

Classification  
 Physics Abstracts  
 61.30G — 68.10C

## Temperature dependence of the anchoring strength coefficient at a nematic liquid crystal-wall interface

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(Reçu le 3 janvier 1984, révisé et accepté le 23 février 1984)

**Résumé.** — La force d'ancrage du méthoxybenzylidène butylaniline (MBBA) en fonction de la température est mesurée par la méthode de la transition de Freedericksz dans une cellule mince ( $l < 2,5 \mu\text{m}$ ) traitée par un surfactant. Pour  $T_{\text{NI}} - 20^\circ\text{C} < T < T_{\text{NI}}$ , le paramètre  $B$  varie approximativement de 0,065 à 0,013 erg/cm<sup>2</sup> dans la phase nématique. On discute la relation entre  $B$  et le paramètre d'ordre nématique.

**Abstract.** — The anchoring strength coefficient  $B$  is measured as a function of temperature using a Freedericksz technique in a very thin ( $l < 2.5 \mu\text{m}$ ) surfactant-treated cell of methoxybenzylidene butylaniline (MBBA). In the nematic phase this parameter varies from approximately 0.065 to 0.013 erg/cm<sup>2</sup> for  $T_{\text{NI}} - 20^\circ\text{C} < T < T_{\text{NI}}$ . The relationship between  $B$  and the nematic order parameter is discussed.

### 1. Introduction.

Surfactants have long been used to achieve uniform alignment at a liquid crystal-non-liquid crystal interface. Over the years several studies have been made to determine the liquid crystal anchoring strength,  $B$ , with varying results. Characterizing the surface contribution to the energy as

$$F_s = \frac{1}{2} B(\theta - \Theta)^2, \quad (1)$$

where  $\Theta$  is the undisturbed director tilt angle at the surface and  $\theta$  is the tilt angle in the presence of some force, Naemura [1-3] used a Freedericksz technique to obtain  $B$  for cells of methoxybenzylidene butylaniline (MBBA) aligned by some two dozen different surfactants, finding values ranging between  $10^{-4}$  and  $10^{-2}$  erg/cm<sup>2</sup>. In an attempt not only to improve resolution, but to obtain the coefficients of terms of higher order in  $\theta$  as well, Yang and Rosenblatt [4] studied an ultra-thin cell of MBBA and the surfactant hexadecylamine, finding  $B = 1.2 \times 10^{-2}$  erg/cm<sup>2</sup>. Still other techniques and surface treatments have been used [5-7], resulting in values of  $B$  between  $10^{-4}$  and  $10^{-1}$ . (References [7] and [8], in fact, also report on a temperature-driven surface transition from parallel to planar orientation.) Taking a different tack, several workers have studied [9] the liquid crystal/solid adhesion energy  $W_a$ , typically by means of contact angle measurements. When relating these

results to the anchoring strength [10], values of  $B$  are yet an order of magnitude larger at a surfactant-treated surface.

To date, however, a unified interpretation of the results has been rather difficult. This is due in large part not only to the wide variety of surfactants studied, but to differences in surface treatment from laboratory to laboratory as well. The purpose of this paper, then, is to report the values of  $B$  obtained in a Freedericksz-type experiment, for a single liquid crystal (MBBA) and a single surfactant (dodecyltrimethylammonium chloride, DTAC) as a function of temperature. In addition to helping us understand the basic surface interactions, such a study has important technological implications for devices designed to operate over a large temperature range.

