

Determination of Latent Mesogenic Behavior in Nonmesogenic Compounds by Extrapolation Method

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A homologous series of 8-(4'-n-alkoxybenzoyloxy) quinolines were synthesized by established methods [5,6]. On evaluation by optical microscopy, none of the homologues were found to exhibit mesogenic behavior even in the monotropic condition. Then, each homologue (B) was mixed with a liquid crystal component (A) and binary systems were studied by optical microscopy. Solid-mesomorphic or isotropic-nematic transition temperatures of binary mixtures were determined and plotted to obtain the phase diagram for transition temperatures versus percentage composition of component (A). The nematic-isotropic transition curve was extrapolated to zero mole percentage of component (A) (100%B) to determine the latent transition temperature (LTT) of each nonmesomorphic homologue. The number of carbon atoms in the n-alkyl chain of each homologue versus LTT is plotted and a phase diagram is obtained. The isotropic-nematic transition curve behaves in a normal manner like a curve behaving for a typical nematogenic homologous series, including odd-even effects in its phase diagram. This method is useful to determine the probable temperature at which a nonmesogenic substance can show mesogenic behavior, provided a suitable condition is applied. Also, it is useful to correct the LTT of a homologue from the mesomorphic-isotropic transition curve.

Keywords Liquid crystal mixtures; mixed mesomorphism; monotropy; nematic; smectic

Introduction

The liquid crystal or mesomorphic state of matter is a physically distinct state of matter, intermediate to the crystalline solid and the isotropic liquid. Theoretically, all substances should exhibit this unique intermediate state in addition to normal states of matter, viz., solid, liquid, and gas. Sometimes, unexpectedly on synthesis of a new homologous series, all the novel compounds are nonmesomorphic. In the present work, an attempt is made to search for the latent ability of non-liquid crystal component (homologue), i.e., probable temperature at which a non-liquid crystal substance can exhibit liquid crystal behavior [latent transition temperature (LTT)] by extrapolation of mesomorphic–isotropic transition curve at 100 mole percent of non-liquid crystal component of a binary system. The transition points might

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lie below its melting point. Thus, a search for their virtual transition temperature is of importance.

Experimental

Synthesis

Synthesis of 8[4'-n-Alkoxybenzoyloxy] Quinolines. p-n-Alkoxy benzoic acids were synthesized by the modified method of Dave and Vora [2]. p-n-Alkoxy benzoic acids were refluxed with freshly distilled excess of thionyl chloride till evolution of sulfur dioxide gas ceases. Excess of thionyl chloride was distilled off. The p-n-alkoxy benzoyl chloride was directly treated with an ice-cooled solution of 8-hydroxy quinoline in pyridine, dropwise. The resulting reaction mixture was warmed through constant shaking for about half an hour. Then, it was kept overnight. The next day, the product was decomposed and allowed to settle with the formation of the ester. Final products were filtered, washed, dried, and purified by alcohol crystallization [4–13].

Characterization

Products were characterized by hot stage polarizing optical microscopy to determine the transition and melting temperatures as recorded in Table 1. Some representative samples were selected for elemental analysis as recorded in Table 2.

Twelve binary systems consisting of various components, 12 homologues of nonmesomorphic homologous series 8(4 - n-alkoxybenzoyloxy) quinolines, and a common component (A) 4-*n*-octyloxy benzoic acid [Sm.101.0°C, Nm.108.0°C, and Iso.148.0°C] are thoroughly mixed by the method of [6,8,12,13] Dave and Lohar [7], Lohar and Doshi [5], and Doshi and Ganatra [9]. 4-*n*-Octyloxy benzoic acid was prepared by the modified method of Dave and Vora [2].

Sr. No.	n -alkyl group- C_nH_{2n+1}	Transition temperatures in °C				
		Smectic	Nematic	Isotropic		
1	Methyl	_	_	180.0		
2	Ethyl	—	—	132.0		
3	Propyl	—	—	117.0		
4	Butyl	—	—	103.0		
5	Pentyl	—	—	112.0		
6	Hexyl	—	—	93.0		
7	Heptyl	—	—	76.0		
8	Octyl	—	—	84.0		
9	Decyl	—	—	82.0		
10	Dodecyl	—	—	88.0		
11	Tetradecyl	—	—	91.0		
12	Hexadecyl	—	—	88.0		

Table 1. Transition temperatures of 8[4'-n-alkoxybenzoyloxy] quinolines

		%	% Theoretically		% Observation		
Sr. No.	R = n-alkyl chain	С	Н	N	С	Н	N
1	C ₁₈ H ₁₅ O ₃ N	73.72	5.12	4.78	73.62	5.16	4.84
2	$C_{22}H_{23}O_3N$	75.64	6.59	4.01	75.55	6.50	4.04
3	$C_{30}H_{39}O_3N$	78.09	8.45	3.03	78.01	8.38	3.10

 Table 2. Combustion analysis data

Transition and melting temperatures of all the binary systems $[A+B_1,B_2,-B_{12}]$ and pure components (Table 1) were observed through hot-stage polarizing optical microscopy.

Results and Discussion

The geometrical structure and shape of the ester homologous series 8[4'-n-alkoxybenzoyloxy] quinolines determine that they have the potential to exhibit liquid crystal mesophases. However, all homologues of the series under discussion were found to be nonmesogenic.

The LTTs of all the homologues determined by extrapolation method are recorded in Table 3. The phase diagrams of some selected binary systems are represented in Figs. 2 and 3. Transition temperatures derived from each phase diagram of the binary system (B_1-B_{12}) are shown in Fig. 4.

