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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

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**To cite this Article** Cuculescu, Iuliana , Bena, Rodica and Smeianu, Gabriela(1989) 'Determination of the anchoring constant for a compensated binary cholesteric mixture', *Liquid Crystals*, 4: 4, 457 – 465

**To link to this Article:** DOI: 10.1080/02678298908035493

**URL:** <http://dx.doi.org/10.1080/02678298908035493>

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## Determination of the anchoring constant for a compensated binary cholesteric mixture

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*(Received 6 October 1988; accepted 28 October 1988)*

The optical transmission and the electric power was simultaneously recorded for the binary compensated cholesteric mixture cholesteryl chloride + cholesteryl nonanoate (70 : 30 molar). The values of the critical voltages  $U_1$  and  $U_2$  (at which the planar texture changes into a conic focal one, and the cholesteric-nematic transition take place) at different temperatures were obtained. The temperature dependence of the anchoring constant is determined.

### 1. Introduction

By applying an electric or a magnetic field to a liquid crystal cell, new equilibrium configurations are induced [1]. The critical fields at which different distortions appear depend both on the material constants (elastic constants, anisotropy of the dielectric permittivity, pitch of cholesteric mesophase) and on the anchoring of the liquid crystal molecules on the solid walls between which it is incapsulated.

In this paper, the work of [1] is extended to a mixture of cholesteric liquid crystals, its molecules being weakly anchored on the walls (non-processing electrodes). The experimental values obtained for the critical voltage are correlated with theoretical expressions for them and the temperature dependence of the anchoring constant is determined for a binary compensated cholesteric mixture.

### 2. Theory

To describe the isothermal, static behaviour of an incompressible liquid crystal, the molecules of which are weakly anchored on the walls of the cell between which it is incapsulated, the continuum theory equations

$$\left. \begin{aligned} \left(\frac{\partial F}{\partial \theta'}\right)' - \frac{\partial F}{\partial \theta} &= 0, \\ \left(\frac{\partial F}{\partial \varphi'}\right)' &= 0. \end{aligned} \right\} \quad (1)$$

are used [1]. Where  $F$  is the free energy density of the liquid crystal

$$\left. \begin{aligned} F &= F_1(\theta, \theta', \varphi') + F_2(\theta), \\ F_1 &= \frac{1}{2}[f(\theta)(\theta')^2 + g(\theta)(\varphi')^2 - 2K_2 \tau \cos^2 \theta \cdot \varphi' + K_2 \tau^2], \end{aligned} \right\} \quad (2)$$

$$\left. \begin{aligned} f(\theta) &= K_1 \cos^2 \theta + K_3 \sin^2 \theta, \\ g(\theta) &= \cos^2 \theta (K_2 \cos^2 \theta + K_3 \sin^2 \theta), \end{aligned} \right\} \quad (3)$$

$$\left. \begin{aligned} F_2 &= -\frac{1}{2} \frac{D^2}{\varepsilon_a \sin^2 \theta + \varepsilon_\perp} \\ \varepsilon_a &= \varepsilon_\parallel - \varepsilon_\perp. \end{aligned} \right\} \quad (4)$$

Here,  $K_i$  ( $i = 1, 2, 3$ ) are the elastic constants of the liquid crystal,  $\tau$  is related to the pitch of the cholesteric helix ( $\tau = 2\pi/p_0$ ),  $\theta$  and  $\varphi$  are the polar angles of the director in a reference system centred at the middle of the liquid crystal cell, with  $Oz$  normal on the wall plane (the solid boundaries are at  $z = \pm p$ ).  $\varepsilon_a$ ,  $\varepsilon_\parallel$ ,  $\varepsilon_\perp$  are respectively the values of the anisotropy of the dielectric permittivity, the dielectric permittivity in a direction parallel and perpendicular to the director,  $D$  is the  $Oz$  component of the electric induction, which is related to the applied voltage by

$$U = \int_{-p}^p \frac{D dz}{\varepsilon_\parallel \sin^2 \theta + \varepsilon_\perp \cos^2 \theta}. \quad (5)$$

Symbol ‘‘ ‘ indicates the derivative with respect to  $z$ .