For the case of perpendicular ( $\Theta = 0$ ) alignment, equation (1) reduces to  $F_s = \frac{1}{2} B\theta^2$ . For finite  $B$  it can be shown [11] that, in a Freedericksz experiment, the threshold magnetic field  $H_{\text{th}}$  is reduced from the rigid anchoring value and is given by the expression

$$\cot \left[ \frac{\pi}{2} \frac{H_{\text{th}}}{U_3} \right] = \frac{\pi K_3}{lB} \frac{H_{\text{th}}}{U_3} \quad (2)$$

where  $l$  is sample thickness,  $K_3$  the bend elastic constant, and  $U_3$  the threshold field for rigid anchoring, i.e.,  $U_3 = \pi/l(K_3/\Delta\chi)^{1/2}$ . Here  $\Delta\chi$  is the volume magnetic susceptibility anisotropy. Equation (2) can

be made more physically transparent by expanding  $H_{th}/U_3$  about 1 :

$$\frac{H_{th}}{U_3} = 1 - \frac{2K_3}{IB} + o\left(\frac{K}{IB}\right)^2. \quad (3)$$

Thus, it is seen that the deviation of  $H_{th}$  from the rigid anchoring case scales as the ratio of the bulk energy to the surface energy. Moreover, it is clear from equation (3) that a larger deviation and thus far better experimental resolution can be achieved by using extremely thin cells in conjunction with higher magnetic fields. It is precisely this advantage which I exploit to obtain  $B$ .

## 2. Experimental.

The results from two separate samples (A and B) are reported. The liquid crystal cells consisted of a pair of 12.7 mm diameter,  $\lambda/20$  fused silica windows, separated by mylar spacers. The sandwich was housed in a brass holder, with the tilt angle and position of one window relative to the other adjusted by a three point screw mount. The windows were cleaned in a soap solution, followed by sonication in acetone and ethanol baths. They were then dipped into a solution of DTAC (Eastman Organic Chemicals) in ethanol ( $2 \times 10^{-4}$  mol/l for sample A;  $1 \times 10^{-4}$  mol/l for sample B) and allowed to dry. Just prior to mounting, the windows were gently rubbed with a Kimwipe and blown with purified nitrogen to remove any remaining dust. (This procedure was compared to one without rubbing, with no qualitative differences.) After mounting, the windows were adjusted for maximum parallelism by observing the reflected interference pattern from a monochromatic light source. Near the center of the windows, the gradient of the cell thickness was estimated to be less than  $0.01 \mu\text{m}/\text{mm}$ .

Since it is crucial to know the precise cell thickness, a reflection interferometry scheme was utilized. The cell was mounted on a precision rotation stage with angular resolution of approximately 20 arcsec. The beam from a He-Ne laser was directed perpendicular to the cell and at its centre. Upon rotation of the cell about an axis perpendicular to the beam, the reflected beam broke up into three distinct colinear spots when imaged onto a screen. The intensity of the center spot, corresponding to reflection from the cell cavity, went to zero whenever  $m\lambda = 2l \cos \phi$  [12], where  $\lambda$  is the wavelength of the light ( $6.328 \times 10^{-5}$  cm),  $\phi$  is the rotation angle, and  $m$  an integer. It should be noted that due to refraction, the sample had to be translated during rotation to maintain the position of the beam in the center of the window at the cavity. Using this technique it was found that  $l = 2.47 \pm 0.015 \mu\text{m}$  (sample A) and  $l = 2.46 \pm 0.015 \mu\text{m}$  (sample B).

After measuring the cavity spacing, the cell was filled from the side with MBBA (3M Corp.) in the isotropic phase and allowed to cool into the nematic. Optical microscopy was used to verify perpendicular ( $\Theta = 0$ , cf. Eq. (1)) alignment. The entire assembly was then mounted in a 3.8 cm diameter cylindrical brass oven, surrounded first by an insulating air pocket and then by a phenolic jacket. Temperature was controlled and measured by a pair of Fenwal UUA33J4 thermistors in conjunction with a Yellow Springs Instrument model 72 controller. Magneto-resistance effects were deemed insignificant [13] and overall temperature control was better than 10 mK.

The oven was placed in the bore of a Bitter magnet and an optical birefringence scheme was used to observe the Freedericksz transition. The field was scanned at 2 000 G/min for sample A and 4 000 G/min for sample B. Because of imperfect orientation of the cell relative to the field, a small rounding of the transition was noted, leading to an uncertainty of approximately 200 G in determining  $H_{th}$  (i.e., less than 1% of  $H_{th}$ ).

