

NEMATIC ORDER NEAR A TRICRITICAL NEMATIC-SMECTIC A PHASE TRANSITION <sup>★</sup>S.B. RANANAVARE, V.G.K.M. PISIPATI <sup>1</sup> and J.H. FREED*Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853, USA*

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A symmetric tricritical point (TCP) is demonstrated for the nematic-smectic A transition by blending two nearly identical isomers and by showing that the difference in coexistence values of the nematic order parameter  $S$  goes to zero with TCP exponent  $\beta_2 = 1$  as  $T_{TCP}$  is approached. A horizontal  $\lambda$ -line is associated with an observed universal behavior of  $S$  when a new scaling of  $T$  is used.

## 1. Introduction

The nematic to smectic A (NA) phase transition in liquid crystals has been a subject of extensive study in recent years. The original theories due to McMillan [1] and de Gennes [2] suggested that this transition could be first or second order. De Gennes, using a Landau expansion of the smectic free energy, emphasized the coupling between the smectic or density order parameter,  $\psi$  and the nematic or orientational order parameter  $S$ . When large fluctuations in  $S$  are permitted, this can cause the phase transition to be first order. A nematic phase of large extent, however, would result in  $S$  being saturated, thereby reducing the importance of the coupling term, so the transition becomes second order. McMillan used a molecular-field theory to obtain a similar conclusion. He predicted that the extent of the nematic range would depend on a parameter  $\alpha$  which measures the orientational-translational (or density) coupling, such that as  $\alpha$  is increased, the nematic range shrinks, and the coupling leads to a first-order transition. These theories thus imply the existence of a tricritical point (TCP) at the crossover from second- to first-order behavior. De Gennes and McMillan also predicted that the NA transition (for

which the space and order parameter dimensionalities are respectively,  $d=3$  and  $n=2$ ) should be very similar to that of superfluid helium, and Alben [3] predicted a <sup>3</sup>He/<sup>4</sup>He-like TCP in binary liquid-crystal mixtures. However, the theoretical story is more complex, and Halperin, Lubensky and Ma [4] argued that the NA transition can never be truly second order, which, of course rules out the possibility of a TCP. This controversy has spurred experimental studies by AC or adiabatic calorimetry [5-8], light scattering [9], and X-ray scattering [10] which have shown that the NA transition can indeed be continuous when measured to the dimensionless temperature  $(T - T_{NA})/T_{NA} \approx 10^{-5}$ . A better understanding of the transition can come from detailed studies of NA tricriticality such as the study of the cross-over between critical and tricritical exponents. Reviews by Lubensky [12] and Johnson [13] give further details on these matters, and a recent article by Garland and co-workers [8] summarizes recent studies. Also, the Landau and molecular-field theories for the tricritical point are discussed by Longa [14].

One prediction of the McMillan theory is that the parameter  $M = T_{NA}/T_{NI}$  (where NI refers to the nematic-isotropic phase transition) is a measure of the effectiveness of the orientational-translational coupling such that  $M = 0.87$  (obtained for  $\alpha = 0.7$ ) would correspond to the TCP, and there would be a continuous second-order transition for  $M < 0.87$ . Doane et al. [15], in an early NMR study of

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<sup>1</sup> Permanent address: Department of Physics, Nagarjuna University, Nagarjuna, Nagar 522 510, India.

$\Delta S = S_A - S_N$  at a first-order  $T_{NA}$  for a homologous series have confirmed that both  $\Delta S$  and  $M$  decrease with decreasing chain length. The more recent studies have been consistent with these observations.

