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An Experimental Study of the Smectic A-Smectic C Transitions in Monolayer, Partially Bilayer and Bilayer Systems

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An Experimental Study of the Smectic A-Smectic C Transitions in Monolayer, Partially Bilayer and Bilayer Systems

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The smectic A-smectic C (A-C) transition in several compounds has been shown to be mean-field-like (MF) with a substantial tricritical crossover effect. However, a simple MF behaviour, i.e., with negligible tricritical influence, had not been reported till recently. The heat capacity measurements of the MIT group in two compounds exhibiting the bilayer A_2-C_2 transition revealed such a behaviour. It is of interest to investigate whether a simple MF behaviour can be observed for partially bilayer A_d-C_d and monolayer A_1-C_1 transitions also. We report the first systematic order parameter measurements in the vicinity of the A_2-C_2, A_d-C_d and A_1-C_1 transitions. The data analysed in terms of power law and extended mean field expressions provide clear evidence of a simple MF behaviour in all three cases. The significance of this result is discussed.

Keywords: smectic A-smectic C transition, tilt angle measurements, mean-field model

INTRODUCTION

The smectic A-smectic C (A-C) transition in several compounds has been shown to be mean-field like (MF) with a substantial tricritical crossover effect.[1-3] Studies on materials exhibiting monolayer phases indicate that the tricritical influence is controlled by the temperature range of the A phase[4] and/or the strength of the transverse dipole moment of the constituent molecules.[5] However, a simple MF behaviour, i.e., with negligible tricritical influence, had not been reported till recently. The heat capacity measurements of Garland and coworkers[6] have shown such a behaviour for two compounds exhibiting the A_2-C_2 transition. The present study was undertaken to investigate whether a simple MF behaviour can be observed for the A-C transition in monolayer and partially bilayer systems as well. In this communication we report the first systematic order parameter measurements in the vicinity of the bilayer A_2-C_2, the partially bilayer A_d-C_d and the monolayer A_1-C_1 transitions.

MATERIALS AND METHODS

The compounds used were 4-n-heptacylphenyl-4'-(4"-cyanobenzoyloxy)benzoate (7APCBB) [A_2-C_2], 4-cyanoethylphenyl-4'-decyloxycinnamate (CEPDOC) [A_d-C_d], *trans*-1,4-cyclohexane-di-n-octyloxybenzoate (TCOB) [A_1-C_1]. The relevant transition temperatures are given in Table I. The experiments were conducted using a computer-controlled Guinier diffractometer (Huber 644) described elsewhere.[7] The accuracy in the determination of the wave vector is 2×10^{-4} Å^{-1} while the resolution in the equatorial direction (also the scanning direction) is 1×10^{-3} Å^{-1} half width at half maximum. The temperature was maintained to a constancy of 5 mK during each measurement.

RESULTS AND DISCUSSION

Figure 1 shows the temperature variation of the layer spacing in 7APCBB and gives an idea of the precision of the layer spacing measurement. The tilt angle in the C phase has been evaluated using the expression

$$\phi = \cos^{-1}(d_c/d_A) \tag{1}$$

where d_c and d_A are the layer spacing values in the A and C phases, respectively. (For these compounds it was observed that the temperature dependence of the layer spacing in the A phase is not negligible. Hence, instead of considering the value of d_A in Equation (1) to be a constant, it was evaluated at each temperature by linearly extrapolating the data in the A phase.) The efficacy of using Equation

TABLE I

Transition temperatures and fit parameters. The number underlined in the fourth column indicates that the transition is isotropic-smectic A

