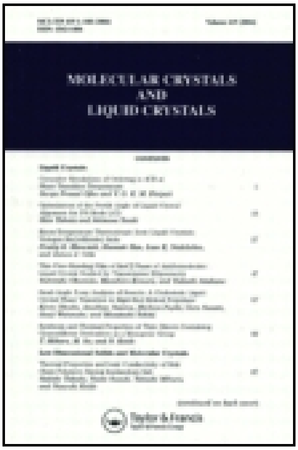

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Phase Transition Studies in Liquid Crystals across I-N and N-S_c Phases in Alkoxy Benzoic Acids – Density Measurements

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Density is one of the simple and accurate techniques to obtain the information regarding the nature of the transition and pre transitional effects across any phase transformation in liquid crystals. Density is measured with temperature in well known alkoxy benzoic acids with alkoxy chain number from 3 to 12 and 16. Even though the density measurements are carried on some of the homologues in this series, we have carried out systematic studies on all the homologues available and the results are compared with the literature values. Whereeever there is deviation the reasons for such deviations are explained.

Keywords: alkoxy benzoic acids; homologues; phase transition studies

I. INTRODUCTION

In the area of soft condensed matter physics, the dilatometric studies (the density) of liquid crystal (LC) phase transitions involving different structural organization is an intriguing topic of study. The density studies involving temperature variation across different phase transformations in LC materials are long known [1–7] to provide information regarding the nature of the phase transition and the growth of the pretransitional effects. If these investigations are carried out in a

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homologous series, the influence of the molecular structure (i.e., the rigidity/flexibility components of the molecule) on the thermal stability of the LC phase can be studied. Further, such studies provide complimentary and confirmatory experimental evidence for these results obtained by using other techniques [1,7] like polarizing thermal microscopy (TM) and differential scanning calorimetry (DSC) regarding the determination of phase transition temperatures, the nature of the transition and the thermal stability of the phase of interest.

p-n-alkoxy benzoic acids form a homologous series of compounds with alkoxy chain number $n = 3$ to 16, exhibit two different types of phase variants. The lower homologues with $n = 3$ to 6 exhibit only nematic phase while higher n value compound with $n = 7$ to 12 and 16 exhibit smectic-C phase along with the nematic phase. These compounds form a family which has been extensively studied as they form inter and intra molecular hydrogen bonding [8–12]. Further, the dilatometric studies have been reported in the case of compounds with $n = 7$, 8 and 9 across IN and NC transitions and they observed that the values obtained for the density jumps across IN transition show high values compared to those observed in other liquid crystal compounds which exhibit IN transition [1].

This manuscript describes the dilatometric studies across IN and NC phase transitions and the pre transitional effects computed on the high temperature side of the IN transition.

II. EXPERIMENTAL

The densities were carried out with a U-shaped bicapillary pyknometer in conjunction with a digital cathetometer. The capillaries of the pyknometer having diameter about 300microns and 25 cm long. The volume of the pyknometer is about 1 ml. The bottom of the pyknometer contains about 96% of the total volume of the sample.

p-n-alkoxy benzoic acids (99.9% purity) ($n = 3$ to 12 and 16) are supplied by Frinton laboratories, New Jersey, USA, and the compounds are used as it is. The absolute error in the measurement of density is $\pm 10^{-4}\,\mathrm{g\,cm^{-3}}$. The cooling rate during the measurement was $0.5\,\mathrm{K\,h^{-1}}$.

III. RESULTS AND DISCUSSION

The transition temperatures from dilatometric studies (Table 1) are reasonably in good agreement with those reported in literature [12] and values supplied by the company.

TABLE 1 Transition Temperatures Observed in Dilatometric Study*

Alkoxy chain number	IN transition temp. (°C)	NC transition temp. (°C)
3	155.8	—
4	160.0	—
5	150.0	—
6	154.0	—
7	147.4	102.2
8	146.6	93.6
9	144.9	117.5
10	137.0	115.6
11	140.7	119.8
12	137.2	127.5
16	150.3	120.3

*Literature values [12].

