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# A Two-State Boltzmann Model for Polar A-Smectics

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# A TWO-STATE BOLTZMANN MODEL FOR POLAR A-SMECTICS

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Abstract : Assuming a head to head and side by side association of the molecules, a two-state Boltzmann distribution model is proposed which explains the temperature dependence of the thickness of the smectic-A layers observed with polar single-tailed mesogens.

In a preceding paper [1], we proposed a model describing the bilayer structure of the smectic A mesophases observed with cyano mesogens. In this model, the smectic layers are formed by the intimate and random mixture of single molecules and of pairs of molecules associated head to head. As a result, the thickness of the smectic layers, ranging from one to two molecular lengths, is a function of the degree of association. On the other hand, the layer spacing $d$ of a cyano and a nitro smectogen in the smectic A phase was recently measured with X-ray at a variety of temperatures[2]; it was shown that $d$ is very much dependent upon temperature, and that its rate of increase diminishes as the temperature is lowered for the cyano derivative, whereas, quite interestingly, it grows appreciably for the nitro derivative. In the present letter, we show a very simple thermodynamic approach of the association phenomenon of polar smectogens, that might be of use in interpreting the unusual thermal properties of the smectic A mesophase reported above.

In a crude over-simplification, we assume that the molecules are all associated either side by side (Fig. 1-a) or head to head (Fig. 1-b). The corresponding energies of association are $E_s$ and $E_h$, respectively. Located in the smectic layers, the dimers are supposed not to be submitted to any special lateral interactions ; *i.e.*, there is no energy of exchange between the two dimeric species.

Using Boltzmann's statistics, one can then estimate the probabilities $p_h$ and $p_s$ of finding the molecules in the head to head and in the side by side association mode,

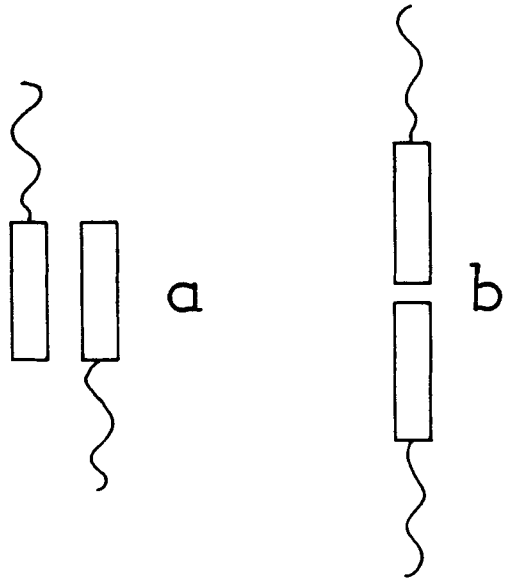


FIGURE 1 Side by side (a) and head to head (b) association of the molecules

respectively :

$$p_h = \exp(-E_h / kT) \quad \text{and} \quad p_s = 1 - p_h = \exp(-E_s / kT)$$

From the obvious relationship : $p_h / p_s = \tau / (1 - \tau)$, where $\tau$ is the degree of head to head association, one finds :

$$\tau / (1 - \tau) = \exp(-\delta E / kT)$$

where $\delta E = E_h - E_s$. It is clear that when $\delta E \ll kT$, $\tau \simeq 1/2$ ; when $\delta E > 0$, $\tau < 1/2$ ; and when $\delta E < 0$, $\tau > 1/2$. Now, in view of the magnitude (up to a few Debyes) of the dipolar moments usually carried by the smectogenic molecules under consideration and of their lateral distances (down to a few Angströms), it is reasonable to expect values for $e = \delta E / kT_0$ ($T_0$ = 300°K) in the range from - 10 to + 10.

To illustrate the thermal behavior of such systems, we calculated the degree of association $\tau$ as a function of temperature $T$ for different values of the parameter $e$ (Fig.2).

Assuming [1] that the head to head dimers are twice as long as the single molecules, and that their molecular area, $\sigma$, is very close, if not identical, to that of the single molecules, we also calculated