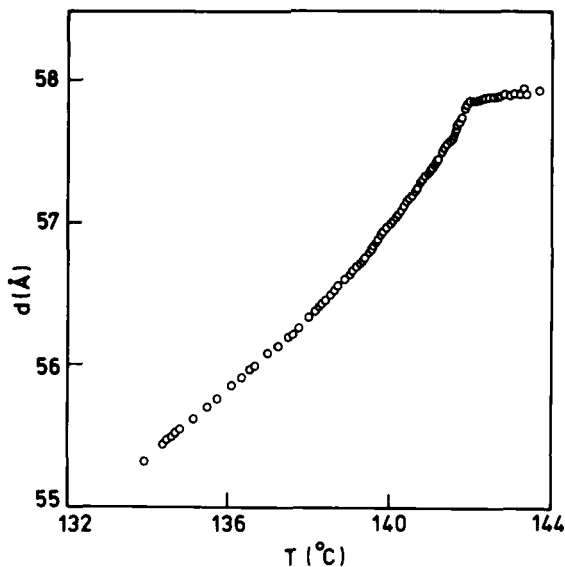| Compound	Transition	T_{AC} (°C)	T_{NA} or T_{IA} (°C)	ϕ_o	R	t_o
7APCBB	A_2-C_2	141.6	144.5	2.43	0.067	1.45×10^{-2}
DB8ClCN	A_2-C_2	117.2	155.1	-	-	[a]2.65×10^{-2}
CEPDOC	A_d-C_d	59.5	109.0	1.53	0.222	9.45×10^{-2}
TCOB	A_1-C_1	118.8	<u>178.3</u>	1.23	0.168	1.57×10^{-1}
$\overline{8}$S5	A_1-C_1	55.0	63.0	[b]2.43	-	[a]6.5×10^{-3}

a: Ref.6   b: Ref.9

FIGURE 1 Thermal variation of the layer-spacing for 7APCBB.
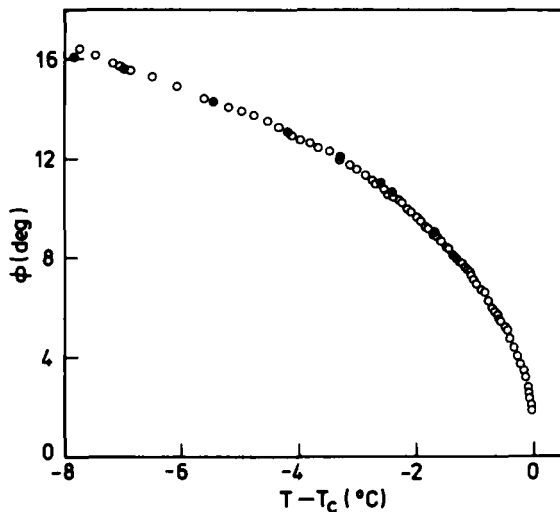
FIGURE 2 Temperature dependence of tilt angle ϕ for 7APCBB. ● are the data points obtained from "four spot" photographs.

(1) was verified by determining ϕ directly from a photographic ("four-spot" pictures) technique. It was found that the values evaluated from the two methods are in good agreement with each other. The variation of ϕ as a function of temperature in 7APCBB is shown in Figure 2.

Earlier studies have shown that the A-C transition can be well described by an extended mean field expression[8] of the type

$$F = F_0 + at\phi^2 + b\phi^4 + c\phi^6 \qquad (2)$$

where F_0 is the non-singular part of the free energy, $t = [(T_c - T)/T_c]$, T_c being the A-C transition temperature; a, b and c are positive coefficients for a continuous transition. Minimising the free energy in the C phase, we get

