COMMENTS

Nature of the Smectic A-to-Nematic Phase Transition of 8CB Revisited

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Not including the references[1−6] mentioned in the preceding comment[7] is regrettable. Nonetheless, those references do not necessarily support the view[7] that the SmA−N transition in 8CB and other liquid crystals[5,6] is, "without doubt", second order.

In Table 1 of ref 8, the density at 33.56 °C was incorrectly reported and should be 0.98916 g cm^{-3}, and least-squares fits of the density $\rho(\theta)$ versus θ in the smectic A "intermediate" and nematic phase regions, where $\theta = t - t'$, t is the temperature at which the density is measured, and t' is a temperature at the center of each region, gave the best correlation coefficients (in excess of 0.997) for equations of the form

$$\rho(\theta) = a + b + c\theta^2 + d\theta^3 \tag{1}$$

Such correlation, even if for "apparent" densities, points to the likely existence of a third intermediate phase in the region where the viscosity variation with temperature is different from that in both the smectic A and nematic phases. The comment also refers to Figure 6 in ref 4, which shows that the densities for the smectic A phase of 8OCB obtained using an Anton Paar density meter are higher than those from more accurate density measurements. This does not rule out the possible existence of an intermediate phase extending over about 0.07 K [8] within the 1 K temperature range between the datum at the highest temperature in the smectic A phase and the datum at the lowest temperature in the nematic phase, where no data were collected.

Impurities intentionally added or intrinsic to the synthesis or purification procedure affect the density of a liquid crystal, lower or raise the transition temperature, and bring about a two-phase region in the vicinity of a first-order transition.[9] Whereas a sharp "best" value of 307.0942 K is calculated by Żywociński and Wieczorek[6] for the SmA−N transition temperature T_{AN} for 8CB, Oweimreen[9] obtained broad and sharp SmA−N and N−I transitions, respectively, from a heating cycle on an 8CB sample. The broadness of the SmA−N transition is attributable to the coexistence of smectic A and nematic phases or the existence of an intermediate phase in the immediate vicinity of the SmA−N transition. The densities in this region are neither for the smectic A phase nor for the nematic phase. The inclusion of data from such a region by Żywociński et al.[5] and Żywociński and Wieczorek[6] in their $V(t)$ versus t fits, where $t = |(T - T_{AN})/T_{AN}|$, to the equation

$$V(t) = At^{1-\alpha}(1 + Dt^{1/2}) + Bt + C \tag{2}$$

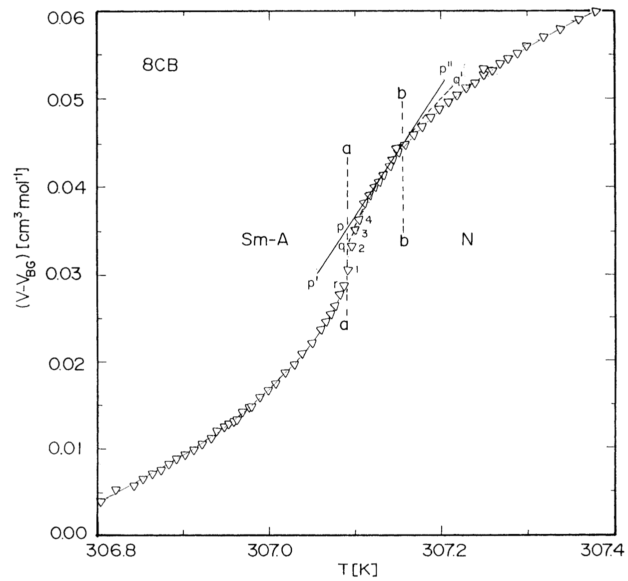

Figure 1. *V* versus *T* plot for the results from dilatometric measurements on 8CB, reproduced as given in Figure 1 of ref 6. The added constructions illustrate the probable existence of an intermediate (or two-phase) region somewhere between the temperature T_{AN} indicated by line aa and a temperature indicated by line bb and a probable finite change in volume at T_{AN}.

in the nematic phase region ($T > T_{AN}$) and the equation

$$V(t) = A't^{1-\alpha}(1 + D't^{1/2}) + B't + C' \tag{3}$$

in the smectic A phase region ($T < T_{AN}$) casts doubt on their conclusion that the SmA−N transition is second order on the basis of the smallness of the $C - C'$ values. A single fit using eq 2 (or eq 3) for all the data above and below T_{AN} is possible if t is defined as T/T_{AN}. If such a fit turns out to be statistically significantly inferior to the fits in the separate regions, such doubt would be confirmed. In the absence of published[5,6] numbers, only the following qualitative analysis is possible.