We have undertaken an extensive study of the TCP and cross-over between first- and second-order behavior in the  $nO, m$  homologous series [i.e. the  $N(p\text{-alkoxy benzilidene})\text{-}p\text{-}n\text{-alkyl-anilines}$  with  $n$  and  $m$  the number of carbon atoms in the alkoxy and alkyl-aniline chains respectively] for  $4 < n < 8$  and  $1 < m < 8$ . In a recent article [16], we showed the dominant role played by the alkoxy chain length in governing the order of the NA transition: for  $n > 5$  ( $< 5$ ) the transition is first (second) order and for  $n = 5$ ,  $m > 8$  ( $< 8$  except for 5O, 6) leads to a first- (second-) order transition. Thus, for example 4O, 6 (with  $T_{NI} - T_{NA} = 23^\circ$ ) has a second-order transition, while 6O, 4, which has the same length and the same  $T_{NI} = 77.6^\circ\text{C}$ , exhibits a weak first-order transition (with  $T_{NI} - T_{NA} = 8^\circ$ ). Though surprising, we find this to be a quite general phenomenon for  $nO, m$  and  $mO, n$  mixtures subject to the above restrictions. We report here on our study of 4O, 6 and 6O, 4 mixtures. This may be regarded as a "minimum perturbation" series, since the difference  $n - m = 2$  is a minimum consistent with a cross-over from second-order to first-order NA transition. In fact, from our studies reported below we find that  $S(x)$  at constant  $T$  and  $P$  (where  $x$  is mole fraction of 4O, 6) is linear with  $x$ , consistent with ideal solution behavior. Also preliminary X-ray results on 4O, 6 and 6O, 4 mixtures [17] show their smectic layer spacings ( $d$ ) to be very nearly equal, but their intermolecular separation ( $r$ ) within a smectic layer does vary with  $x$  in a small, but monotonic fashion consistent with  $r(6O, 4) < r(4O, 6)$ .

In the present work, utilizing differential scanning calorimetry (DSC) and ESR with a spin probe, we first demonstrate that these methods can be utilized rapidly and accurately to determine the 4O, 6/6O, 4 concentration at the TCP. We show that for the  $nO, m$  series, there is a universal dependence of  $S$  in the nematic phase upon a dimensionless  $T$  different from the frequently utilized  $t_N = 1 - T/T_{NI}$  but related to the McMillan parameter  $M$ . Related behavior of  $S$  in the smectic A phase is also found. We suggest that this universal behavior demonstrates the crucial role played by the nematic order parameter in the smec-

tic phase transition. Most significantly, we clearly demonstrate, from the measured values of  $S$ , the existence of a symmetric tricritical point that is a direct analogue of the  $^3\text{He}\text{-}^4\text{He}$  superfluid transition, and an estimate of the associated critical exponent  $\beta_2$  is made. After considering the source of the difference in behavior between 4O, 6 and 6O, 4, we briefly consider the implications of our results for current theories of the NA transition and the TCP.

## 2. Phase diagram and tricritical point

We have located the TCP in 4O, 6/6O, 4 mixtures by the DSC technique of Navard and Cox [18]. We find it to be at mole fraction of 4O, 6:  $x = 0.805 \pm 0.01$  for which  $M = 0.955$ . We wish to emphasize again that we find this method is both reliable and very convenient to use. We have systematically studied the nematic order parameter,  $S$ , of the large and rigid spin probe CSL (5  $\alpha$ -cholestane) by ESR for an extensive range of 4O, 6/6O, 4 mixtures. It is well known from many previous studies that CSL accurately reports on the overall or "backbone" molecular ordering within liquid-crystalline phases [19,20] and its low concentration ( $10^{-4}$  molar) hardly perturbs the phase behavior<sup>#1</sup>. We show, in fig. 1, the phase diagram for the 4O, 6/6O, 4 mixtures based upon the DSC studies. Both DSC and ESR methods could be conveniently employed to determine the phase transitions as a function of  $T$  and  $x$ , and to within the accuracy of the present measurements ( $\pm 0.1^\circ\text{C}$  in  $T$  and  $\pm 1\%$  in  $x$ ) they are in good agreement. Indeed the TCP could be accurately determined from the ESR measurements (cf. fig. 2b2). We find the ESR method to be the more sensitive and no less convenient.

This phase diagram looks remarkably like the one obtained by McMillan [1] from his simple theoretical model (if % 6O, 4 is replaced by the parameter  $\alpha$ ), i.e. a greater fraction of 6O, 4 would, by increasing the  $d/r$  ratio, enhance the orientational-translational coupling term. The main disagreement with

<sup>#1</sup> We checked the transition temperatures and the transition enthalpies of the liquid crystal with and without probe, and to within our experimental resolution, we did not find any differences.