The LTT of each homologue is plotted versus the number of carbon atoms in the *n*-alkyl chain of left *n*-alkoxy terminal group. The phase diagram obtained is represented in Fig. 1. Careful observation of the phase diagram of the series (Fig. 1) indicates that the solid–isotropic transition curve shows descending tendency as the series is ascended. The curve falls up to fourth homologue and then a rising and falling tendency is observed in a zigzag manner. The isotropic–nematic transition curve falls, rises, and then falls in a normal manner like a mesomorphic homologous series. The isotropic–nematic transition

Sr. No.	Homologue	LTT in °C		
1	Methyl	126.5		
2	Ethyl	128.0		
3	Propyl	80.0		
4	Butyl	44.0		
5	Pentyl	56.0		
6	Hexyl	52.0		
7	Heptyl	55.0		
8	Octyl	68.0		
9	Decyl	79.0		
10	Dodecyl	83.0		
11	Tetradecyl	83.0		
12	Hexadecyl	60.0		

Table 3. Latent transition temperatures





curve shows odd-even effect like the mesomorphic series. The isotropic-nematic transition curves for odd and even homologues merge into each other at the 10th homologue.

p-n-Alkoxy benzoic acids are mesomorphic (liquid crystal) in nature, because the dimerised p-n-alkoxy benzoic acid has two phenyl rings bonded through hydrogen bonding in its structure. On esterification, hydrogen bonding breaks and quinoline molecule



Figure 2.



Figure 3.

is bridged through the -COO-group. Thus, liquid crystal property is expected to be maintained like the *p*-*n*-alkoxy benzoic acids. However, liquid crystal property practically disappears on esterification. Of course, the transition temperatures of non-liquid crystal ester homologue under discussion are lowered, as compared to the corresponding *p*-*n*-alkoxy benzoic acid, just like a liquid crystal homologous series. Thus, disappearance of liquid crystal characteristics of *p*-*n*-alkoxy benzoic acids on linking with 8-hydroxy quinoline



Figure 4. Homologous Series: 8[4'-n-alkoxybenzoyloxy] quinoline.

is attributed to the absence of intermolecular anisotropic forces of attraction of suitable magnitude depending upon the molecular shape, size, polarity, polarizability, aromaticity, effect due to lateral and terminal end groups, etc. The non-liquid crystal behavior of all of the homologues is attributed to their either high crystallizing tendency due to stronger intermolecular forces of attraction or weaker intermolecular forces of end-to-end and lateral attraction than optimum intermolecular and isotropic forces of attraction of suitable magnitude required for the formation of mesophase as a consequence of molecular rigidity, flexibility, and molecular bending. The intermolecular forces of attraction are unable to resist thermal vibrations imposed upon sample specimen homologues under discussion. Therefore, molecules of all of the homologues under the influence of the exposed heat disalign on the plane of the surface but do align at an angle less than 90°C. Thus, disaligned molecules of the sample homologues fail to maintain, or restrict to maintain, parallel orientational order of molecules. Thus, molecules of the sample homologues are randomly oriented without any regularity in floating condition. Under this situation, mesophase formation does not appear to occur. Hence, the entire homologous series 8[4'-n-alkoxy benzoyloxy] quinolines is nonmesomorphic in character. Therefore, all homologues of the series sharply pass from solid to isotropic liquid without exhibition of any liquid crystal state.

Twelve binary systems of 12 nonmesomorphic homologues consisting of $A+B_1$, $A+B_2-A+B_{12}$ were studied under hot-stage polarizing optical microscopy. The extent of composition range over which liquid crystal mesophase is observed depends upon the degree of similarities of the molecules of components A and B, of a binary system in shape, size, polarity, polarizability, etc. Solute molecules are structurally compatible and conducive to liquid crystal mesophase formation. Therefore, mixed liquid crystals are formed over a wider composition range either enantiotropically and/or monotropically in the respective phase diagram of the binary system. The eutectic points in the phase diagrams for binary systems meet melting point curves to the left of the respective eutectic points. Therefore, eutectic points of the binary systems under discussion are in equilibrium with the nematic liquid phase. In all of the binary systems, the isotropic liquid could be supercooled to the mesophase. The metastable monotropic mesophase formation observed is within sufficient range of composition and temperature, leading to smooth extrapolation of the melting/transition curve. Thus, reliable extrapolation of curve to zero mole percent of component (A) (or 100 mole percent of B) of binary systems is easily achieved for all the components (B) as shown in Table 3. Hence, the LTTs of all the homologues are reliable. Reliable LTTs are plotted versus the number of carbon atoms in the *n*-alkyl chain of left *n*-alkoxy terminal, which gives rise to a phase diagram for a non-liquid crystal homologous series under discussion. This phase diagram of a non-liquid crystal homologous series very well matches with a phase diagram of the mesogenic series. Thus, reliable extrapolation and hence the extrapolation method is useful to test and correct the LTT of an individual component of a binary system or a homologue of a non-liquid crystal homologous series.

Conclusion

The reliability of the LTT of a nonmesomorphic homologue of a homologous series or the nonmesomorphic component of a binary system depends upon the similarity in molecular structure of mixing components, homogeneity of a binary mixture, and melting point difference of both components constituting the binary mixture with the condition that mixing components should not mutually interact. The evidence obtained by the present investigation places the extrapolation hypothesis on sound ground.

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