For weak anchoring of the molecules on the walls (non-processing electrodes) a free interfacial energy of the form:

$$W = A(\mathbf{v} \cdot \mathbf{n})^2 + B, \quad (A > 0) \quad (6)$$

is supposed to appear at both contact surfaces, where  $A$  and  $B$  are constants,  $\mathbf{v}$  is the unit vector normal to the exterior surfaces of the electrode, and  $\mathbf{n}$  is the director. In addition  $A$  is called the anchoring constant. The boundary conditions are

$$\left. \begin{aligned} g(\theta) \varphi' &= K_2 \tau \cos^2 \theta, \\ f(\theta) \cdot \theta' \pm A \sin 2\theta &= 0, \quad \text{at } z = \pm p, \end{aligned} \right\} \quad (7)$$

and the accepted solutions of equations (1) will minimize the free energy (per surface unit)

$$\left. \begin{aligned} \tilde{F}(\bar{\theta}) &= \int_{-p}^p F dz + 2A \sin^2 \bar{\theta}, \\ \bar{\theta} &= \theta(\pm p), \\ \pm \bar{\varphi} &= \varphi(\pm p). \end{aligned} \right\} \quad (8)$$

In addition to the planar uniformly twisted arrangement ( $\theta = 0$ ;  $\varphi' = \tau$ ), non-parallel distortions are possible, namely

$$\left. \begin{aligned} \theta(z) &= \theta(-z); \quad \varphi(-z) = -\varphi(z), \\ \theta'(0) &= 0; \quad \theta(0) = \theta_m; \quad \varphi(0) = 0. \end{aligned} \right\} \quad (9)$$

Writing the prime integrals for equations (1), and determining the integration constants, it follows that the critical voltage  $U_1$  which breaks the planar arrangement is given by

$$\frac{\varepsilon_a U_1^2}{4} = K_1 \left( \frac{\pi}{2} - \bar{\lambda}_c \right)^2 + K_3 \tau^2 p^2,$$

where

$$\lambda_c = \arcsin \sqrt{\left( \frac{\frac{D_1^2 \epsilon_a}{\epsilon_1^2} - K_3 \tau^2}{\frac{D_1^2 \epsilon_a}{\epsilon_1^2} - K_3 \tau^2 + \frac{4A^2}{K_1}} \right)}, \quad (10)$$

The critical voltage  $U_2$  inducing the cholesteric-nematic transition is then given by

$$\sqrt{\left( \frac{4K_3}{U_2^2 \epsilon_a - \frac{4K_2^2 \tau^2 p^2}{K_3}} \right)} \operatorname{arcch} \sqrt{\left( \frac{\epsilon_a U_2^2 - \frac{4K_2^2 \tau^2 p^2}{K_3}}{\epsilon_a U_2^2 - \frac{4K_2^2 \tau^2 p^2}{K_3} - \frac{16A^2 p^2}{K_3}} \right)} = 1. \quad (11)$$

From this result it is possible to obtain an expression for the anchoring constant  $A$ ,

$$A = \frac{\sqrt{K \cdot K_2}}{4p} \sqrt{(\epsilon_a U_2^2 - 4K_2 K \tau^2 p^2) \operatorname{th} \frac{\sqrt{(\epsilon_a U_2^2 - 4K_2 K \tau^2 p^2)}}{2\sqrt{(K \cdot K_2)}}}, \quad (12)$$

where  $K = K_3/K_2$ .

### 3. Experimental

For the experiment, the binary compensated cholesteric mixture, cholesteryl chloride + cholesteryl nonanoate (70:30 per cent molar) (the compensation temperature  $t_c$  is 20°C [2, 3]) was encapsulated between tin oxide plane-parallel transparent electrodes. The cell thickness was  $L = 2p = 30 \mu\text{m}$ . The optical transmission and the electrical power were recorded simultaneously in the thermostated sample at the temperatures 24, 27, 35.4, 45.7 and 53.5°C. The experimental arrangement is shown in figure 1.