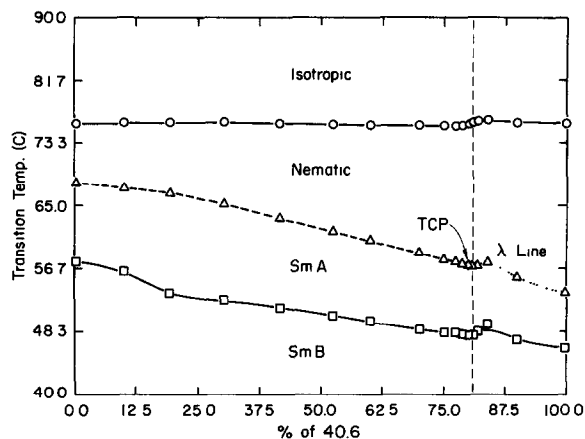


Fig. 1. Phase diagram for mixtures of 4O, 6 and 6O, 4 from DSC and polarizing microscopy studies in the temperature versus mole percent 4O, 6 plane. The phases are labeled, and the tricritical point  $T_{TCP}$  and  $\lambda$ -line are noted. The error in  $T_{NI}$  and  $T_{NA}$  is  $< \pm 0.5^\circ\text{C}$  (whereas for  $T_{AB}$  it is  $< \pm 1.5^\circ\text{C}$ ). (The equal divisions of the ordinate are computer rounded, cf. fig. 2 caption.)

the McMillan model is the significantly larger value of  $M$  we obtain for the TCP. Similar trends and phase diagrams were also obtained for mixtures of 4O, 7/7O, 4 and of 4O, 8/8O, 4 [21].

We show in fig. 2a the orientational order parameters measured at the NA phase transition for a range of  $x$  plotted as a function of  $T_{NA}(x)$  (with  $T_{NA}$  versus  $x$  given in fig. 1). The plot in fig. 2a to the right of the TCP (i.e.  $x < 0.80$ ) shows the values of  $S_N$  and  $S_A$  in coexistence at  $T_{NA}(x)$  corresponding to a first-order transition, whereas the single line (within experimental uncertainty) to the left of the TCP is the  $\lambda$ -line associated with the second-order transition. Fig. 2a may be compared with the equivalent results for  $^3\text{He}$ - $^4\text{He}$  mixtures [22]. In particular, in the latter case one plots mole fraction (m.f.) of  $^3\text{He}$  versus  $T(\text{m.f.})$ , the transition temperature. As Brisbin et al. [5] pointed out  $S_A - S_N = \Delta S$  is the "non-ordering density" for the N-A transition analogous to the m.f. difference in the  $^3\text{He}$ - $^4\text{He}$  case. In the latter case, it is known that "the two branches of the phase separation curve are linear near the [TCP] meeting there at a finite angle, and that the lambda line emerges precisely from this peak" [22]. This is exactly the character of the phase diagram in fig. 2a for the NA phase transition. It is, to our knowledge, the first such demonstration for a liquid-crystalline

