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N–S_A Transition First or Second Order: Tricritical Point (TCP) in N(*p*-*n*-pentyloxy benzylidene)*p*-*n*-alkyl anilines?

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The nature of the nematic–smectic A (NA) phase transition is discussed in the light of the available experimental data on N(*p*-*n*-pentyloxy benzylidene)*p*-*n*-alkyl anilines, 50.m series of compounds. The experimental data elucidate the interesting aspects and it is confirmed that the 50.m homologues have a unique place in nO.m compounds. The nature of the NA transition, its dependence on the nematic thermal range, the length of the alkoxy and alkyl chains are discussed. The experimental evidence suggests the presence of TCP near the 50.m homologues.

INTRODUCTION

The nematic–smectic A (NA) transition was realized either as a first-order or a second-order transition by extensive theoretical and experimental studies in recent years.[1–6] Kobayashi,[1] McMillan[2] and de Gennes[7] independently proposed different theoretical models and showed that this transition could be either first or second order. de Gennes, using a Landau expansion of the free energy, emphasized the crucial role played by the nematic order fluctuations and its coupling to the smectic A order parameter which can lead to a first order NA transition. McMillan using mean field theory, predicted for a large l/d (l = length and d = diameter of the molecule) the nematic range shrinks and the NA transition becomes first order. These theories thus imply the existence of a tricritical point (TCP) at the cross over from a second order to a first order transition. Extensive reviews[8–11] describe some of the theoretical and experimental developments in liquid crystal multicritical phenomena and the properties of the NA transition. The experimental studies by adiabatic calorimetry,[12–15] light scattering[16] and x-ray studies[12] have shown that the NA transition can indeed be continuous when measured to $(T-T_{NA})/T_{NA} \simeq 10^{-5}$. Further recent calorimetric studies in N(*p*-*n*-heptyloxy benzylidene)*p*-*n*-heptyl aniline (70.7)[18] showed a first order NA transition and concluded that for $T_{NA}/T_{NI} \simeq 0.99$ a TCP occurs. Contrary to this observation a number of other nO.m com-

pounds[19–23] with M $\simeq$ 0.96 exhibited a first order N–A transition. In a recent article in the 40.6 + 60.4 binary mixtures of nO.m series the TCP occurred at M = 0.955.[24]

A systematic study on a number of nO.m compounds (n = 4 to 8 and m = 4 to 12) by different experimental techniques is carried out in order to study the nature of the NA transition, its dependence on the nematic and smectic ranges and the McMillan parameter M = T_{NA}/T_{NI}. As a part of this program we present here the experimental results at the NA transition in some of the N(*p*-*n*-pentyloxy benzylidene) *p*-*n*-alkyl anilines, which occupy a unique position in nO.m series.

EXPERIMENTAL

The 50.m compounds were prepared by condensation of *p*-*n*-pentyloxy benzaldehyde and the appropriate aniline in refluxing absolute ethanol for four hours in the presence of a few drops of glacial acetic acid. The crude compounds obtained after removing the ethanol were recrystallized repeatedly from absolute ethanol and this process was continued until constant transition temperatures are observed. The transition temperatures are in agreement with the literature values.[25]

A capillary pyknometer with a diameter of about 0.35 mm was used for density measurements. Two capillaries (each 40 cm.) are arranged at the top of a bulb in U shape. The amount of the sample within the dilatometer was about 4 gm. The changes in the level of the liquid crystal were measured with a cathetometer to $\pm$0.01 mm. The absolute error in the density is $\pm$0.0001 gm/cm^3. The permitted temperature control is 0.1°C for a length of time ranging from 0.5 to 3 h. The absolute accuracy in temperature measurements is $\pm$0.1°C. The rate of cooling used was 0.1°C per hour.

RESULTS AND DISCUSSION

The nematic and smectic A thermal ranges, nematic–smectic A (T_{NA}) transition temperatures, the McMillan parameter M = T_{NA}/T_{NI} and the density jumps ($\Delta\rho/\rho\%$) at the NI and NA phase transitions for 50.m compounds are presented in Table I. For comparison the data of the compounds in 40.m, 60.m and 70.m homologous series are included which exhibit the same order of the nematic range and the M value with those in 50.m homologous series. Figure 1 illustrates the density variation with temperature on either side of the NA phase transition ($\pm$5°C) in 50.m compounds along with 60.4 and 70.1. The salient features are:

1. The isotropic–nematic (IN) transition is found to be first order in all nO.m compounds exhibiting a density jump of the order of 0.3 $\pm$ 0.1.

2. A small but noticeable density jumps are observed in case of 50.6,[26] 50.8[27] and 50.12[26] homologues of 50.m series at the NA transition. The jumps and thermal expansion coefficient α suggest a questionable weak first order tending to a second order. Further it is observed the jump decreases with the increase in the alkyl chain length. The other compounds 50.4, 50.5, 50.7 and 50.10[26,28] show no density jump

TABLE I

Compound	N-Range °C	S_A-Range °C	$T_{NA°C}$	T_{NA}/T_{NI}	Δρ/ρ at IN in %	Δρ/ρ at NA in %
50.4	16.8	0.5	52.4	0.951	0.22	—
50.5	23.4	1.3	54.4	0.933	0.34	—
50.6	11.2	8.4	61.7	0.968	0.30	0.10
50.7	13.3	8.7	64.8	0.962	0.33	—
50.8	8.0	15.8	68.0	0.977	0.25	0.08
50.10	8.8	13.0	67.0	0.974	0.46	—
50.12	2.9	17.7	71.0	0.992	0.32	0.06
60.4	7.8	11.1	69.1	0.978	0.42	0.24
60.5	10.0	13.6	75.0	0.972	0.27	0.22
70.1	12.0	4.4	61.0	0.965	0.20	0.46
70.4	2.1	9.8	74.6	0.994	0.28	0.43
70.5	2.8	11.4	79.3	0.990	0.34	0.25
40.10	12.0	17.9	64.7	0.961	0.22	0.02
40.12	8.0	17.6	69.5	0.977	0.39	0.02

and the density curve is continuous at the NA transition (Figure 1) suggesting the transition to be of second order. The X-ray diffraction,[29] ESR[30] and refractive index[27,28] studies on 50.8 and 50.10 concur with the density results in confirming the NA transition to be of second order.