The constructions added to Figure 1 of ref 6 for 8CB and shown in Figure 1 in this comment allow the reader to focus on the data between the dashed lines aa (close to 307.09 K) and bb (close to 307.17 K). Because there is no such thing as a perfectly "pure" liquid crystal, it is likely that points 1, 2, 3, and 4 (which extend over less than 0.015 K in the vicinity of the SmA−N transition) belong, as mentioned above, to neither the smectic A phase nor the nematic phase and need to be excluded. On excluding points 1 and 2 (which are closest to T_{AN}), the smooth curve qq′ through the remaining points between aa and bb hints at a possible volume change represented by the distance qr. On excluding points 1, 2, 3, and 4, the straight line p′p″ through the remaining points between aa and bb hints at a possible volume change represented by the distance pr. This volume change is unlikely to be affected and may even increase if all the data to the right of line bb are considered.

Dilatometric results from heating and cooling runs for 8OCB, graphically presented together in Figure 4 of ref 5, are reproduced separately in this comment as Figure 2a and b for

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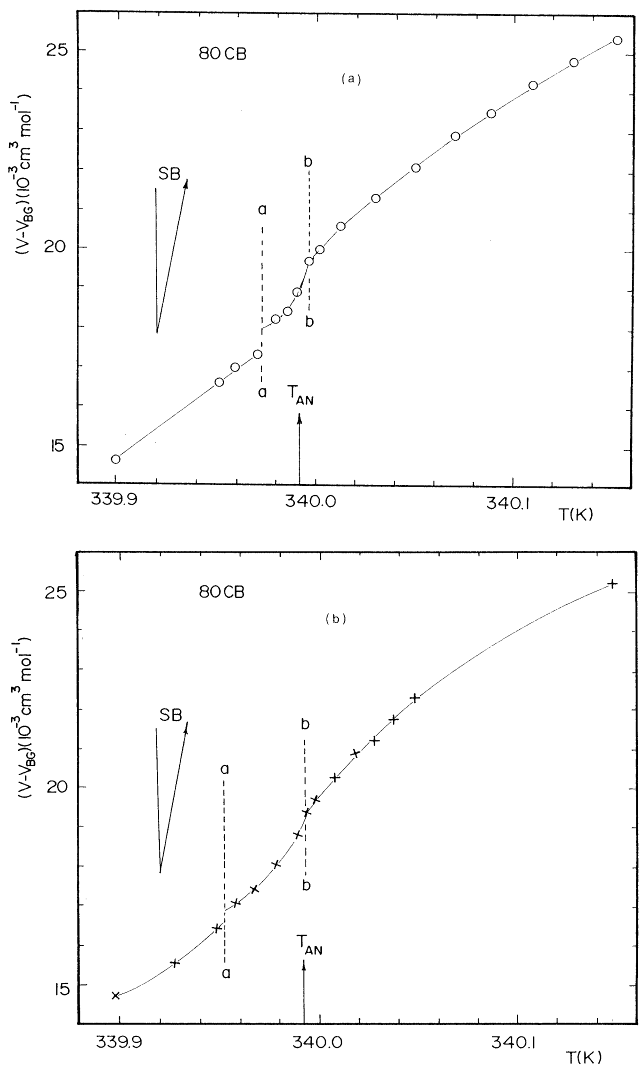

Figure 2. V versus T plots for the results from dilatometric measurements for (a) heating (○) and (b) cooling (+) runs on 8OCB, reproduced from Figure 4 of ref 5. The constructions illustrate a probable volume change at the temperature indicated by line aa and the probable existence of an intermediate phase somewhere between the temperatures indicated by lines aa and bb.

heating and cooling runs, respectively. Could an intermediate phase exist somewhere between the temperatures indicated by lines aa and bb in Figures 1 and 2a and b? Could a fit that uses data from the combined heating and cooling runs (Figure 4 of ref 5) mask a likely, however weak, first-order transition indicated by a kink, or possibly two, in the separate heating and cooling runs (Figure 2a and b), particularly because cooling back to the original smectic A structure could take a long time? Could the inclusion of data close to the SmA−N transition, where a two-phase region or an intermediate phase may exist, obliterate very small volume changes at T_{NA}?

