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J. Lohar

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## A STUDY OF MIXED LIQUID CRYSTAL FORMATION IN MIXTURE OF p-METHOXY AND p-ETHOXY BENZOIC ACIDS

J. M. LOHAR

Applied Chemistry Department, Faculty of Technology and Engineering,  
M. S. University, Baroda, India

**Résumé.** — Il est connu que parmi les composés alkoxy de l'acide benzoïque, ceux à haut poids moléculaire présentent des propriétés mésomorphes. Les deux premiers membres de cette série ne montrent pas de mésophases, certainement à cause de leur très haut point de fusion. Cependant, on a déjà remarqué que leurs mélanges présentent des propriétés mésomorphes. Une étude détaillée du mélange binaire des acides p-méthoxy et p-éthoxy met en évidence une mésophase nématique intermédiaire dans un intervalle de température extrêmement court. Par surfusion, cet intervalle de température n'est pas élargi. Les températures virtuelles de transition nématique-liquide, déduites par extrapolation des courbes d'équilibre entre ces deux phases, montrent qu'il existe une grande différence entre le point de fusion et cette température virtuelle. Ceci est une condition non favorable à l'existence d'une mésophase.

**Abstract.** — The higher members of p-substituted alkoxy benzoic acid series are well known mesogenes. The first two members fail to exhibit liquid crystallinity individually probably due to considerably higher melting points, however, their mixture is reported to show mixed mesomorphism. A detailed study of the binary system of p-methoxy benzoic acid with p-ethoxy benzoic acid reveals the exhibited nematic mesophase region to be extremely small. Even the metastable monotropic liquid crystallinity does not extend much beyond either side of the eutectic. The latent transition temperatures for both these acids ascertained by smooth extrapolation on either side of the transition curve suggest a wide difference between the melting point and the corresponding latent transition temperature, a condition not conducive to exhibition of mixed liquid crystallinity.

**1. Introduction.** — The molecular features which are considered to be the essential characteristics of thermotropic liquid crystals have been summarised [1] as elongated and rectilinear molecules with *flat* segments as benzene rings and existence of strong dipoles and easily polarisable groups in the molecules. All but the first two members of the p-p' substituted alkoxy benzoic acids which meet with the enumerated essentials quite fairly, exhibit liquid crystallinity over a range of temperature. These molecules get endowed with sufficient linearity due to formation of dimers.

Despite the minimum requirements being present all the time and formation of dimers, the first two members viz. p-methoxy and p-ethoxy benzoic acids do not exhibit liquid crystallinity individually. Yet, their mixture is reported to exhibit mesomorphism [2]. As details concerning such an exhibition of mesomorphism are not available, an attempt of studying such a binary system of the two acids and their individual binary systems with p-methoxycinnamic acid as a liquid crystalline component, has been made under this investigation with a view to understand their behaviour towards exhibition of mixed mesomorphism.

**2. Experimental.** — **2.1 PREPARATION OF p-ETHOXY-BENZOIC ACID.** — The acid was prepared by boiling under reflux for 2-3 hours 1 mole of p-hydroxybenzoic acid, dissolved in 2 moles of aqueous potassium hydroxide with 1.1 moles of ethyl iodide. Under these conditions little or no esterification takes place; the free acid liberated by the addition of concentrated hydrochloric acid was crystallised thrice from small volumes of glacial acetic acid. The fine crystalline acid was obtained in white prism like crystals. The yield was practically quantitative. M. P. 197 °C [3].

**2.2 PREPARATION OF p-METHOXYCINNAMIC ACID.** — 20.4 g of anisaldehyde and 39 g of malonic acid were dissolved in 50.0 c. c. of pyridine to which a few drops of piperidine were added and heated for one hour under reflux on a water bath. A rapid evolution of CO<sub>2</sub> takes place. The reaction was completed by boiling the solution for five minutes. Then it was cooled and poured into excess of water containing enough hydrochloric acid to combine with pyridine. The p-methoxycinnamic acid separated was filtered off, washed with water and recrystallised from alcohol several times and dried. The yield was practically quantitative. White shining crystals were obtained. M. P. 172-188 °C [4].

2.3 PURIFICATION OF p-METHOXYBENZOIC ACID (ANISIC ACID). — It was purified by repeated crystallisation from water. Fine white needles were obtained. M. P. 183.4 °C.

2.4 PURIFICATION OF p-AZOXYANISOLE. — It was purified by repeated crystallisation from alcohol. Fine yellow needles were obtained. M. P. 118-136 °C.

2.5 METHOD OF STUDY. — The usual optical method has been employed for the study [5].

3. Results and discussion. — A study of the phase diagram (Fig. 1) reveals the enantiotropic mixed meso-

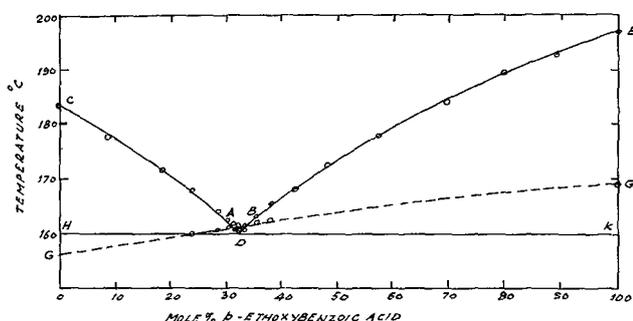


FIG. 1. — Nematic mixed liquid crystal formation.

morphic region within the mole % range of 31.0 to 34.0 of p-ethoxybenzoic acid which is indeed extremely small. Even the metastable monotropic transitions on supercooling do not extend beyond 23.76 mole % on the left and 37.61 mole % on the right side of the eutectic. The temperature range over which mixed nematic mesophase is exhibited varies between 0.5-1.5 °C which too strangely enough is small. The maximum temperature for nematic liquid-isotropic liquid transition is 161.4 °C, simultaneously the eutectic being 160.0 °C. All this looks strange in face of the expected ease with which mesomorphic property could show up over a much wider range of molar concentration and temperature.

