase diagrams are given separately in this manuscript (see Fig. 1).

Table 1. Temperatures derived from phase diagrams

	Nonmesomorph $X{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}Y$			Mole% of component (A)										
	X	Y		0%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
B_1	CH_3	CH_3	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	(58.0)	(58.5)	(67.0)	72.0	80.0	84.0	88.0	90.0
			I	91.5	93.0	84.0	76.0	71.5	70.0	93.0	96.0	103.0	113.0	116.0
B_2	Cl	CH_3	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	—	—	(86.5)	(85.5)	(87.5)	85.0	84.0	90.0
			I	128.0	129.5	127.0	120.0	111.5	104.5	97.5	90.5	91.5	111.0	116.0
B_3	CH_3O	Br	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	—	—	—	(70.0)	(70.0)	(71.0)	(79.0)	(105.0)
			I	120.0	120.5	113.0	101.0	91.5	84.0	81.0	84.0	90.0	101.0	116.0
B_4	CH_3O	Cl	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	—	(73.0)	(69.5)	(70.0)	(71.0)	(73.5)	(80.0)	(105.0)
			I	93.0	93.5	87.0	77.5	86.5	81.0	83.5	86.0	89.0	99.0	116.0
B_5	Cl	$COCH_3$	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	—	—	(66.5)	(69.5)	(69.5)	(71.5)	(76.0)	(105.0)
			I	133.0	139.0	138.0	131.5	123.0	112.0	100.0	90.0	88.0	90.5	116.0
B_6	Cl	Cl	S	—	—	—	—	—	—	—	—	—	—	—
			N	—	—	—	—	—	(58.5)	(60.5)	(64.0)	(69.0)	(77.0)	(105.0)
			I	112.0	107.0	101.5	92.5	82.0	77.5	79.0	81.0	85.0	92.0	116.0
B_7	Cl	Br	S									(63.0)	(68.0)	
			N	—	—	—	—	—	(59.0)	(60.5)	(68.0)	(70.0)	(74.0)	(105.0)
			I	125.0	123.0	116.5	107.5	98.0	87.0	82.0	83.0	87.0	92.5	116.0

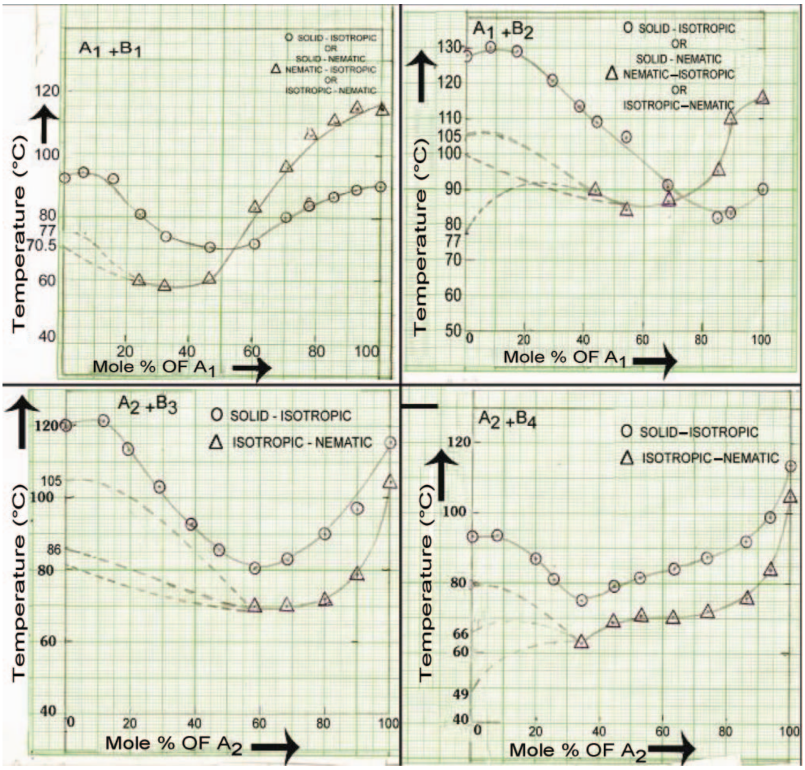


Figure 1. Phase behavior of representative binary systems of sets i and ii.