Three different types of fits by Żywociński et al.[5] for 8OCB data gave $C - C'$ values of 11×10^{-7}, 29×10^{-7}, and 7×10^{-7}. On the basis of the proximity of these values to a total estimated uncertainty of 3×10^{-7} in $C - C'$, it was decided[5] that $\Delta V_{AN} \approx 0$ and that the transition is, "without doubt",[7] second order. By substituting the lowest of the ΔV_{AN} values and a dp/dT_{AN} value estimated from the data of Cladis et al.[10] into the Clausius−Clapeyron equation (which, incidentally, is an equation for a first-order transition), a value of 0.4 J mol^{-1} was obtained[5] for ΔH_{AN}. This value was contrasted with the ΔH_{AN} value of 0.4 J mol^{-1} obtained for 8CB by Thoen et al.[11] and relied upon, as Thoen et al.[11] did, to arrive at the conclusion that the SmA−N transition for 8OCB is second order. As already mentioned,[12] the extreme slowness of the heating rate (0.6 mK/h) in the adiabatic calorimetric (AC) study[11,13] and the unavoidable heat dissipation effects, however small, could result in underestimating ΔH_{AN} for 8CB. Thoen et al.[13] claim that differential scanning calorimetric (DSC) measurements yield higher ΔH values because they include pretransitional effects along with a true latent heat effect. The ΔH values given in Table 1 in their paper[13] do not support this claim; 7 out of 10 of them are higher than the ΔH values obtained for the same transitions by DSC.[14] Thus, a low and doubtful ΔH_{AN} for 8CB[11,13] is used to corroborate a ΔH_{AN} value estimated for 8OCB[7] from a doubtful ΔV_{AN} value. Reasonably careful DSC measurements give a ΔH_{AN} value of 40 J mol^{-1} for 8CB[12,14] and 8OCB.[12] Using this value and the dp/dT_{AN} value estimated from the data of Cladis et al.[10] in the Clausius−Clapeyron equation, a ΔV_{AN} value of 7×10^{-5} cm^3 g^{-1} is obtained. This is comparable to the value of 10×10^{-5} cm^3 g^{-1} obtained by Oweimreen[8] for the volume change across the smectic A-to-intermediate phase transition and to the value of 5×10^{-5} cm^3 g^{-1} indicated by the distance pr in Figure 1.

Evidence that density measurements using a vibrating densitometer exaggerate the ΔV_{AN} value does not, by itself, automatically mean that $\Delta V_{AN} = 0$ for 8CB. Even if, for the sake of argument, the finite ΔH_{AN} values obtained in many DSC studies[15−22] and the finite ΔV_{AN} values obtained from measurements using a vibrating densitometer[2,21] are put aside, the ΔV_{AN} value of 0.00048 ± 0.00014 cm^3 mol^{-1} obtained by Leadbetter et al.,[22] the results from high pressure[23,24] and diamagnetic susceptibility[25] measurements on 8CB, and the observation[9,17,20,26] of a SmA−N two-phase region for impure 8CB samples together point to a very weak first-order SmA−N transition for 8CB. In addition, dilatometric measurements by Torza and Cladis[27] on p-cyanobenzylidene (CBOOA), a bilayer smectic like 8CB, yielded a ΔV_{AN} value of $(5.0 \pm 2) \times 10^{-5}$ cm^3 g^{-1}. Clearly there is enough evidence in the literature to indicate that the SmA−N transition in 8CB in particular, if not in bilayer smectics in general, is likely to be very weakly first order.

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