At values of the d.c. applied voltage  $U_1(t)$ , the initial planar texture changes into a focal conic one. This is also stressed by the change of the characteristic slope for  $I(U)$  and by the modification of the optical transmission (see figures 2(a), (b), (c), (d), (e)). At values of d.c. applied voltage  $U_2(t)$ , the focal conic texture changes into a finger print arrangement; at voltages higher than  $U_2(t)$  the cholesteric-nematic transition

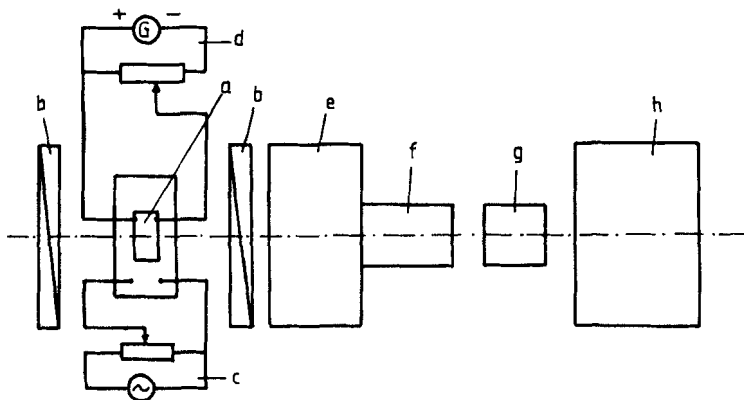
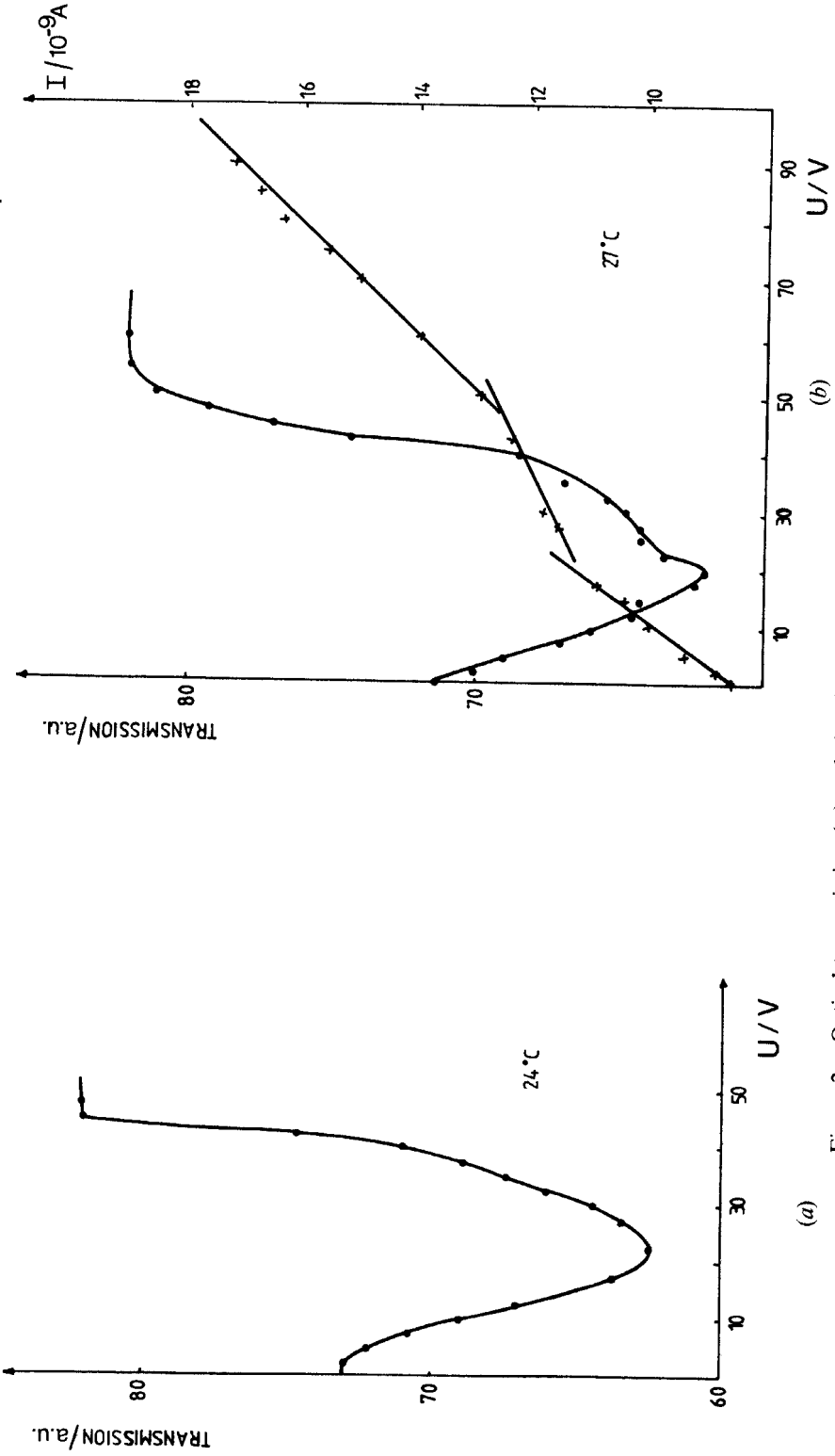