$$\phi = R^{1/2}[(1 + 3t/t_0)^{1/2} - 1]^{1/2} \tag{3}$$

Here $R = (b/3c)$, and $t_0 = (b^2/ac)$ is identified to be the full width at half height of the heat capacity curve. From Equation (3) one can see that for $|t| \ll t_0$, $\phi \sim t^{1/2}$ implying a simple MF behaviour (i.e., contributions from the 6th order term in Equation (2) are negligible) and for $|t| \gg t_0$, $\phi \sim t^{1/4}$ which describes the MF-tricritical like behaviour. Thus in this model the dimensionless parameter t_0 assumes an all important role describing the cross-over from a simple MF region near the transition to a tricritical-like region away from the transition. The temperature range over which mean-field behaviour can be observed is controlled by the magnitude of t_0; the smaller this value, the narrower is the MF region. The interesting fact is that in the monolayer cases t_0 was found to be small[3,9] the highest reported value being 6.5×10^{-3} for a compound referred to as $\overline{8}$S5. With these facts in mind, we fitted the tilt angle data for 7APCBB to Equation (3). Figure 3(a) shows that the fit is excellent. The value of t_0 obtained ($= 1.45 \times 10^{-2}$) is larger than that obtained previously for the monolayer cases but is somewhat smaller than the one obtained for another compound (DB8ClCN) having an A_2-C_2 transition.[6] A possible reason for the latter could be the narrow temperature range of the smectic A phase in 7APCBB (2.9°C) as compared to DB8ClCN (≈ 38°C). The large value of t_0 indicates that the MF region is substantial. The specific heat data obtained by Wen *et al.*,[6] for 7APCBB is reproduced in Figure 3(b) which shows a step-like variation across the transition supporting this observation. This feature combined with the absence of any pretransitional increase of specific heat on the C side, suggests that the coefficient c in Equation (2) is very small. In the limiting case of $c = 0$, the temperature variation of tilt angle can be described by a simple power law:

$$\phi = \phi_0 t^{1/2} \tag{4}$$

where, $\phi_0 = (a/b)^{1/2}$ and the specific heat will have a step-like jump.

Figure 3(a) also shows the fitting of the tilt angle data to Equation (4). From the excellence of the fit to Equation (4) and the step-like specific heat variation, one can conclude that for this compound, the coefficient c is indeed negligibly small and a MF expression with up to 4th order terms only is sufficient to describe the data.

Having observed that a simple MF model can describe the tilt angle data in the bilayer C_2 phase, it is interesting to see whether this could be true even in partially bilayer and monolayer C phases also. Since, at least in monolayer systems it has been demonstrated that the temperature range of the A phase influences the nature of the A-C transition,[3] we selected materials having a large temperature range ($\gg 50$°C) of the A phase. Figures 4 and 5 show the thermal variation of tilt angle for CEPDOC (A_d-C_d transition) and TCOB (A_1-C_1 transition) and the fits to
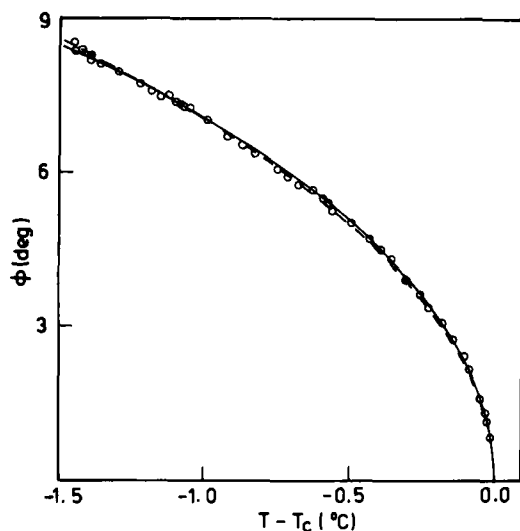
FIGURE 3(a) ϕ vs. $T - T_c$ plot for 7APCBB showing fits to Equation 3 (solid line) and Equation 4 (dashed line). Only every fifth data point is plotted here to present a clear view of the picture.
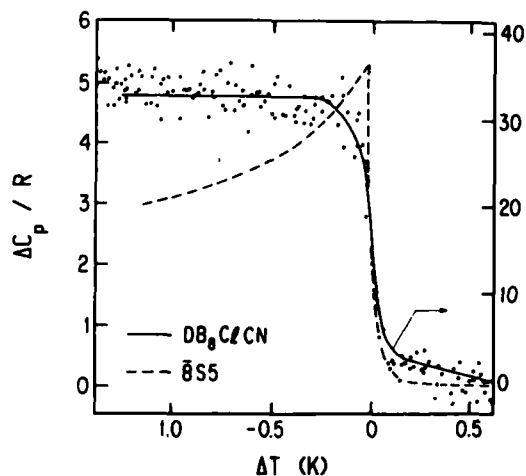

FIGURE 3(b) A detailed view of the excess molar heat capacity associated with the A_2-C_2 transition in 7APCBB. Also shown for comparison are the data for the A_2-C_2 transition in DB_8ClCN and the A_1-C_1 transition in $\overline{8}S5$. [Reference 6].