The estimated molar volume (molecular weight/density) in the isotropic phase per an increment of methylene unit estimated at $T_{(IN+5)}$ is in the range of $15.99 \times 10^{-6}\,m^3 \cdot mol^{-1}$ and agrees with the literature data available on nO.m compounds and the values reported for the normal liquids [1,13,14] whose values vary between 15 to $17 \times 10^{-6}\,m^3 \cdot mol^{-1}$. Figure 1 illustrates the variation of molar volume with the alkoxy chain number with a slope value of $16.1 \times 10^{-6}\,m^3 \cdot mol^{-1}$.

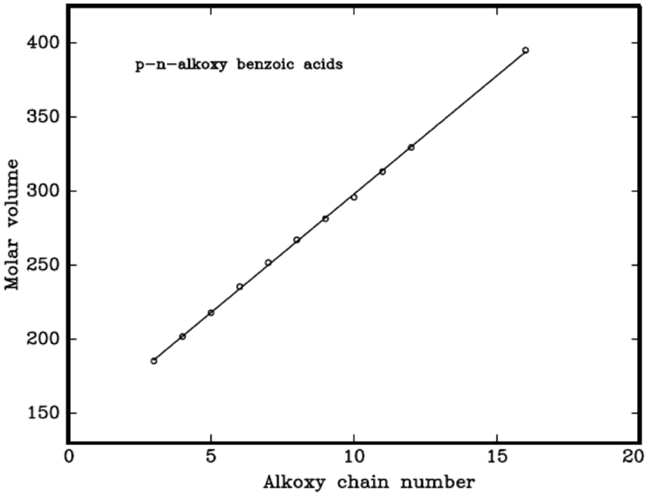

FIGURE 1 Change of molar volume with the chain length.

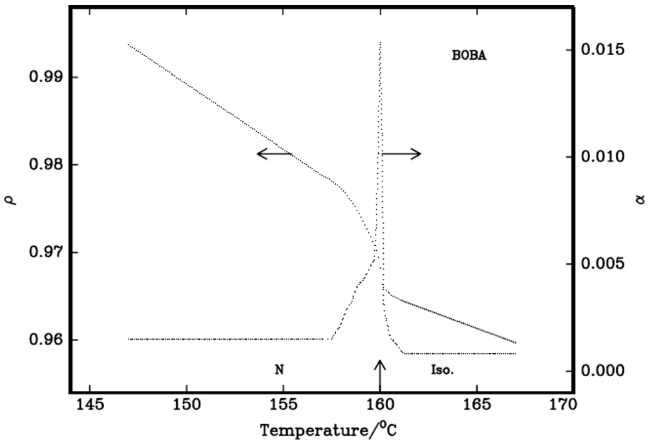

FIGURE 2 Variation of density and thermal expansion coefficient with temperature in 4Oba.

The temperature variation of density ρ(T) and the thermal expansion coefficient α(T) for all the compounds was carried out in all the compounds and the results in the case of $n = 4$, 7 and 16 are shown in Figures 2–4. The slopes observed in different phases show an increasing trend as one goes from isotropic to higher order LC phases as expected. However, the values are found to be relatively higher in

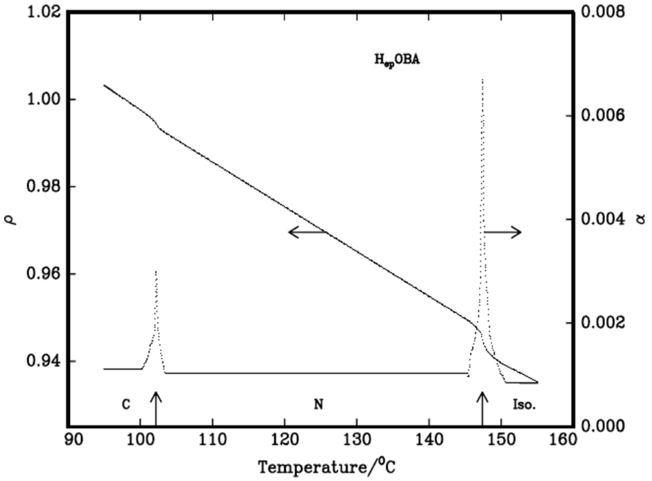

FIGURE 3 Variation of density and thermal expansion coefficient with temperature in 7Oba.