A careful examination of the phase diagrams reveals the fact that the nematic–isotropic (or vice versa) transition curve in set 1 (binary systems $A_1 + B_1$ and $A_1 + B_2$) meets the solid-isotropic (or nematic–isotropic) liquid curve to the right of the corresponding eutectic points, i.e., the triple points are to the right of the eutectic point. In set 2, where first component A_2 is monotropic nematic, a triple point is absent in phase diagram.

The formation of mixed liquid crystals in the binary systems (see Table 1) is clearly understood as the molecules are being aligned in a typical manner in their mixed melts. In the mixed melts, a set of molecules belonging to mesomorph (A_1 or A_2) get mixed with another set of molecules belonging to nonmesogen (Schiff's bases). The nonmesomorphs differ from the mesomorphic molecules in two respects, namely, magnitude of the polar nature of the terminal groups and central bridge linking two phenyl rings. But the effect of central bridge being negligibly small, the former effect of the polarity of terminal end groups is considerably more. The mesomorphic components A_1 and A_2 has terminal groups with sufficient polar nature, which give rise to terminal attractions in ample measure. Therefore, on heating the binary mixtures, they form mesophase of the nematic variety for all the binary systems under discussion. Only a binary system ($A_2 + B_7$) form smectic variety of mesophase in addition to nematic mesophase.

Thus, formation of nematic variety of mesophase occurs due to terminal attractions, which offer resistance to thermal vibrations maintaining an end-to-end alignment over a range of temperature. As mesomorphic molecules get mixed with nonmesomorphic molecules (B_1, B_2 ... B_7), they acquire an environment of considerably less terminal attractions. Naturally, the forces operative in the direction of maintaining an end-to-end orientations of molecules get interrupted by the entry of such nonmesomorphic molecules causing a kind of disturbance.

Obviously, the mesomorphic molecules of the mixed melt are not able to offer enough resistance to the thermal vibrations on heating to higher temperature and, hence, converted to isotropic liquid somewhat, earlier than their usual transition temperature. Hence depression in transition curve is caused. The disturbance offered by the nonmesomorphic molecules is limited and increases with increasing proportion of their composition. The minimum proportion of composition needed to disrupt completely; the mesomorphic alignment of the mesogenic melts in turn depends upon the polar nature of its own terminal groups.

In the case of a majority of nonmesomorphic Schiff's base, the component required to disruption is 50% or more. Thus, mesophase is prolonged as monotropic mesophase, which helps in setting a smooth trend to the transition curve and allows real curvature or a proper bend characteristics of component B up to 24 to 50 mol% of mesomorphic component A_1/A_2. The mesomorphic–isotropic (or vice versa) transition curves of all the binary systems have been extrapolated through possible paths in keeping with the smoothness of the transition curves as set in by their mesomophic–isotropic (or vice versa) transition versus their concentration in mole percent of the liquid crystalline component at constant atmospheric pressure. The range of LTT or different values of LTT determined from phase diagrams for nonmesomorphic components are reported in Table 2.

Careful examination of LTT range or different two or three values of LTT for each Schiff's base under the present investigation are quite comparable with those reported earlier.

Table 2. Relative comparison of LTT in °C reported earlier

Nonmesomorph $X-C_6H_4-CH=N-C_6H_4-Y$			LTT in °C present investigation for nematic/smectic mesophase	LTT in °C reported earlier			
X	Y	Schiff's base		Ref.-AVD	Ref.-KJG	Ref.-JML/AVD	Ref.-CGJ
CH_3	CH_3	B_1	70.5–77.0	64.0	86.0	—	—
Cl	CH_3	B_2	77.0–100.0–105.0	—	72.5	73.0	—
OCH_3	Br	B_3	81.5–105.0 (81.5–86.0–105.0)	82.0	—	82.0	100.0
OCH_3	Cl	B_4	49.0–80.0 (49.0–66.0–80.0)	42.0	—	42.0	92.0
Cl	$COCH_3$	B_5	45.0–118.0 (49.0–106.0–118.0)	43.0	—	—	—
Cl	Cl	B_6	70.0–102.0 (70.0–78.5–102.1)	75.0	—	75.0	—
Cl	Br	B_7	Nm. 58.0–74.0	72.5	—	—	—
			(58–67–74)	—	—	—	—
			Sm. (for A_2) 86.0				