The sample birefringence was measured using an automatically compensating Pockels cell. Since some recent modifications have been made, a description of the apparatus is in order. Briefly, the sample and Pockels cell were placed between crossed polarizers oriented at  $45^\circ$  with respect to the field (Fig. 1). The dc compensation voltage on the Pockels cell was modulated by a small ac voltage at  $\nu = 2800$  Hz.

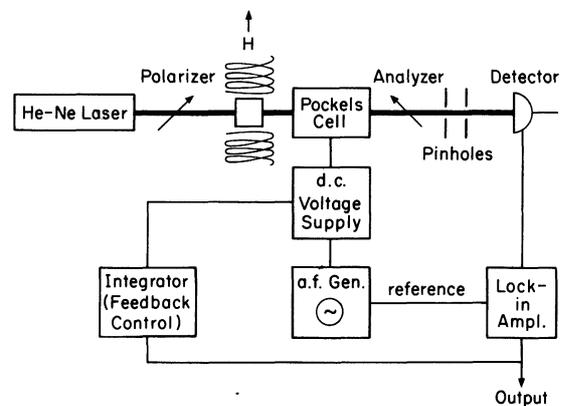


Fig. 1. — Schematic representation of birefringence apparatus.

For sufficiently small total birefringence, the signal  $V$  at the detector had three frequency components, zero,  $\nu$ , and  $2\nu$ , such that  $V_\nu \propto (\delta_s - \delta_p)$ .  $\delta_s$  and  $\delta_p$  were the dc phase shifts due to the sample and Pockels cell birefringences, respectively, and  $\delta_s = \int_0^l k \Delta n dz$ ,

where  $k$  is the wavevector of light and  $\Delta n$  the local birefringence. The output of the lock-in amplifier, proportional to  $V_\nu$ , was integrated and used to automatically adjust the Pockels cell voltage  $V_p$  so that

$\delta_p$  was equal to  $\delta_s$ , resulting in  $V_v = 0$ . Thus,  $V_p$  (proportional to  $\delta_s$ ) was recorded on an XY plotter vs. applied field  $H$ . Sensitivity in  $\delta_s$  was approximately  $10^{-4}$  rad, corresponding to  $\Delta n \sim 4 \times 10^{-6}$  for  $l \simeq 2.5 \mu\text{m}$ . Both the sample and electronics response times were fast relative to the field sweep rate, although a smoothing filter in the magnet power supply resulted in a small amount of hysteresis when the field was swept in both directions across  $H_{th}$ . This hysteresis component of the uncertainty in determining  $H_{th}$  was about 30 G for sample A and 60 G for sample B.

**3. Results.**

Figures 2 and 3 show the threshold fields  $H_{th}$  vs.  $T_{NI} - T$  for samples A and B, respectively.  $T_{NI}$  was found to be  $45.13 \pm 0.03$  °C in sample A and  $45.31 \pm 0.03$  °C in sample B. The error bar represents an overall uncertainty of approximately  $\pm 200$  G in determining  $H_{th}$ . The solid lines represent the theoretical values for  $H_{th}$  calculated for several values of  $B$  from equation (2) and from the data for  $K_3$  and  $\Delta\chi$  in reference [14]. Note that the case of  $B = \infty$  corresponds to rigid anchoring, i.e.,  $H_{th} = U_3$  as defined in equation (2).