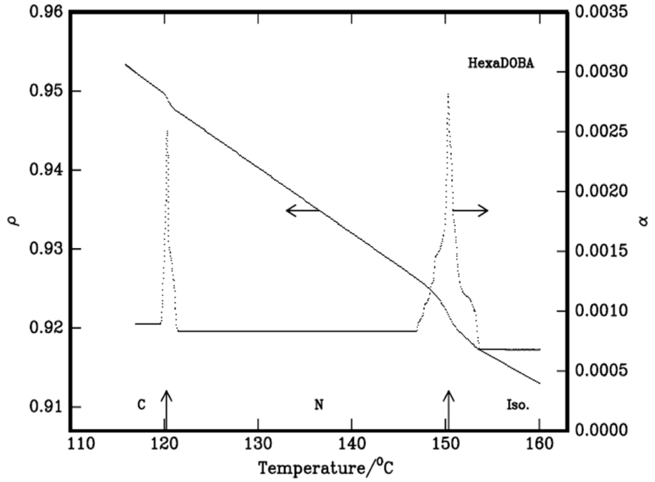

FIGURE 4 Variation of density and thermal expansion coefficient with temperature in 16Oba.

some compounds and lower in others [Table 2] compared to those found in nO.m compounds [5].

Isotropic – Nematic (IN) Transition

The density is found to decrease with the increase of temperature in all phases including the isotropic phase of all the compounds except in the vicinity of phase transition where it shows an increase, before it attains equilibrium value of the next (lower temperature) phase. The density jump, $(\Delta\rho/\rho)$ is calculated as the vertical distance between the density values (ρ_1 and ρ_2) obtained by the linear extrapolation from either sides of the transitions, (which are in fact the average value of the above two extrapolated density values i.e., $[\{(\rho_1 - \rho_2)\}/\{(\rho_1 + \rho_2)/2\}]$.

The observed percentage of density jumps $(\Delta\rho/\rho)$ in these compounds vary between 0.22%, to 1.11% in the compounds and the values are found to be with in the range reported for other compounds which exhibit IN phase transition [8,9] except for the compounds with $n = 4$, 7, 8, 11 and 12 compounds which show high values and these values agree with reported values for which the dilatometry was reported [Table 2] [8–11]. However, it is not uncommon to get high or lower density jump values. The thermal expansion coefficient maxima observed for these compounds are given in Table 2. These values suggest the first order nature of the transition as expected at an IN interface.

TABLE 2 The Density Jump, Thermal Expansion Coefficient Maxima and the Density Slope in Different Phases of the Alkoxy Benzoic Acid Compounds

Compound	Phase variant	% of $(\Delta\rho/\rho)_{\text{I-N}}$	$\alpha_{\text{I-N}} \times 10^{-4}\,{}^\circ\text{C}^{-1}$	% of $(\Delta\rho/\rho)_{\text{NC}}$	$\alpha_{\text{N-C}} \times 10^{-4}\,{}^\circ\text{C}^{-1}$	$(\text{d}\rho/\text{dT})_{\text{iso}} \times 10^{-4}\,{}^\circ\text{C}^{-1}$	$(\text{d}\rho/\text{dT})_{\text{N}} \times 10^{-4}\,{}^\circ\text{C}^{-1}$	$(\text{d}\rho/\text{dT})_{\text{C}} \times 10^{-4}\,{}^\circ\text{C}^{-1}$	Ref.
3-acid	N	0.31	32.2	—	—	2.5	4.4	—	
4-acid	N	0.95	153.3	—	—	10.7	14.5	—	[8]
5-acid	N	0.29	31.7	—	—	6.8	9.4	—	[8]
6-acid	N	0.35	29.6	—	—	5.0	6.6	—	
7-acid	NC	0.55 (0.97)	67.0	0.16	30.0	8.5	10.3	11.2	[9]
8-acid	NC	0.63 (1.28)	51.3	0.22	29.3	9.8	11.5	12.7	[9]
9-acid	NC	0.44 (.88)	41.1	0.05	15.7	5.9	6.3	7.3	[10,11]
10-acid	NC	0.22	36.6	0.04	11.1	5.9	7.1	8.0	
11-acid	NC	0.99	84.3	0.25	37.3	9.8	14.9	17.5	
12-acid	NC	1.11	53.9	0.35	30.0	11.0	13.6	15.5	
16-acid	NC	0.44	28.2	0.11	25.0	7.10	8.30	9.00	