Note: Nm, nematic mesophase; Sm, smectic mesophase. AVD = A.V. DOSHI; JML = J.M. LOHAR; KJG = K.J. GANATRA; CGJ = C.G. JOSHI.

The binary systems consisting of nonmesomorphic Schiff's bases having terminal end groups of insufficient polarity are $-CH_3$, $-Cl$, $-Br$, and $-COCH_3$. The degree of mesomorphism exhibited is much limited since the mesomorphic–isotropic transition curves cut B_1 and B_2 (or do not cut B_3 to B_7) solid-isotropic curves at the point to the right of the corresponding eutectics with prolonged monotropy, which leads to extrapolate a more real curvature or proper bend causing variance of few °C. Thus, persistence of monotropy to a large extent leads extrapolation to more accurate determination of LTT.

Polarity concept is further supported by initial slope values of the nematic–isotropic liquid (or vice versa) transition curves. The group slope values are mutually differ for set 1 and set 2 as well as with previously reported values by earlier researchers. However the order of polarity and hence the group efficiency order derived in the present investigation very well matche with earlier work. The order of group efficiency for nematic derived is $-OCH_3 > -Cl \approx -CH_3 > -COCH_3 > -Br$.

Thus initial slope and hence group slope value may vary with the first component (A_1/A_2) but finally the group efficiency order derived on the basis of polarity concept as well as order of polarity remains unaltered with reference to earlier work[2].

4. Conclusion

The extrapolation method to determine LTT of nonmesomorphs is quite dependable when nonmesomorphic substances are structurally similar to mesomorphic substances and possess sufficiently polar terminal end groups, for homogeneous binary mixtures and melting points of the constituent components do not differ to a large extent. For greater dependability of the extrapolation method, the eutectic point should preferably be in equilibrium with the anisotropic liquids. However, the evidence obtained by the present investigation raises the reliability and credibility of the extrapolation method to determine LTT of nonmesomorphs.

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References

[1] Doshi, A. V., & Vyas, P. R. (1991). *Acta Ciencia. Indica*, *XVII C*(4), 379.

[2] Gray, G. W., & Winsor, P. A. (1974). *Liquid Crystals and Plastic Crystals*, Ellis Horwood: Chichester, Volume 1, Chapter 4, pp. 103–172.

[3] (a) Doshi, A. V., & Joshi, N. N. (1993). *J. Ind. Chem. Soc.*, *70*, 807–809 (b) Doshi, A. V., & Ganatra, K. J. (2000). *J. Ind. Chem. Soc.*, *77*, 322–325 (c) Doshi, A. V., & Lohar, J. M. (1993). *Proc. Indian Acad. Sci. Bangalore*, *105*, 209–214 (d) Doshi, A. V., & Makwana, N. G. (2008). *J. Ind. Chem. Soc.*, *85*, 262–266 (e) Doshi, A. V., & Prajapati, H. R. (2007). *J. Ind. Chem. Soc.*, *84*, 658–660 (f) Doshi, A. V. (1987). Study of Mesomorphism and Extrapolation of its Charecteristics, PhD thesis, Saurashtra University, Rajkot, Gujarat, India (g) Doshi, A. V., & Patel, V. R. J. (2008). *Ind. Chem. Soc.*, *85*, 267–272 (h) Doshi, A. V., & Prajapati, H. R. (2011). *Der Pharma Chemica*, *3*(1), 123–133 (i) Doshi, A. V., & Patel, V. R. (2010). *Der Pharma Chemica*, *2*(6), 429–436.