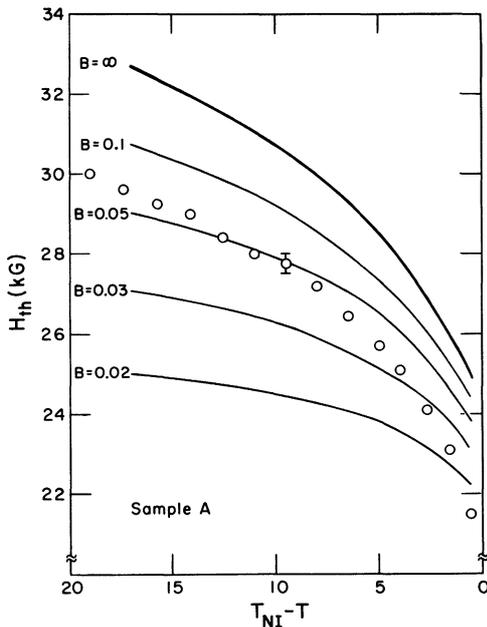


Fig. 2. —  $H_{th}$  vs. reduced temperature for sample A ( $l = 2.47 \mu\text{m}$ ). Solid lines represent calculated threshold fields for various values of  $B$  using the data of reference [14].

The reliability of the  $K_3$  and  $\Delta\chi$  data is of paramount concern in the data analysis. In an earlier work, Naemura [2] obtained a value of  $B$  of order  $3 \times 10^{-3}$  erg/cm<sup>2</sup>, implying that the actual values of  $K_3$  were somewhat larger than those obtained by de Jeu *et al.* [14]. In fact, Yang and Rosenblatt [4] operating at approximately  $T_{NI} - T = 6$  °C, scaled  $K_3$

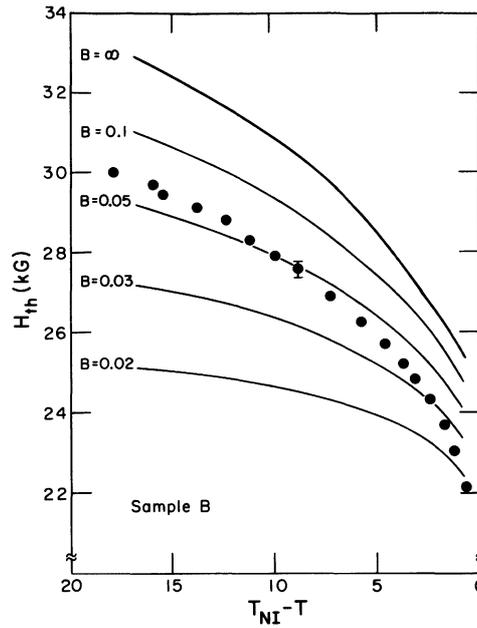


Fig. 3. — Same as figure 2, except for sample B ( $l = 2.46 \mu\text{m}$ ).

in reference [14] in order to account for Naemura's weak anchoring results. Subsequently, however, I have remeasured  $H_{th}$  in both a thick ( $l = 76.4 \pm 0.2 \mu\text{m}$ ) and thin ( $l = 2.85 \pm 0.03 \mu\text{m}$ ) sample, using a more highly concentrated solution of DTAC surfactant, finding results in the thick sample consistent with reference [14]. To see this, equation (3) can be rewritten as

$$lH_{th} = \pi \sqrt{\frac{K_3}{\Delta\chi}} - \frac{2\pi}{lB} \sqrt{\frac{K_3^3}{\Delta\chi}}. \quad (4)$$

Since the ratio of the quantity  $lH_{th}$  for the thin sample to the thick sample was measured to be about 0.93 over the entire temperature range, the correction term which scales as  $(lB)^{-1}$  must be relatively small. From this two conclusions can be drawn :

- 1) the values of  $B$  are larger by one to two orders of magnitude than those found by Naemura and,
- 2) in light of (1), the corrections for non-rigid anchoring to my experimental values for  $\sqrt{K_3/\Delta\chi}$  would be about 0.3 % in the  $l = 76.4 \mu\text{m}$  sample.

My experimental values for  $\sqrt{K_3/\Delta\chi}$ , moreover, differed by less than 2 % from those of de Jeu *et al.* [14]. Thus, for consistency, I have chosen to use the values of  $K_3$  and  $\Delta\chi$  from reference [14] in the analysis of my data. [As an aside, upon using the correct value of  $K_3$ , the value of  $B$  in reference [4] (referred to as  $G$  in that paper) should be 0.015 erg/cm<sup>2</sup>. The qualitative behaviour and conclusions discussed therein, however, remain unchanged. In addition, using de Jeu's values for  $K_3$ , Naemura's results [1-3] for  $B$  would also be larger than the values given in those papers.]