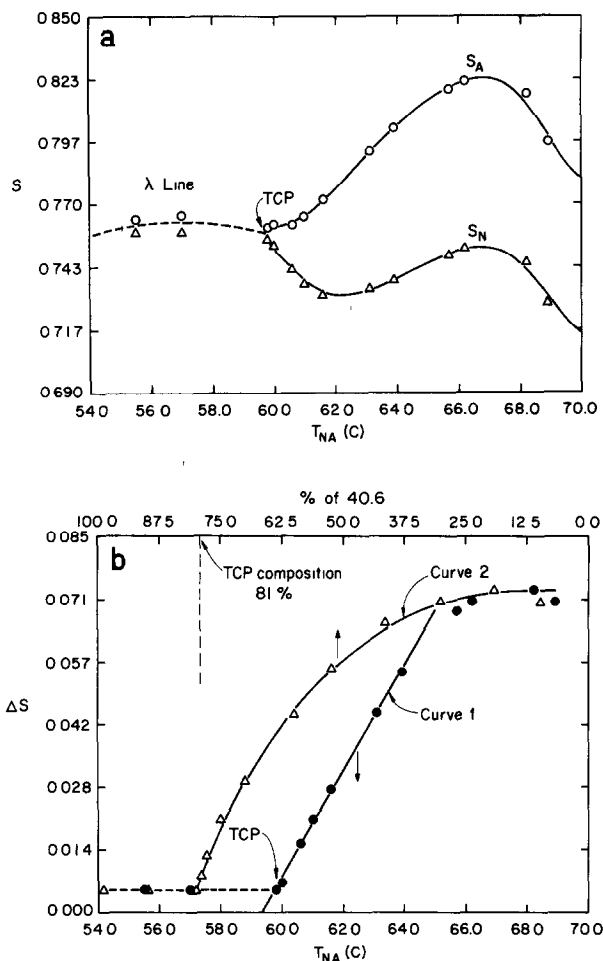


Fig. 2. (a) Phase diagram for mixtures of 4O, 6 and 6O, 4 shown as a plot of nematic (or orientational) order parameter  $S$  versus the NA phase transition temperature,  $T_{NA}(x)$ . The coexistence region and the  $\lambda$ -line are shown. The error in  $S$  is  $< \pm 0.0025$ . (b)  $\Delta S \equiv S_A - S_N$  at the NA phase transition versus (1)  $T_{NA}(x)$  and (2) mole percent of 4O, 6. Note that for curve (1) use the lower abscissa, whereas for curve (2) use the upper one as indicated by the vertical arrows. In (1) the straight-line fit yields an exponent  $\beta_2 = 1.00 \pm 0.005$ . In (2) the TCP is accurately located. (In these figures the ordinate is divided into six equal divisions; the numerical values between the exact end values have however been computer rounded for convenience.)

TCP. Note that in the present case the  $\lambda$ -line is horizontal (and is discussed below).

To continue with the analogy between the  $^3\text{He}$ - $^4\text{He}$  superfluid transition and the NA transition we note that for the former,  $\Delta$  (the chemical potential difference between  $^3\text{He}$  and  $^4\text{He}$ ) is the conjugate field

$g$  to the m.f., whereas for the latter one may take as the conjugate field  $g$  to  $\Delta S$  one that couples to the orientational order of the molecular long axis. Brisbin et al. [5] and others have done this by varying the alkoxy chain length in a different homologous series; we have kept the molecular length  $d$  constant but have continuously (but gently) varied the  $d/r(x)$  ratio. Thus  $x$  regarded as a monotonic function of  $r(x)$  [or  $d/r(x)$ ] can play the role of the conjugate field. Thus fig. 1 is in the “ $T$ - $g$ ” plane permitting one to study critical-to-tricritical cross-over of unrenormalized exponents. (The nearly linear dependence of  $T_{NA}$  on  $x$  in fig. 1 indicates the very mild variation in conjugate field.) The recent studies of specific heat and smectic coherence length have shown the cross-over of the exponents  $\alpha$ ,  $\nu_{\perp}$  and  $\nu_{\parallel}$  from the superfluid ( $n=2$ ,  $d=3$ ) value to the mean-field tricritical value. In fact, the anisotropic scaling relationship  $\alpha + 2\nu_{\perp} + \nu_{\parallel} = 2$ , explained by Lubensky [8], and Nelson and Toner [23,24] was found for all the systems investigated #2.

Instead, we may readily study the tricritical exponent  $\beta_2$ , defined by  $\Delta S \propto (T_{TCP} - T_{NA})^{\beta_2}$  from fig. 2a or alternatively from  $\Delta S$  versus  $T_{NA}(x)$  plotted in fig. 2b1. The very good linear fit, yielding  $\beta_2 = 1.00 \pm 0.05$ , which is the well-known mean-field prediction expected for the TCP, is obtained as shown. This result is thus further confirmation of the existence of a NA TCP and hence of the second-order character of the NA transition for  $T_{NA} < T_{TCP}$ .