Equations (3) and (4). The two equations describe the data equally well for both compounds over the entire temperature range implying that the influence of the 6th order term in Equation (3) is negligible just as in the case of 7APCBB. This is reflected in the computed values of t_0 (Table I); both compounds have t_0 values higher than any reported so far. Two points are worth noting: 1) TCOB has a small tilt angle, even deep in the C phase—$\phi \sim 11°$ at $(T_c - 10)°C$. This appears to be due to a small a/b ratio (see Table I), which together with large values of b/c, suggests that the coefficient b is large. 2) In the bilayer phases (7APCBB and
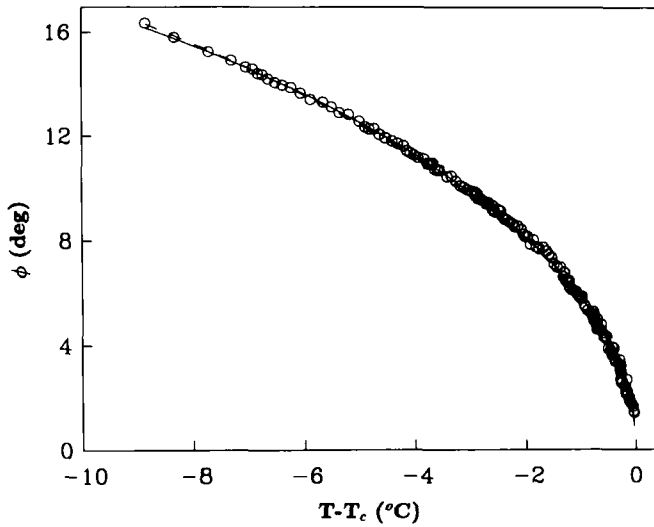
FIGURE 4 ϕ vs. $T - T_c$ plot for CEPDOC showing fits to Equation 3 (solid line) and Equation 4 (dashed line).
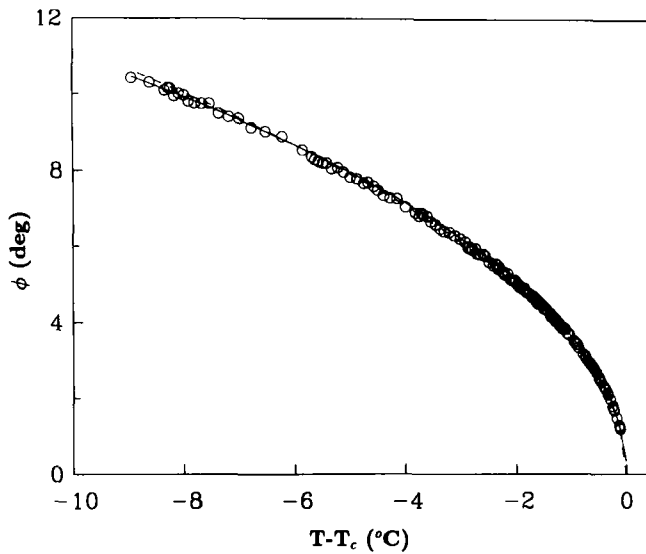

FIGURE 5 ϕ vs. $T - T_c$ plot for TCOB showing fits to Equation 3 (solid line) and Equation 4 (dashed line).

DB8ClCN), an increase of the A phase range by a factor of about 10 increases t_0 by a factor of about 2 whereas in the monolayer case (TCOB) an increase of the A phase range by a factor of about 7 increases t_0 by a factor of about 25 times.

A possible explanation for the observation of simple MF behaviour in the bilayer compounds even when the temperature range of the A phase is small is that the smectic A order is saturated before the transition to the C phase takes place, thus reducing the MF-tricritical crossover effect. It would appear that a larger temper-

ature range is required to saturate the smectic A order in the partially bilayer and monolayer cases.

Acknowledgment

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