$$d / l = 2 / (2 - \tau)$$

where $l$ is the molecular length (Fig. 3). As expected,

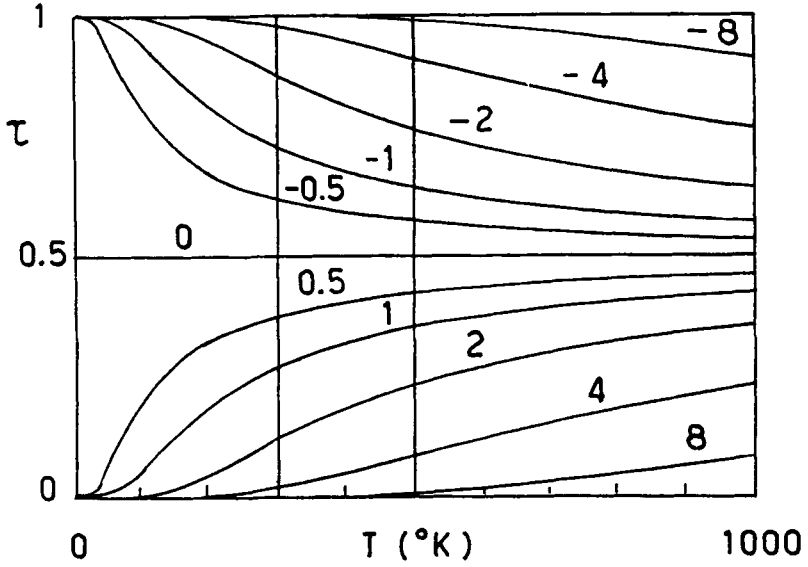


FIGURE 2 Temperature dependence of the degree of head to head association as a function of $e = \delta E / kT_0$

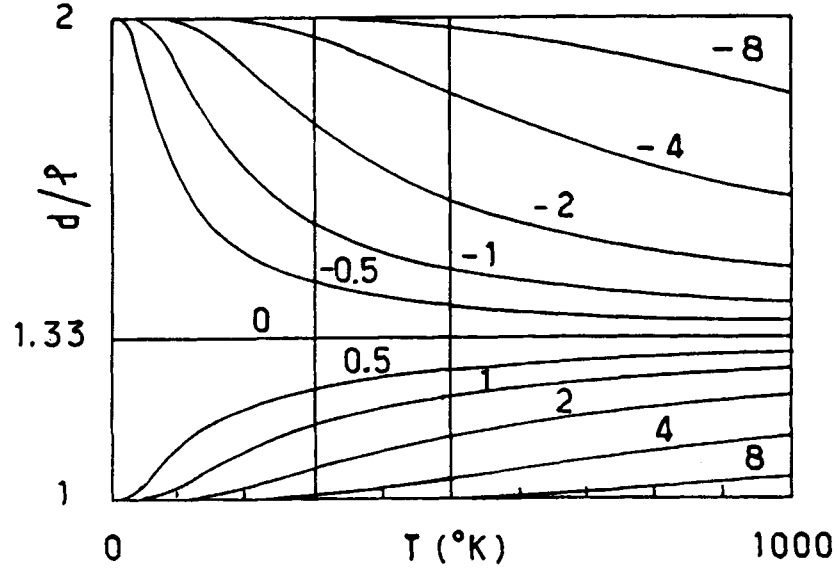


FIGURE 3 Temperature dependence of the layer thickness $d$ compared with the molecular length $l$ as a function of $e = \delta E / kT_0$. Smectics usually occur in the temperature range between 300 and 500°K.

$\tau$ decreases from 1 to 1/2, and as a consequence $d/l$ decreases from 2 to 4/3, when $e$ goes from - 10 to 0 and when $T$ goes to infinity ; correlatively, $\tau$ increases from 0 to 1/2, and $d/l$ increases from 1 to 4/3, when $e$ goes from 10 to 0 and when $T$ goes to infinity. It is of interest to note that, in a given temperature range (e.g. 300°K < $T$ < 500°K), the curvature of the curves d($T$) is turned upwards or downwards depending upon the value of $e$.

In spite of its extreme simplicity, the model used in this letter seems fairly suitable to provide us with an elementary explanation, first, of the temperature dependence of the layer spacing in the smectic A phase, and second, of the rate of change of the spacing with temperature, depending upon the nature of the polar single-tailed mesogens considered [2]. In order to account for the existence of single-layered, double-layered and partially bilayered A smectics, it is apparently sufficient to invoke the difference in energy of the head to head and side by side association of the molecules. It should be emphasized that whenever this difference is small, the layer thickness is found to have values around 1.33 molecular lengths, in agreement with what has so frequently been encountered in practice [3].

However, this model must be developed — and such a work is in progress — to take into account a series of factors which should affect the thermodynamic state of the system. Thus, when the degree of head to head association of the molecules grows, the number of paraffin tails per unit area of smectic layer increases, the paraffin tails extend over a larger distance, and the corresponding conformational entropy decreases. Furthermore, the lateral interactions between the dimeric species must probably not be neglected, and the side by side association must be generalized to cover dimers as well as multimers. When the interactions between head to head dimers and side by side molecular associations are less favorable than those between like species, one can expect the mixture not to be perfectly homogeneous. The mixture would then exhibit fluctuations which in certain cases could even induce "phase separations" within the smectic layers, leading to transverse modulations of the layers, similar to those described by the Bordeaux group [4]. Finally, the molecules can very well associate with themselves, not only in the way described above, *i.e.* head to head and side by side with perfect overlapping, but also side by side with partial overlapping, depending upon the distribution of the interacting sites along the molecules. In this general case, the Boltzmann distribution of the states of the system would involve many levels of energy.

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