### 3. The orientational order parameter and the NA transition

We now examine in figs. 3 and 4 the respective behavior of  $S_N$  and  $S_A$  versus  $T$  for 14 different 4O, 6/6O, 4 mixtures corresponding to  $x$  ranging from 0 to 1. We use  $t_N$  and  $t_A = 1 - T/T_{NA}$  respectively in the dimensionless abscissas of figs. 3a and 4a. In fig. 3a there is a large spread of such curves attributable to the large range of  $\Delta T_N(x) = T_{NI}$

$-T_{NA}(x)$  versus  $x$ . However, when  $S_N$  is plotted in fig. 3b versus  $t_N^U = (T_{NI} - T)/\Delta T_N = t_N/(1 - M)$  a single universal curve is obtained! We have observed this identical behavior for 16 other cases of pure compounds and mixtures from the  $nO$ ,  $m$  homologous series [21]. Note that this universal curve is obtained not only for those mixtures exhibiting a second-order transition, but it applies to the cases of first-order transitions after replacing  $T_{NA}$ , the observed phase transition temperature by  $T_{NA}^*$  ( $< T_{NA}$ ). This is to be regarded as the temperature at which the second-order transition would have occurred if a first-order transition had not. We obtained  $T_{NA}^*$  empirically as the single adjustable parameter (for each  $x$ ) to have  $S_N$  versus  $t_N^U$  fall on the universal curve in fig. 3b. Our results for  $T_{NA} - T_{NA}^*$  are consistent (within our experimental uncertainties) with the simple Landau theory summarized below.

In order to interpret the success of this scaled  $t_N^U$  we first note the following. (1)  $S_{NA}$ , the order parameter in the nematic phase at the second-order  $T_{NA}$  (or apparent  $T_{NA}^*$  for first-order cases) is equal to  $0.760 \pm 0.005$  for all members of the homologous series; in fact, the constancy of  $S_{NA}(x)$  with  $x$  showed up in fig. 2a as a horizontal  $\lambda$ -line. (2)  $S_{NI}$ , the value of  $S_N$  at the NI transition, is nearly the same for all members of the homologous series. Let us now incorporate these observations into the simple Landau theory for the NA transition. We first write the free energy in terms of nematic and smectic order parameters in the usual manner as [2,5]

$$F = \alpha(T, x)\psi_0^2 + \frac{1}{2}\beta_0(T, x)\psi_0^4 + \gamma\psi_0^6 + (\delta S^2/2)\chi(T, x) - C(T, x)\delta S\psi_0^2, \quad (1)$$

where  $\delta S$  is the *change* in  $S$  induced by the coupling to  $\psi_0^2$ , and where we have explicitly denoted the expansion parameters in terms of their functional dependence on  $T$  and  $x$  for the 4O, 6/6O, 4 mixtures (for other members of the  $nO$ ,  $m$  series we shall regard  $x$  in a more general sense). In eq. (1),  $\alpha = \alpha_0[T - T_{NA}^*(x)]$  (and is not to be confused with McMillan's  $\alpha$  parameter). One optimizes  $F$  with respect to  $\delta S$  leading to  $\delta S = C\chi\psi_0^2$ , which can be substituted back into eq. (1). It then follows that a tricritical point is predicted for  $\chi(T_{NA}(x)) = 2\beta_0/C^2$ . For  $\chi(T_{NA}(x))$

#2 The only careful study of the *smectic* order parameter near (but not at) the tricritical point is due to Chan et al. [25], who used the Landau model for the critical exponent. But the variation of their critical exponent is instead consistent with cross-over [22] from the 3D XY model to the mean-field (tricritical) exponent.