Figure 1. Experimental arrangement for optical and electrical measurements. (a) liquid crystal sample; (b) polarizers; (c) heating control; (d) electrical circuit (e) monochromator SPM-2; (f) photomultiplier; (g) amplifier; (h) recorder.



(a) (b) Figure 2. Optical transmission (●) and electrical current (x) versus applied voltage.

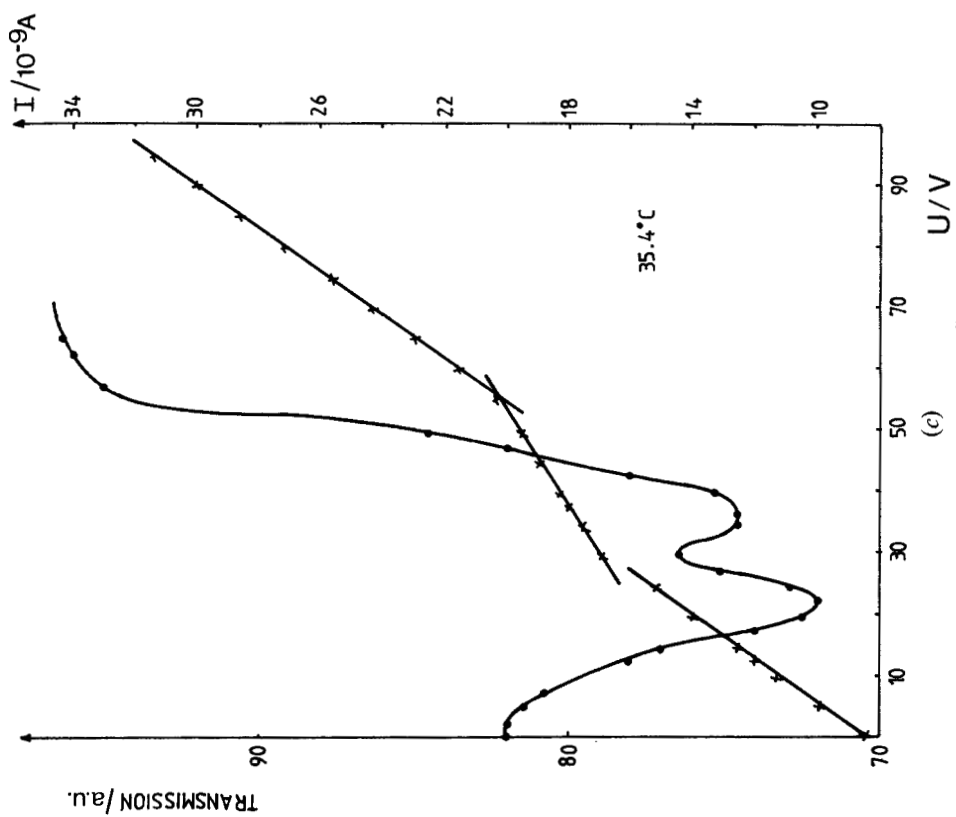
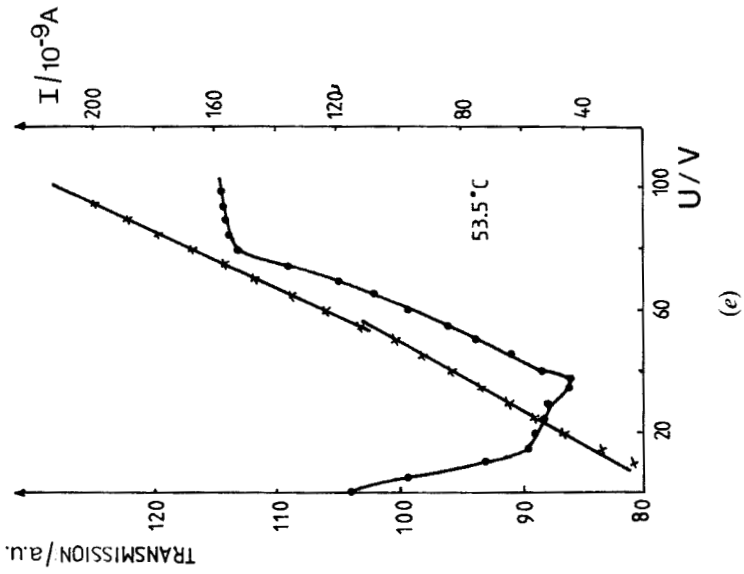
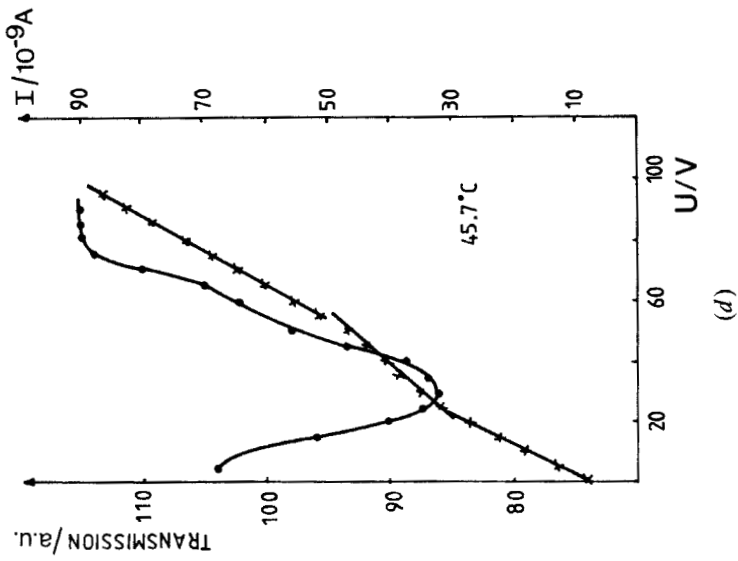


Figure 2 (continued)



(e)



(d)

Figure 2 (continued)

