Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: P. R. Alapati, A. Arulsankar, B. Gogoi, T. K. Ghosh & Nagappa (2001): SM A — SM C TRICRITICAL POINT IN TBBA AND TBDA MIXTURES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 61-68

To link to this article: http://dx.doi.org/10.1080/10587250108023948

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 61-68
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Sm A – Sm C Tricritical Point in TBBA and TBDA Mixtures

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Terephtal-bis-p-n-decylaniline (TBDA) exhibit a weakly first order Sm A – Sm C Phase Transition Whereas TBBA, a lower homologue of the same series, exhibit a second order Sm A – Sm C transition. In order to investigate the tricritical point (TCP) of Sm A – Sm C transition, a systematic study of binary mixtures of TBBA + TBDA are undertaken. DSC and polarizing thermal microscopy studies infer the TCP of the Sm A – Sm C Transition at the weight percent of 80.05 TBDA in TBBA. We report here a systematic study of the approach of TCP by DSC and density measurements as a function of temperature in few compositions of TBBA + TBDA on both sides of the tricritical point.

Keywords: First order transition; Sm A – Sm C transition; Tricritical point

INTRODUCTION

The smectic A and the smectic C phases are characterized by a one-dimensional density wave whose wave vector is along (Sm A) or tilted (Sm C) with respect to the molecular director. The molecules maintain translational invariance within the smectic planes. If the constituent molecules are optically active the Sm C^* phase will be observed instead of the Sm C phase. Experimentally, the Sm A – Sm C

(Sm A – Sm C*) transition is generally found to be second order. Although, it was initially proposed that this transition might exhibit helium like critical behaviour[1], subsequent studies have clearly shown that Sm A – Sm C as well as the Sm A – Sm C* transition is mean-field-like with a sixth order term in the Landau free energy expansion[2-5]. Lien and Huang[6] predicted that the Sm C – Sm A transition can be driven to become first order by large fluctuations of a nearby Sm A – Isotropic transition. However, the existence of a first-order Sm A – Sm C transition does not appear to have been established experimentally so far except in few higher homologues of Terephthal-bis-p-n-alkylaniline series of compounds viz., TBDA and TBNA. However, a first order Sm A – Sm C* transition was observed in some ferroelectric liquid crystals exhibiting high spontaneous polarisation. Sm A – Sm C tricritical points are also reported[7-12] either as fluctuation mediated weak first order Sm A – Sm C transitions, weak first order transitions due to the strong coupling between the chiral group to the orientational order, or due to the narrow Sm A thermal range and also in the vicinity of N-S_A-S_C multicritical points.

Higher homologues of TBĀA series of compounds viz., TBDA and TBNA exhibit first order/weakly first order Sm A – Sm C transition,[13,15] whereas TBH_pA and lower homologues exhibit a second order Sm A – Sm C transition. We report here a systematic study of the Sm A – Sm C tricritical point (TCP) in binary mixtures of TBDA + TBBA using Differential Scanning Calorimetry (DSC) and density studies. The only other study of the Sm A – Sm C TCP in TBĀA homologous series was reported by Prasad et al[8] using X-ray diffraction studies.

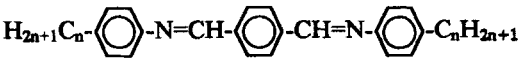
EXPERIMENTAL

The compounds TBBA and TBDA were synthesized following the standard procedure given in the literature[13] and repeatedly recrystallized from absolute ethanol-benzene mixture until the observed transition temperatures were constant. The mixtures of TBDA+TBBA were prepared in ethanol-benzene mixture and the solvent was removed under vacuum using Rotoevaporator. The transition temperatures were determined by using Perkin-Elmer DSC-2. Various phases

exhibited by these mixtures were characterized by observing their textures under a polarizing microscope attached with an indigenous hot stage. The temperature resolution of the microscopic observation was 0.1°C. Density measurements were carried out with a bicapillary pyknometer[14]. The diameter of the capillary was about 0.35 mm and the accuracy in the density measurement was ±0.1 Kg m^{-3}. The permitted cooling rate was 2°C hr^{-1} and temperature accuracy was ±0.1°C.

