

# Comment on On the Nature of the Smectic A-to-Nematic Phase Transition of 8CB

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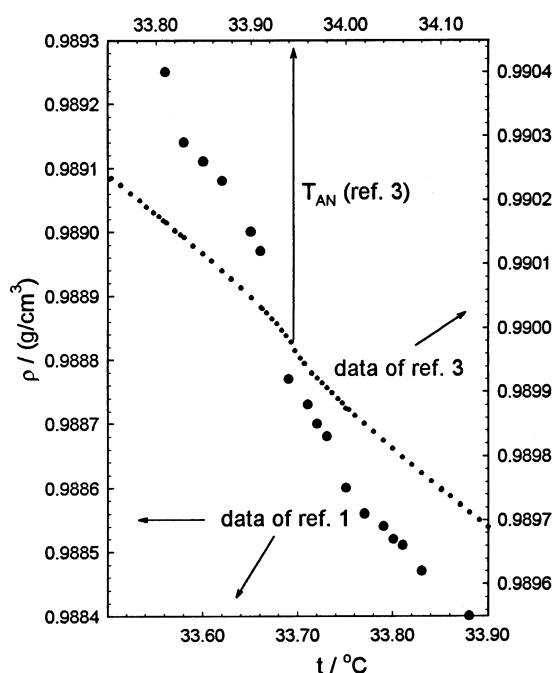
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The paper by Oweimreen<sup>1</sup> commented on hereafter describes density measurements of one of the most thoroughly investigated liquid crystalline compounds, 8CB. The main goal of the paper is to prove that a new “intermediate” phase exists between smectic A (SmA) and nematic (N), referred to as “more ordered nematic” or “less ordered smectic”. The first-order character of the transition from smectic A to this intermediate phase is suggested. A detailed discussion of earlier results by other authors for 8CB and other compounds exhibiting the SmA–N phase transition is also presented. The author,<sup>1</sup> however, does not cite or comment on the paper<sup>3</sup> reporting the most precise molar volume measurements of the same phase transition for the same compound, 8CB, published in the same journal in 1999. The present comment provides a missing comparison between the results obtained by Oweimreen<sup>1</sup> using a Paar densimeter and the dilatometric measurements by Żywociński and Wieczorek.<sup>3</sup>

Density measurements<sup>1</sup> and our volumetric measurements<sup>3</sup> converted to density are shown in Figure 1. It is immaterial for the present discussion that the transition temperatures of both samples differ by 0.26 ° and that absolute densities are different. Both temperature scales have the same resolution and are shifted to show the data in the same temperature range on both sides of the transition temperature. Also, density scales of the same resolution are shifted, but the problem here is not the absolute accuracy of the measurements but the precision necessary to judge whether the transition is continuous or first order. As we mentioned earlier in a detailed description<sup>4</sup> of our method, it gives, with all necessary corrections, the precision to better than 1 ppm. However, we allow for possible systematic error in density up to 0.001 g/cm<sup>3</sup>, which is not important provided that only the character of the phenomenon is studied.

As can be seen in Figure 1, the data from the Paar densimeter, although somewhat scattered, show a clear jump in density, which is assigned by the author<sup>1</sup> to the first-order phase transition, whereas our dilatometric data show a rather weak inflection point, which we interpret as a continuous phase transition (for a detailed analysis, see ref 3). The discrepancy between density measured with the aid of a Paar instrument (vibrating U-tube filled with a sample) and density obtained from direct dilatometric measurements has already been reported by other authors<sup>5–7</sup> and was recently well-documented and explained by Żywociński.<sup>8</sup> The present case shown in Figure 1 seems identical to the case exhibited in Figure 6 of ref 8. The studies<sup>8</sup> were carried out on an SmA-to-N phase transition in compound 8OCB, which was also studied by Oweimreen<sup>2</sup>. The subject seems extremely important because many scientists make use of densimeters with mechanical oscillators but are not aware of the errors that could possibly appear during such measurements. We repeat briefly a simple explanation of the



**Figure 1.** Comparison of the density changes near the SmA–N phase transition obtained by Oweimreen<sup>1</sup> (●) using a Paar densimeter and by Żywociński and Wieczorek<sup>3</sup> (○) from direct dilatometric measurements.

above discrepancies, showing that the “apparent density” measured by a densimeter with a vibrating U tube depends on the viscosity of the sample.

The continuous transitions in 8CB and 8OCB have already been proven without any doubt (refs 3 and 9, respectively), but the apparent density shows a clear jump, suggesting a first-order transition. Such results can be consistently explained by large viscosity changes at the transitions from less viscous nematics to very viscous smectics. It seems obvious that the vibrations of the mechanical oscillator filled with a viscous liquid must be damped because the liquid must locally flow when the tube, and a column of the liquid inside it, undergoes deformations (bending) during vibrations (see ref 9 for detailed proof). Barbosa and Palangana<sup>7</sup> reported a similar situation for the transition from the isotropic phase of low viscosity to the extremely viscous hexagonal phase, but they give an erroneous explanation.

Because the density data from the dilatometer are the results of direct measurements, obviously, measurements of the apparent density obtained with the aid of a Paar instrument cannot be trusted in the cases described above.

The second problem is the existence of the intermediate phase<sup>1</sup>. It seems to be just an artifact of the lines guiding the eye drawn in Figure 1 of ref 1. In Figure 1 of this comment, the points without connecting lines are simply scattered, and there are too few of them to draw a conclusion about the presence of another transition of the second order. Such a transition is invisible in our study (see Figures 1–3 of ref 3).

The discussion and the references given by Oweimreen<sup>1</sup> relate also to the calorimetric measurements of the SmA–N phase transition. Earlier work by Oweimreen and Morsy<sup>2</sup> reports the calorimetric measurements of 8CB and other compounds from *n*CB and *m*OCB homologous series. In such a context, it is

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surprising that both papers<sup>1,2</sup> do not refer to the work by Thoen et al.,<sup>10</sup> which represents the best thermal study of the SmA–N transition ever made. Moreover, the new phase transition was found by Oweimreen and Morsy<sup>2</sup> in DSC measurements, but it is completely invisible in the most precise measurements from adiabatic calorimetry and the data most thoroughly analyzed by Thoen et al.<sup>10</sup>

It has to be mentioned that the resolution of our dilatometric measurements is comparable to that of Thoen's adiabatic calorimetry, and our results give the same critical exponents for the SmA–N phase transition. Also, our volume jump,  $\Delta V_{\text{NI}}$ , estimated for the nematic-to-isotropic phase transition in 8CB<sup>11</sup> and the enthalpy jump,  $\Delta H_{\text{NI}}$  from Thoen et al.<sup>10</sup> are both perfectly consistent when related using a known  $(dp/dT)_{\text{coex}}$  value and the Clapeyron relation. In conclusion, the claim made in ref 1 on the basis of the data presented there that the SmA–N transition is first order in 8CB is clearly incorrect.

## References and Notes

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