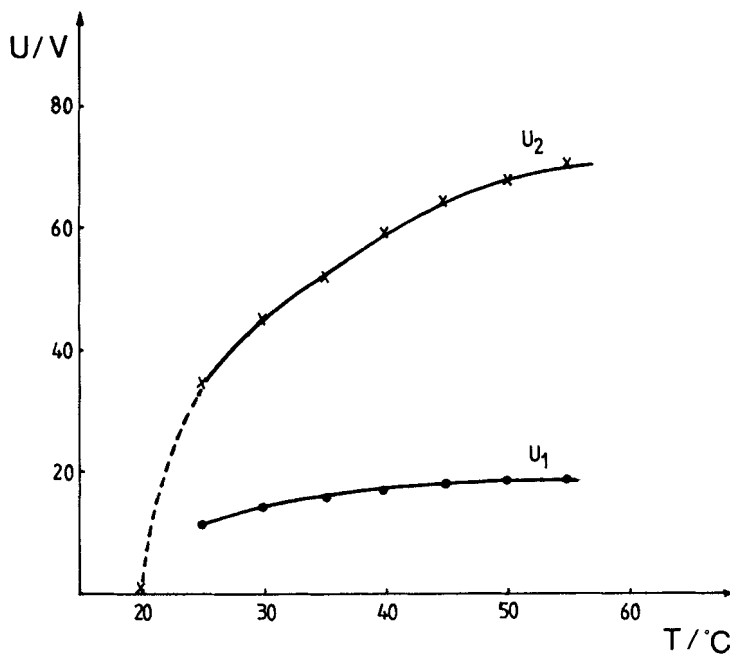


Figure 3. Temperature dependence of the critical voltages  $U_1$  and  $U_2$ .

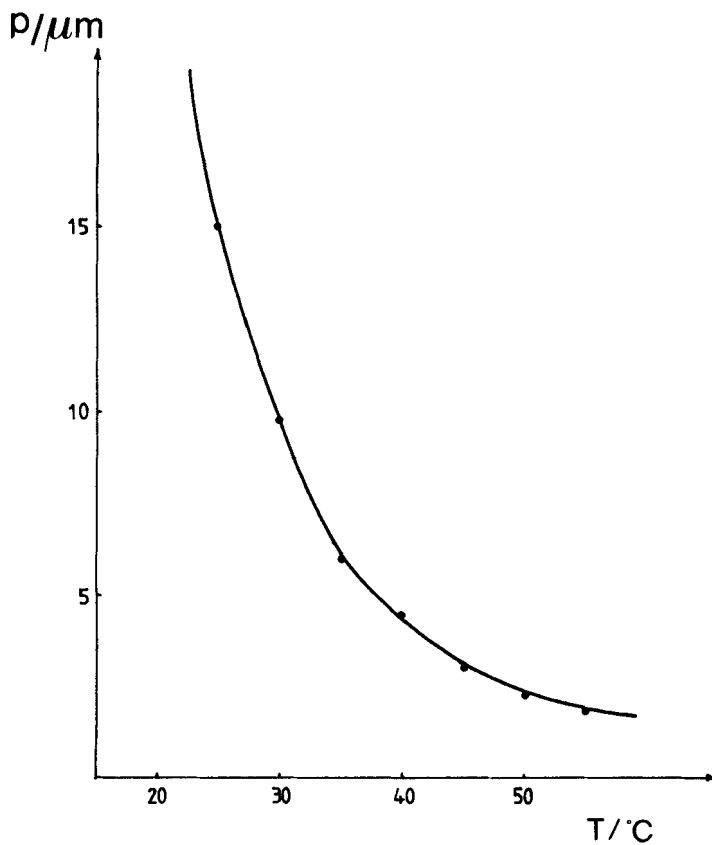


Figure 4. The temperature dependence of the pitch for the mixture.