RESULTS AND DISCUSSION

Molecular structure of Terephthal-bis-p-n-alkylaniline compounds is shown below.



TBDA (n=10) and TBBA (n=4)

The Isotropic – Smectic A and Smectic A – Smectic C phase transition temperatures and entropy change (ΔS/R) at these transitions in seven compositions of weight percent of TBDA in TBBA are presented in Table 1.

TABLE 1 I-S_A and S_A-S_C phase transition temperatures and entropy change (ΔS/R) at these transitions in different compositions of weight percent of TBDA in TBBA.

% TBDA	Transition Temperature/°C		Sm A Thermal Range/°C	Entropy change (ΔS/R)	
	I-S_A	S_A-S_C		I-S_A	S_A-S_C
100	190.90	189.02	1.88	1.81	0.152
93.55	193	187.3	5.70	1.79	0.098
85.15	198.6	184.7	13.90	1.67	0.048
82.80	197.6	181.6	16.00	1.68	0.028
81.06	197.2	181.1	16.1	1.62	-
80.26	198.9	182	16.90	1.63	-
80.05	199.5	182.2	17.30	1.56	-
75.39	200.9	177.4	23.5	1.59	-

Smooth variation of entropy change at the Sm A – Sm C transition in different mixtures indicate the existence of Tricritical Point (TCP) near 81% of TBDA.

Variation of entropy change as a function of weight percent of TBDA in TBBA is shown in figure 1. The variation of entropy change ($\Delta S/R$) at Sm A – Sm C transition as a function of scaled parameter, T_{AC}/T_{IA} where (T_{AC} is the S_A – S_C and T_{IA} is the isotropic – smectic A transition temperature) similar to Mc Millan parameter for Nematic – Smectic A transition is shown in figure 2. It appears that the crossover of Sm A – Sm C transition from first order to second order transition

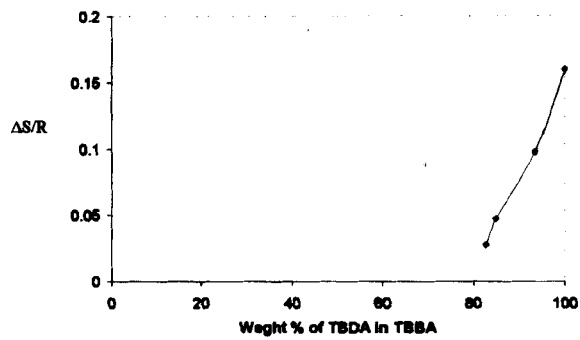


FIGURE 1 Variation of entropy change as a function of weight percent of TBDA in TBBA.

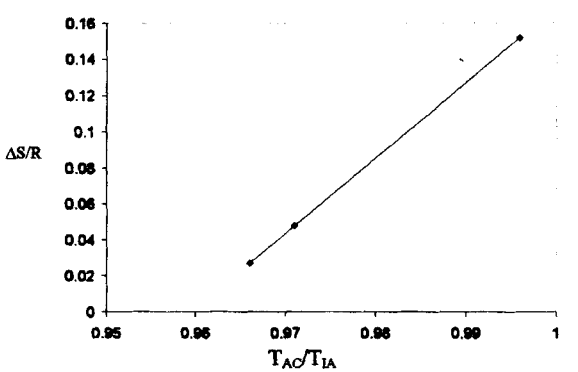


FIGURE 2 The variation of entropy change ($\Delta S/R$) as a function of scaled parameter T_{AC}/T_{IA}

takes place at a T_{AC}/T_{AI} value of 0.960. The ratios $N=h_2/h_1$ (where h_1 and h_2 are the heights of the DSC transition peaks obtained at the Sm A – Sm C transition with two different temperature scanning rates: one (h_2) being twice the other (h_1) keeping the weight of the compound constant) are $1 \leq N \leq \sqrt{2}$ for an isothermal first order transition and 2 for a second order transition[16]. Variation of Navard-Cox parameter ($N=h_2/h_1$) as a function of weight percent of TBDA is shown in figure 3.