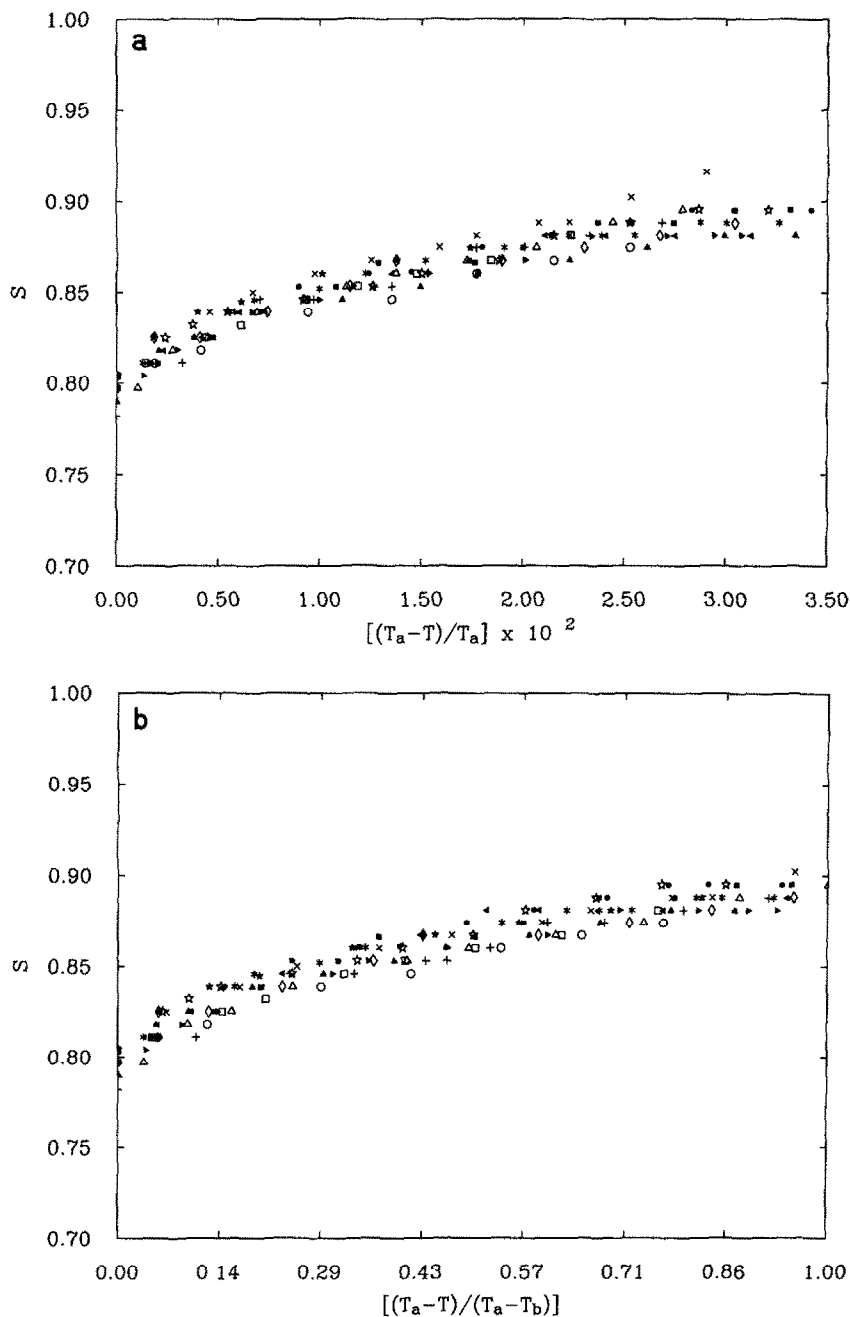


Fig. 4. Graphs of  $S_A$  versus (a)  $(1 - T/T_{NA})$  and (b)  $(T_{NA} - T)/(T_{NA} - T_{AB})$  for the same 14 mixtures of 4O, 6-6O, 4 as in fig. 3. The error in  $S_A$  in these figures is  $< \pm 0.005$ .

$< 2\beta_0/C^2$  there is a second-order transition at  $T_{NA} = T_{NA}^*$ , whereas for  $\chi(T_{NA}(x)) > 2\beta_0/C^2$  there is a first-order transition at  $T_{NA} = T_{NA}^* + \beta^2/16\alpha_0\gamma$ .

Our observation that  $S_{NA} = 0.76$  at  $T_{NA}^*$  in all cases suggests that we may rewrite  $\alpha(T, x) = \alpha(S) = \hat{\alpha}_0(S - S_{NA})$  in eq. (1), with  $\hat{\alpha}_0$  a constant, i.e. the