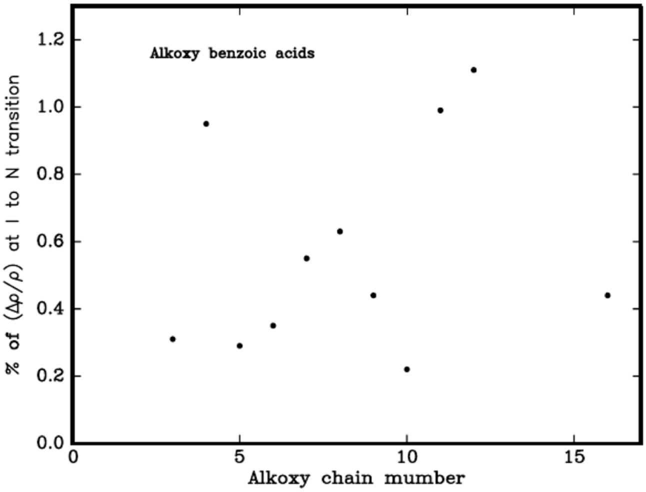

FIGURE 5 Density jumps across IN interface verses chain number.

The density jumps observed across IN interface are plotted against the chain number and is shown in Figure 5.

Nematic – Smectic-C (NC) Transition

The compounds with $n = 7$ to 12 and 16 exhibit smectic-C phase in addition to nematic phase. A transition from an orientational order nematic phase to smectic-C phase possessing additional layered structure with a tilted order is expected to be first order. The observed density jumps which are found to be lower compared to those reported for compounds for which dilatometric studies are reported in literature and the thermal expansion coefficient maxima [Table 2] suggest this particular transition is found to be first order.

Pretransitional Effects Across IN Transition

The observed nonlinear density variation on isotropic side (fluctuation dominated non-linear regions, FDNLR) represents the varied volume swept by the molecules (with characteristic hindered rotational degrees of freedom). As such these fluctuations are accompanied by the density variation, which grows during the condensation of the low temperature LC phase. In the vicinity of the phase transformation, the volume occupied by the molecules with a specified potential energy is influenced by the growth of low temperature mesophases

TABLE 3 $\alpha_{eff.}$ Values, Thermal Span of FDNLR of p-n-Alkoxy Benzoic Acids

Alkoxy chain number	$\alpha_{eff.}$	FDNLR (°C)
3	0.50	2.2
4	0.71	1.4
5	0.35	1.4
6	0.33	1.1
7	0.41	3.3
8	0.29	1.8
9	0.31	2.2
10	0.40	1.6
11	0.52	2.9
12	0.42	3.0
16	0.42	3.4

with a specific molecular structure. Further, the FDNLR on both sides of the interface depends on the LC phase (on the lower temperature side of the transition). The growth of LC phase through the underlying density fluctuation from the isotropic liquid is estimated by an exponent α by fitting the observed density data (in FDNLR for $T > T_C$) to the following relation

$$|\rho_i - \rho_C| \propto |Ti - Tc|^{(1-\alpha_{eff.})} \tag{1}$$

where ρ_I is the observed density at temperature of interest T_i and ρ_C is the observed density at isotropic to nematic transition. As $\Delta T = |T_i - T_C|$ reflects thermal range of pre transition of fluctuation in FDNLR, they imply the longevity of the fluctuations. However, $\alpha_{eff.}$ reflects the strength of the fluctuations. The $\alpha_{eff.}$ values and the data of thermal span of FDNLR are listed in Table 3. The goodness of the fit is demonstrated through the ρ values (>0.996) corresponding to the χ^2 test in the present compounds.

The Salient Features Observed from the Dilatometric Study are

1. Confirmation of the first order nature of IN and NC transitions.
2. The density jumps observed across the two phase transformations agree with the literature values reported for some of the compounds in the series except in one or two compounds.
3. The difference in $\alpha_{eff.}$ and FDNLR values for the compounds suggests difference in the strengths of the fluctuations that the molecule experiences at the phase transition interface.

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