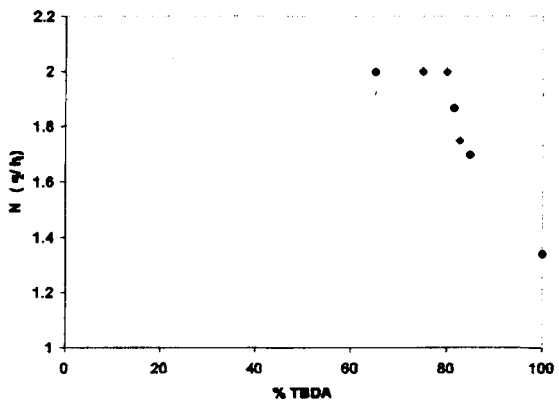


FIGURE 3 Navard-Cox parameter as a function of weight % of TBDA

A constant value of N=2 for mixtures lower than 80.05% TBDA indicates that the transition is second order where as the smooth decrease of N value from 2 at 80.05% TBDA to 1.34 at 100% TBDA indicates that the transition becomes weakly first order in mixtures above 80.05% TBDA. Therefore, the existence of TCP for Sm A – Sm C is established in 80.05% TBDA in TBBA at a T_{AC}/T_{IA} value of 0.959.

The variation of density as a function of temperature in six binary mixtures of TBDA + TBBA viz., 93.55% TBDA, 85.15% TBDA, 82.80% TBDA, 81.06% TBDA, 80.05% TBDA and 75.39% TBDA are shown in figure 4. Rather small

density jumps ($\Delta\rho/\rho\%$) of 0.21 for the mixture 93.55% TBDA, 0.12 for the mixture 85.15% TBDA and 0.08% for 82.8% TBDA are observed at the Sm A – Sm C transition indicating that the transition weaken further as the percent of TBBA is increased. Further a small coexistence region of Sm A and Sm C phases was observed at the transition in these three mixtures. These values are in agreement with density jump ($\Delta\rho/\rho\%$) at Sm A – Sm C transition in pure TBDA which is 0.39[13] whereas it is 0.13 in TBNA[15]. No density jump was observed at the transition for the remaining mixtures studied indicating that the transition is second order. However, the transition is indicated by a very small change in slope of density curve at the smectic A – smectic C transition.

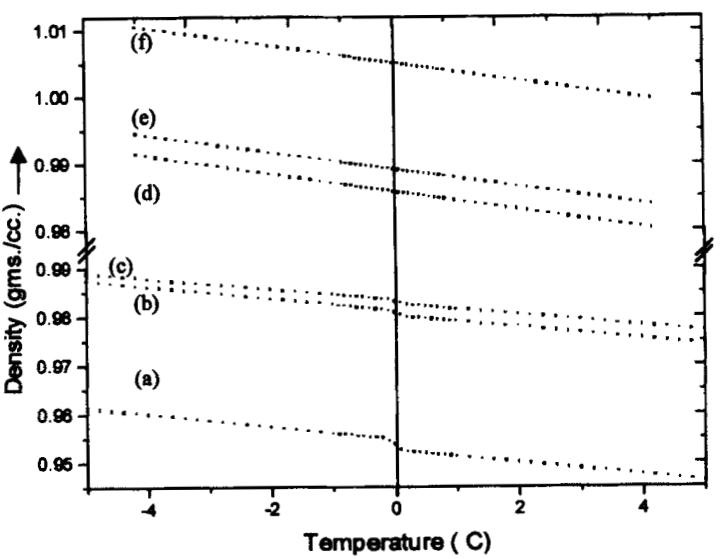


FIGURE 4 The variation of density as a function of temperature (centred on T_{AC}) in six binary mixtures of TBDA + TBBA: (a) 93.55% TBDA (b) 85.15% TBDA (c) 82.80% TBDA (d) 81.06% TBDA (e) 80.05% TBDA and (f) 75.39% TBDA.