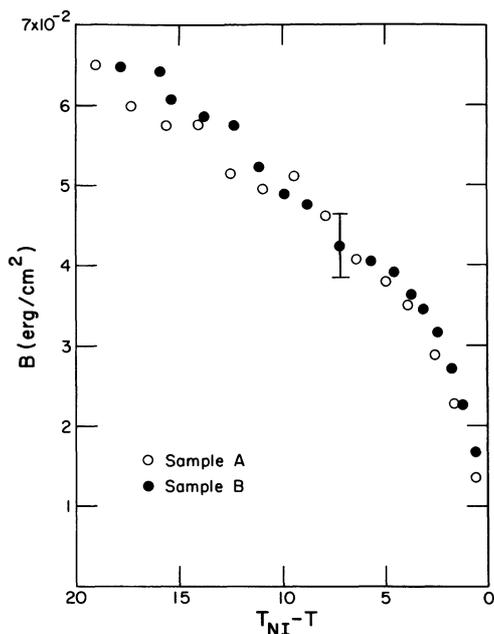


Fig. 4. —  $B$  vs. reduced temperature for the two samples.

Figure 4 shows  $B$  vs.  $T_{\text{NI}} - T$  for the two samples. The error bar represents the scatter in  $B$  due to uncertainty in measuring  $H_{\text{th}}$ . Two sources of systematic error, however, can also push the  $B$  vs.  $T_{\text{NI}} - T$  curve up or down. Since the values of  $K_3$  used in this paper may be as much as 3 or 4 % in error, this would result in an approximately 11 %-14 % error in  $B$ . (A larger  $K_3$  results in a smaller  $B$ .) In addition, a potential error in  $l$  of 0.015  $\mu\text{m}$  would result in a 5 % error in  $B$ . (A larger  $l$  results in a larger  $B$ .) It should be noted that the fractional errors would have even been much larger had thicker samples been used. These errors notwithstanding, figure 4 clearly shows that  $B$  is a strong function of temperature, spanning a significant part of one decade for a twenty degree nematic range.

It is interesting to note that these values of  $B$ , particularly near room temperature, are larger by a factor of 20 to 30 than those of Naemura [2] for the same liquid crystal-surfactant combination. Moreover, his surfactant-solvent solution was some thirty times more concentrated. The value of  $B$  obtained by Yang and Rosenblatt [4] closer to  $T_{\text{NI}}$  and using hexdecylamine as a surfactant is also smaller than the values presented in this paper, although only by a factor of 2. Clearly, the magnitude of  $B$  depends critically upon surface preparation.

In a somewhat speculative attempt to better understand the behaviour of  $B$ , the quantity  $B/\Delta\chi_M^2$  is plotted vs. reduced temperature for the two samples in figures 5 and 6. Here,  $\Delta\chi_M$  is the mass magnetic susceptibility, which is proportional to the bulk nematic order parameter  $S$ . Within error bars, both samples indicate that  $B/S^2$  is relatively independent

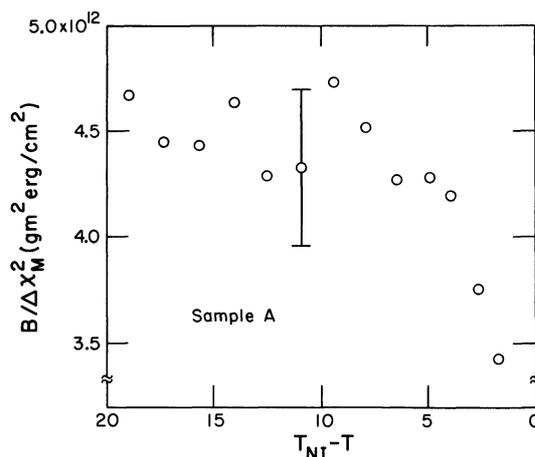


Fig. 5. —  $B/\Delta\chi_M^2$  vs. reduced temperature for sample A. Here  $\Delta\chi_M$ , the mass magnetic susceptibility anisotropy, is proportional to the bulk nematic order parameter.