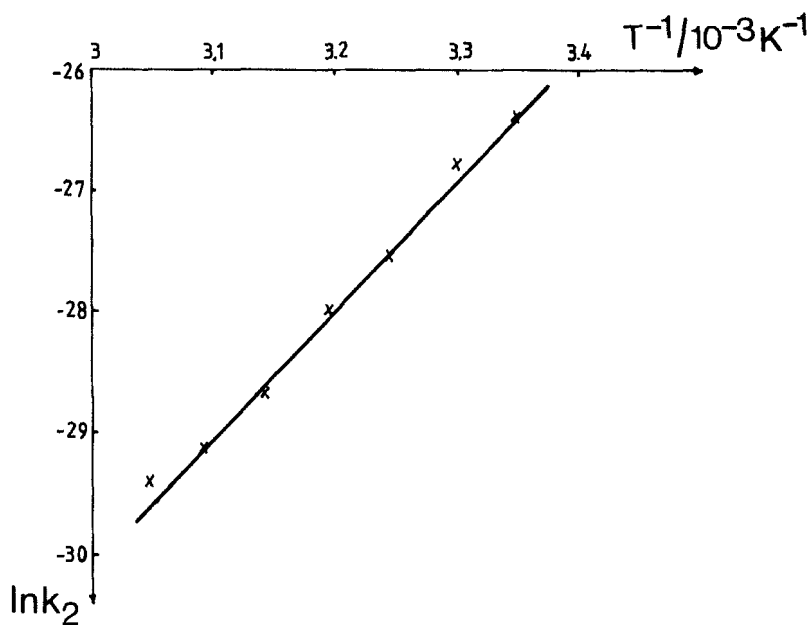
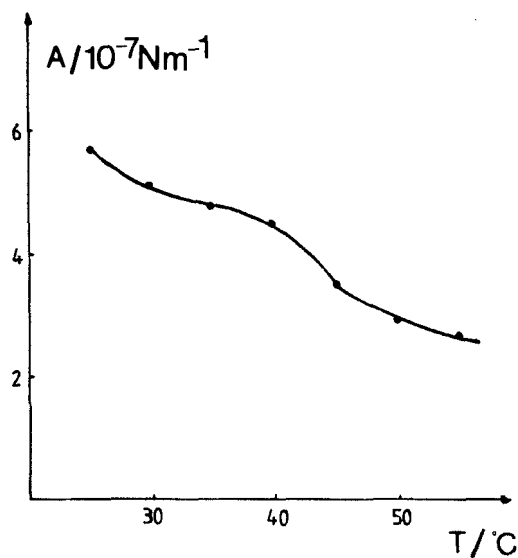
Figure 5.  $\ln K_2$  versus  $1/T$ .

Figure 6. The temperature dependence of the anchoring constant.

begins and the pitch of the mixture becomes infinite. Figure 3 shows the temperature dependence of  $U_1$  and  $U_2$ .

Figure 4 shows the temperature dependence of the pitch [2].

The value for  $\varepsilon_a$  of 0.15 was calculated from the temperature dependence of the refractive indices [4]. ( $\varepsilon_a = \varepsilon_0 \varepsilon_a$ ). The value of  $\varepsilon_a$  is independent of temperature. From the relation [5]:

$$K_2 = \frac{U_1 U_2}{L^2} \varepsilon_a \left( \frac{p_0}{2\pi} \right)^2,$$

the  $K_2(t)$  values were calculated. Figure 5 shows the dependence of  $K_2$  as a function of temperature. The ratio  $K = K_3/K_2 = 0.24$  is also independent of temperature [6]. From this data, using equation (12), we obtained the temperature dependence of the anchoring constant  $A$  (see figure 6).

#### 4. Discussion and conclusions

The texture changes of the mixture cholesteryl chloride-cholesteryl nonanoate (70–30 per cent molar) produced by applying a d.c. electric field are in agreement with those predicted by theory. By using the values of  $U_1$  and  $U_2$  obtained from our experiments, we have estimated the anchoring constant and its temperature dependence. The magnitude of the anchoring energy  $W$  estimated from equation (6) is the same as that obtained by integrating the free energy density for the whole sample thickness (namely  $\sim K_2 \tau^2 L$ ). The decrease of  $A$  with increasing temperature is evident as the molecules adhesion to the walls decreases with the increasing thermal motion.

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