NA transition is driven by the nematic order parameter in the sense that a precise value,  $S_{NA}$  must be achieved for the second-order transition to the smectic phase to occur<sup>#3</sup>. Given that the NI transition occurs at nearly the same  $T_{NI}$  for all 4O, 6-6O, 4 mixtures (cf. fig. 1) with approximately the same value of  $S_{NI}$ , the use of  $t_N^U$  could just be a convenient scaling between the "end points" of the nematic phase consistent with these other facts. In particular, if  $S_N$  versus  $T$  were linear, e.g.  $S_N = S_{NI} + b(x)(T_{NI} - T)$ , then these facts would mean that  $b(x) = (S_{NA} - S_{NI}) / [T_{NI} - T_{NA}^*(x)]$  with a universal curve  $S_N = S_{NI} + (S_{NA} - S_{NI})t_N^U$ . Instead we can plot the McMillan (or Maier-Saupe) [1,2] expression for  $S$  versus  $t_N^U$  with the cut-off of the nematic phase at the common  $S_{NA}$  as shown by the solid line in fig. 3b; with the addition of a second term in the orientational potential [14,19] (e.g. the Legendre polynomial  $P_4$  in addition to  $P_2$ ) we can fit the observed universal curve reasonably well (e.g. with  $P_4 = -0.3P_2$ ). The fact that other homologues of different chain length (yielding different values of  $T_{NI}$ ) also obeys the same universal curve suggests that  $T_{NI}$  is just an adjustable reference temperature for which a common value of  $S_{NI}$  is obtained.

In considering this matter further we have compared the behavior of  $S_N$  with the density  $\rho$  for the two pure components 4O, 6 and 6O, 4. The densities are the same in the isotropic phase and just below  $T_{NI}$ , but for  $T < T_{NI}$  one consistently has  $\rho(6O, 4) > \rho(4O, 6)$  in both the nematic and smectic phases [26]. Our preliminary X-ray data indicate that this is primarily due to a slightly denser packing within a smectic layer for 6O, 4 [i.e.  $r(6O, 4) < r(4O, 6)$ ] but with the same smectic layer spacing [ $d(6O, 4) \approx d(4O, 6)$ ]. Thus, by varying  $x$  one is gently varying the  $r/d$  ratio as noted above. In the spirit of the McMillan model, but not identical to it, we can let  $\alpha = 2 \exp[-(\pi r/d)^2]$ , and otherwise use his model. Based upon the analysis of Lee et al. [27], McMillan's simplified Fourier analysis of the molecular potential along the nematic director is probably adequate, since in our case we have short

alkyl chains, and the molecular length is not varied. (Lee et al. point out that by lengthening the alkyl chain the more general form of the potential is needed, and it will cause a depression in  $T_{IN}$  for longer chains. However, we observe a more complex behavior from the  $n, Om$  homologous series [21].) In the context of the McMillan theory, our results would imply that the orientational-density coupling is very important in driving the smectic phase transition. (This is the term somewhat related to that in  $\delta S \psi^2$  in the Landau expansion, i.e. an increase of McMillan's  $\alpha$  would be consistent with an increase in the coefficient  $C$  in eq. (1).) In fact, the simple McMillan theory (for  $\alpha = 0.6$ ) gives nearly our observed  $S_{NA} = 0.76$ , whereas his result for  $S_N$  and  $S_A$  at a first-order transition [considering it is for an  $\alpha = 0.85$ ] that is too large for our experiments in which  $\alpha$  is only gently varied about the TCP] is not inconsistent with fig. 2a. However, as shown by Longa [14], an additional translational term is probably needed to obtain the correct  $T_{TCP}/T_{NI}$ .

As a last point, we consider whether the nematic order parameter is actually saturated at  $T_{NA}$  (or  $T_{NA}^*$ ). In fact, we see in fig. 4 that  $S_A$  continues to increase with temperature, asymptotically reaching  $S_A \approx 0.89$  before the smectic A to B (AB) transition occurs. Fig. 4 resembles more of a "saturation curve" than did fig. 3. Nevertheless below the smectic B transition,  $S_B$  further increases toward unity. These observations are undoubtedly additional indications of the importance of orientational-translational coupling. To summarize, a substantial orientational order of rather precise magnitude appears to drive the NA transition, with additional orientational ordering occurring after the formation of the smectic A phase. In the smectic A phase,  $S_A$  appears to saturate out until the hexatic packing within the smectic B phase induces the last vestiges of orientational disorder to continue to freeze out.

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<sup>#3</sup> In fact if we let  $\alpha = \alpha(S, x)$  in eq. (1) and expand in terms of  $\delta S = S - S_0$ , then  $\alpha = \alpha_0(x)(S_0 - S_{NA}^*) + \alpha'(S_0, x)\delta S + \dots$ , so that in eq. (1) we can set  $C = -\alpha'(S_0, x)$ , thereby emphasizing the dominant role played by the nematic ordering in the NA transition.

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