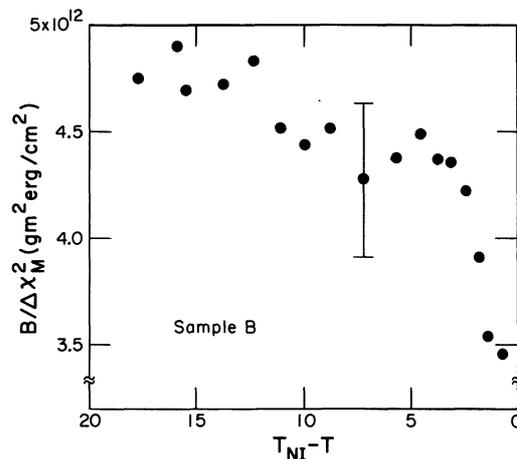


Fig. 6. — Same as figure 5, except for sample B.

of temperature, except in the range  $T_{\text{NI}} > T \gtrsim T_{\text{NI}} - 4^\circ\text{C}$  where  $B/S^2$  begins to fall off.

Utilizing a model involving dispersive forces in a mean field approximation, Saupe [15] has shown that the elastic constant  $K_3$  scales as  $V^{-7/3} S^2$ , where  $V$  is a molar volume. Using similar arguments, one can devise a model in which  $B$  also has a quadratic dependence on the *local* nematic order parameter. In such a model, however, the order parameter in question is  $S_s$ , i.e., the order *at the surface*. Miyano [16] and Tarczon and Miyano [17] have shown that MBBA and pentylcyanobiphenyl (5CB) have non-zero  $S_s$  in the isotropic phase, even going negative for a particular surfactant. Mada and Kobayashi [18] moreover, have shown that  $S_s > S$  in the nematic phase of heptylcyanobiphenyl (7CB) for several different surface treatments. In addition, the density dependence ( $\sim V_s^{-8/3}$ ) of such a simple model would also entail the local density at the surface, which again may differ from the value  $V$  in bulk [19]. Thus, unless

$S_s \simeq S$  for this particular liquid crystal-surfactant system, the result that  $B/S^2$  is relatively constant may be no more than an unfortuitous accident.

In addition to complications arising from the necessity to use  $S_s$  rather than  $S$ , any model for the surface must include the possibility of polar contributions. Naemura, for example, investigated [3] the relative contributions of the polar and dispersive terms at a liquid crystal-wall interface. The importance of polar contributions at a free surface has also been shown in freely-suspended thin films [20]. A treatment which accounts for dipolar terms would, of course, involve odd as well as even terms in the Legendre polynomial expansion of the free energy [21, 22]. In light of all this, figures 5 and 6 represent only a crude qualitative attempt to understand the behaviour of  $B$  in the absence of a rigorous molecular theory.

Theoretically, Parsons has treated [22] the orientational part of the surface tension at a free surface. Okano and Murakami, moreover, have given [23] the dependence of the surface tension on the complex dielectric tensor. To my knowledge, however, a dis-

cussion of the possible temperature dependence of  $B$  at a surfactant-treated surface has heretofore been absent in the literature. Clearly, this quantity has a strong dependence on  $T$ , and needs to be examined more fully, both theoretically and experimentally. Moreover, designers of devices which depend upon surface anchoring and which operate over a large temperature range need to account for the temperature behaviour of  $B$ . Work is continuing to more fully understand the origin of this surface term.

#### Acknowledgments.

The author wishes to thank K.-H. Yang of IBM and G. C. Papaefthymiou of MIT for useful discussions. This work was supported by a grant from the National Science Foundation Solid State Chemistry Program, DMR82-04718, The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation through its Division of Materials Research.

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