Density jumps for mixtures are compared with those of pure TBĀA compounds in Table 2. The variation of density at S_A-S_C transition as a function of thermal range of Sm A phase (Table 2) clearly indicate that the transition becomes weaker as the Sm A thermal range increases and the TCP occur at a Sm A thermal range of about 17°C, whereas in pure compound, TBOA, existence of TCP was reported with a much lower Sm A thermal range of 9.4°C.

TABLE 2 Density jump at Sm A – Sm C transition and Sm A thermal range of TBDA + TBBA mixtures and other TBĀA homologues.

Compound	$\Delta\rho/\rho\%$	T_{AC}/T_{IA}	Sm A Thermal Range (°C)
93.55% TBDA	0.21	0.988	5.80
85.15% TBDA	0.12	0.971	13.90
82.80% TBDA	0.08	0.966	16.00
80.26% TBDA	-	0.964	16.9
80.05% TBDA	-	0.960	17.3
TBDA	0.39	0.996	1.90
TBNA	0.13	-	6.40
TBOA	-	-	9.40

ACKNOWLEDGEMENTS

Financial support from Council of Scientific & Industrial Research (CSIR) and Department of Science & Technology (DST), New Delhi are gratefully acknowledged.

References

[1] P.G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **21**, 49 (1973).
[2] C.C. Huang and S.C. Lien, *Phy. Rev. Lett.*, **47**, 1917 (1981).
[3] C.C. Huang and J.M. Viner, *Phy. Rev. A.*, **25**, 3385 (1982).
[4] R.J. Birgeneau, C.W. Garland, A.R. Kortan, J.D. Litster, M. Michele, B.M. Ocko, C. Rosenblatt, L.J. Yu and J.W. Goodby, *Phys. Rev. A.*, **27**, 1251 (1983); M. Michele and C.W. Garland, *ibid*, **27**, 2624 (1983).
[5] S. Dumrograttana, G. Nounesis and C.C. Huang, *Phys. Rev. A.*, **33**, 2181 (1986); S. Dumrograttana, C.C. Huang, G. Nounesis, S.C. Lien and J.M. Viner, *ibid*, **34**, 5010 (1986).
[6] S.C. Lien and C.C. Huang, *Phys. Rev. A.*, **30**, 624 (1984).
[7] R. Shashidhar, B.R. Ratna, G.G. Nair, S. Krishna Prasad, CH. Bahr and G. Heppke, *Phys. Rev. Lett.*, **61**, 547 (1988) and references therein.
[8] S.K. Prasad, V.N. Raja, D.S.S. Rao, G.G. Nair and M.E. Neubert, *Phys. Rev. A.*, **4**, 2479 (1990).
[9] CH. Bahr and G. Heppke, *Phys. Rev. A.*, **41**, 4335 (1990).
[10] J.B. Goates, C.W. Garland and R. Shashidhar, *Phys. Rev. A.*, **41**, 3192 (1990).
[11] C. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **150B**, 313 (1988).

[12] H.Y. Liu, C.C. Huang, C. Bahr and G. Heppke, *Phys. Rev. lett.*, **61**, 345 (1988).
[13] P.R. Alapati, D.M. Potukuchi, N.V.S. Rao, V.G.K.M. Pisipati and D. Saran, *MOl. Cryst. Liq. Cryst.*, **146**, 111 (1987) and references therein.
[14] P.R. Alapati, D. Saran and S.V. Raman, *Mol. Cryst. Liq. Cryst.*, **287**, 239 (1996).
[15] N.V.S. Rao, V.G.K.M. Pisipati, J.S.R. Murthy, P.B. Rao and P.R. Alapati, *Liquid Crystals*, **5**, 539 (1989).
[16] P. Navard and J.M. Hauding, *J. Thermal Analysis*, **29**, 405 (1984); *Mol. Cryst. Liq. Cryst., Letters*, **101**, 261 (1984); *Mol. Cryst. Liq. Cryst., Letters*, **102**, 265 (1984).