The first detracting factor seems to be that of comparatively higher eutectic. If the eutectic of the mixture could sink considerably lower, then the temperature range could be much bigger than the one actually observed. The relatively high melting points 183.4 °C and 197 °C respectively of these acids do not permit sinking of the eutectic beyond a certain level and induce

the molecules to offer greater resistance to thermal break down. Thus while individually non-mesogenes, they even resist mixed mesomorphic property from appearance in mixed melts.

The second factor of importance seems to be the latent transition temperatures of these acids. The latent transition temperatures can be easily ascertained by smooth extrapolation of nematic-isotropic transition curve on either side. The values obtained are recorded in Table I. The binary mixtures of these acids individually with p-azoxyanisole give rise to nematic-isotropic transition curves which show incipient minimum [5, 6]. Naturally, extrapolation of such curves is rendered difficult thereby making it impossible to look for even approximate values of the latent transition temperatures of these acids from their binary systems with p-azoxyanisole.

But Walter [7], from his study of the binary systems of these non-mesogenes with p-methoxycinnamic acid arrived at certain values for the latent transition temperatures of p-methoxy and p-ethoxy benzoic acids. From the present study of the binary systems of these same non-mesogenes with p-methoxycinnamic acid (Fig. 2 and 3), the values of the latent transition temperatures are ascertained by smooth extrapolation of the nematic-isotropic transition curves. All these values are given in Table I along with those obtained from their own binary system.

At once it can be seen that these values are comparable leaving little or no doubt about the reliability of

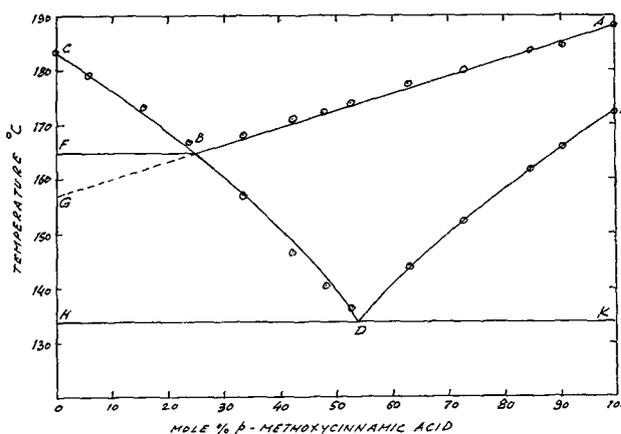


FIG. 2. — Extrapolation of the nematic-isotropic transition curve.

TABLE I

Substance	Latent transition temperatures		
	L. T. T. extrapolated (binary system with p-methoxy cinnamic acid) in °C	L. T. T. extrapolated (binary system of the acids) in °C	L. T. T. extrapolated (Walter [7]) in °C
p-methoxy benzoic acid	157.5	156.5	155.6
p-ethoxy benzoic acid	169.0	169.5	165.0

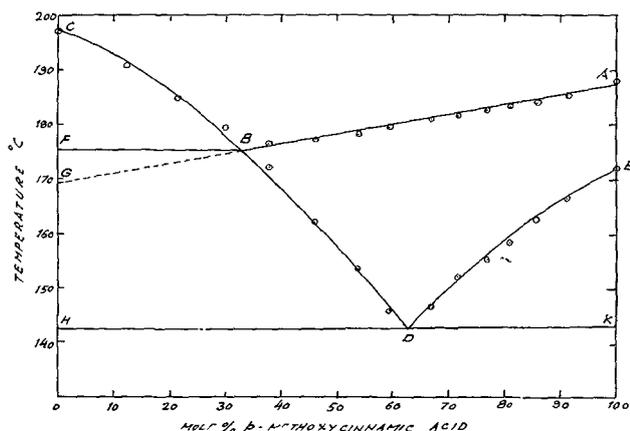


FIG. 3. — Extrapolation of the nematic-isotropic transition curve.

these values. It is clearly noted from Table II that these latent transition temperatures are far off from their normal melting points, the difference being 26.9 °C and 27.5 °C for *p*-methoxy and *p*-ethoxy benzoic acids respectively.

TABLE II

*Difference value between L. T. Ts. and M. P. s.*

Substance	M. P. in °C	L. T. T. extrapolated in °C	Difference
<i>p</i> -methoxybenzoic acid	183.4	156.5	26.9
<i>p</i> -ethoxybenzoic acid	197.0	169.5	27.5

This is such condition as not conducive to exhibition of mixed mesomorphism. Remarkably, the difference between their melting points and latent transition temperatures in both the acids is practically the same indicating thereby that both the acids are equally off from the probable ease of formation of mixed liquid crystals. The higher polarity of the terminal groups will be resulting into much lesser slopes [5, 8] of the isotropic-nematic transition curves, a condition that would decide the proximity of the latent transition temperatures to their normal melting point obtained by extrapolation. Evidently, the terminal groups of both these acids are sufficiently polar; even the initial slopes of the transition curves are much low. These conditions are indeed favourable to greater proximity of latent transition temperatures to their melting points. Yet, the unexpected but factually much wider difference in their latent transition temperatures to their normal melting points leads to only one important thing viz. their unusually high melting points.

The effect of pressure in lowering the melting points of the pure substances as well as their mixed melts will suggest a study of the binary system under suitable pressure conditions which was viewed beyond the scope of the present investigation.

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