3. Discrete density jumps exhibited by the compounds 60.4, 60.5, 70.1, 70.4 and 70.5 at the NA transition confirm this transition as first order. This was further confirmed from the recent ESR study of the orientational order parameter using a nitroxide probe.[30]

4. The higher homologues of 40.m series, 40.10[26b] and 40.12[26b] show a second order NA transition like their lower homologues 40.6,[31] 40.7[32] and 40.8.[33]

5. Different compounds, *viz.*, 40.12, 50.8, 50.10 and 60.4; 50.12 and 70.5; 40.10 and 70.1 exhibit almost identical nematic thermal range as well as the McMillan parameter (M) value but with different smectic A ranges. The NA transition in these compounds is either first order, weak first order or second order. Further it is interesting to note that the compounds 50.6 and 60.5 (the difference between the two compounds being the interchange of end chains) with slight different M values and of comparable nematic range (11.2°C for 50.6 and 10°C for 60.5) show a weak first order and first order NA transitions respectively.[30,34]

The results in the nO.m compounds envisage the decisive role played by the alkoxy chain in governing the NA transition rather than the nematic or smectic thermal range or the alkyl chain length. Furthermore the 40.m series including the higher homologues, irrespective of their nematic range, exhibit a second order NA transition, while 60.m and 70.m series exhibit a first order NA transition including the lower homologues which possess both nematic and smectic A phases (60.3 compound has a nematic range of 13°C. While 70.1 has 12°C). It was further substantiated by the recent studies on the binary mixtures of nO.m compounds; 40.6 + 60.4 and 40.8 + 60.8.[35] The TCP was observed for M = 0.955 in the first binary mixture and for M = 0.978 in the second binary mixture respectively. The M value and the nematic range observed for the TCP in 40.8 + 60.8 mixtures are

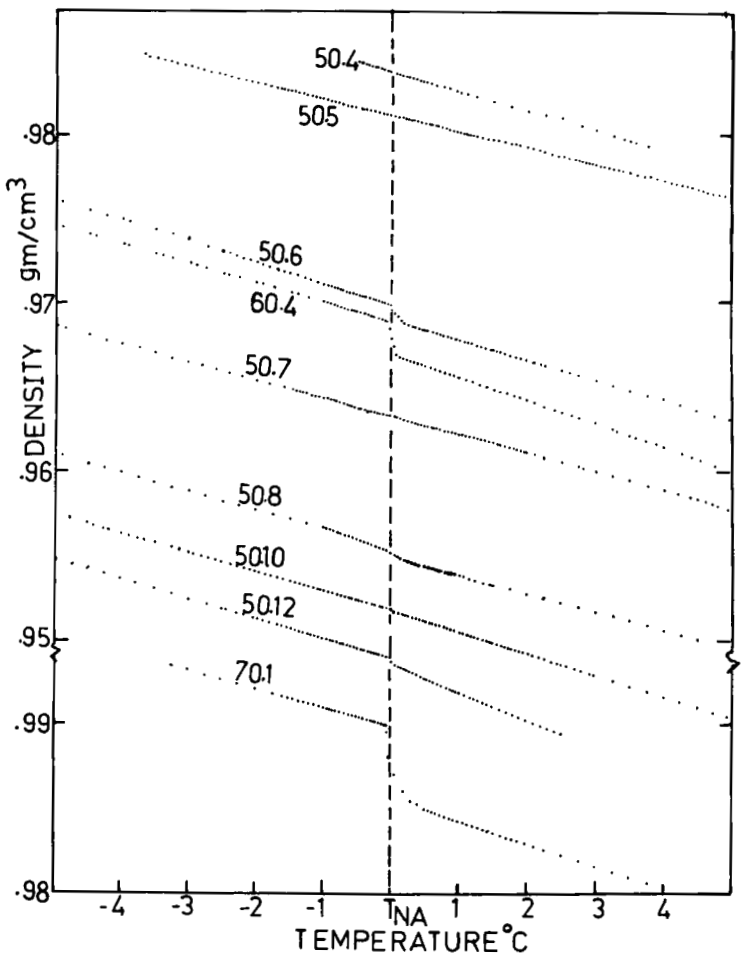

FIGURE 1 Density (gm/cm³) variation with temperature on either side of the NA phase transition (±5°C) in 50.m compounds along with 60.4 and 70.1.

identical with the values reported for the compound 50.8. It suggests an interesting point, *viz.*, the physical properties of the compounds in 50.m series characterizing the NA transition whether to be first order or second order may fall in the vicinity of the TCPs in the binary mixtures of the compounds possessing nematic and smectic A phase in the nO.m homologous series when n takes a value above and below 5 and m is constant. The M value at the TCP in these mixtures is smaller than the values reported for the binary mixtures of $\overline{n}S5$[12] series and nCB[14,36] series. Furthermore, in the nO.m series we believe that the minimum alkoxy carbon chain number should be six for a possible first order NA transition irrespective of the alkyl chain number, the nematic thermal range and the M value. Further experimental investigations are in progress to confirm this conclusively.

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