

Anisotropic interactions between mbba and surface-treated substrates

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ANISOTROPIC INTERACTIONS BETWEEN MBBA AND SURFACE-TREATED SUBSTRATES

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Résumé. — Nous avons déterminé la direction de l'axe facile du directeur et son énergie d'ancrage B_θ aux interfaces MBBA-substrat solide [traité avec des agents tensio-actifs], par la méthode de la transition de Freedericksz. Les résultats expérimentaux indiquent que les interactions stériques, dispersives et polaires sont importantes dans la détermination de l'orientation des molécules sur les lames. Nous avons trouvé des valeurs de B_θ assez faibles et estimons l'anisotropie de tension superficielle du MBBA à environ 10^{-2} dyn/cm.

Abstract. — Easy axis Θ and anchoring strength coefficient B_θ were measured on the interfaces between MBBA and substrates with various surfactants layers, by using wall effects on the Freedericksz transition. Experimental results indicate that steric, dispersive and polar interactions play individual roles in the molecular orienting forces of surface-treated substrates. B_θ values were found to be rather small. MBBA surface tension anisotropy was estimated to be of the order of 10^{-2} dyn/cm.

1. **Introduction.** — Several substrates with surfactant layers exert an orienting effect on liquid crystal (LC) molecules. The surface orientation of LC molecules is characterized using the easy axis (Θ , Φ) and anchoring strength coefficients B_θ and B_ϕ . It is known that LC molecules align homeotropically ($\Theta = 0^\circ$) on the surfactant layer with a long alkyl chain, and the polar angle of the easy axis Θ increases as the surfactant chain length decreases [1]. Also, B_θ values are found to be very small in several cases [1, 2]. However, anchoring strength measurement was rather difficult and experimental data regarding B values were quite limited. This is one of the reason why there is poor understanding of mechanisms for molecular orientation on substrates. Recently, a new method has been developed to measure anisotropic interfacial interactions between nematic LC molecules and substrates by using wall effects on the Freedericksz transition [3]. This paper reports measured Θ and B_θ values between MBBA (p-methoxybenzylidene-p'-butylaniline) and various substrates with serial surfactants layers. It also presents some consideration on molecular orienting forces.

2. **Theoretical.** — Interfacial interaction energy per unit area W_s is represented using polar angle θ_0 and azimuthal angle ϕ_0 for a director at the interface (Fig. 1). Here, conical configuration is considered under the $\partial\theta_0/\partial x = \partial\theta_0/\partial y = 0$ condition. Then W_s is modeled into the form

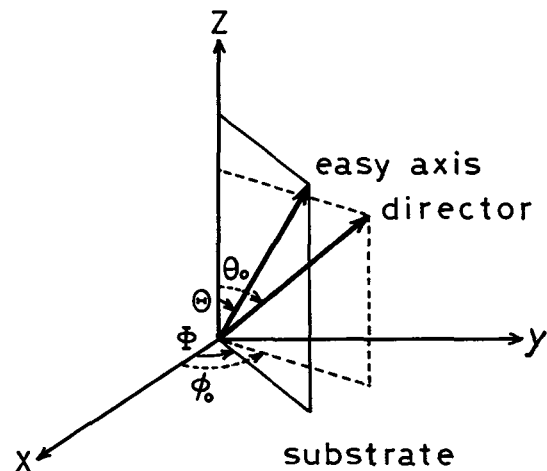


FIG. 1. — Interface notations.

$$W_s = \frac{A}{2} + \frac{B_\theta}{2} \sin^2(\theta_0 - \Theta) + \frac{B_\phi}{2} \int \sin^2(\phi_0 - \Phi) dS, \tag{1}$$

where A , B_θ and B_ϕ are anchoring strength coefficients, Θ and Φ are easy axis components and $\int dS$ means the surface integral for unit area. In case of homeotropic alignment, the third term is omitted. Consider a simple case where the third term can be neglected. Consider a nematic LC layer with thickness l , sandwiched between two parallel substrates with the

same boundary condition. The director deformation under magnetic field H parallel to the substrate is derived from the condition that the total free energy per unit area director dependent terms

$$G_{\theta} = 2 \left(\frac{B_{\theta}}{2} \right) \sin^2 (\theta_0 - \Theta) + \frac{1}{2} \int_{-l/2}^{l/2} (K_{11} \sin^2 \theta + K_{33} \cos^2 \theta) \left(\frac{d\theta}{dz} \right)^2 dz - \frac{1}{2} \int_{-l/2}^{l/2} \chi a H^2 \sin^2 \theta dz \quad (2)$$

are minimum for θ , where K_{11} and K_{33} are Frank elastic constants for splay and bend respectively and χa is magnetic anisotropy. Equilibrium director deformation computation under the magnetic field shows that threshold magnetic fields H_c' depend on both Θ and B_{θ} [3]. These relations enable B_{θ} evaluation from measured Θ and H_c' .

3. Experimental.—Experiments were accomplished using MBBA in the nematic phase. The surfactant

layer was deposited by dipping a substrate in a surfactant solution. Homologous series of n-alkyl trimethyl ammonium salts and n-alkyl amines as well as some other cationic, nonionic and amphoteric surfactants were examined. The *magneto-capacitance method* was used to measure Θ and H_c' for In_2O_3 evaporated glass substrates. The *total reflection method* was used for glass substrates. Measurements were performed for various thickness MBBA layers. l values were determined carefully by using capacitance, optical interference and microscopic focusing measurements together. Measuring procedure details were reported in a previous letter [3].

4. Results.—A summary of experimental results is given in table I. Surfactants with long alkyl chain ($n \geq 10$, n is the number of carbon atoms in the alkyl chain) promote MBBA homeotropic alignment ($\Theta = 0^\circ$). In case of n-alkyl amines, $\Theta = 3^\circ$ was obtained even for $n = 10$ and 12. We used eq. (2) to approximately evaluate B_{θ} from H_c' even for $\Theta \lesssim 5^\circ$, when φ -dependent term has some contributions to the total free energy, although eq. (2) was

TABLE I

Easy axes Θ and anchoring strength coefficients B_{θ} on interfaces between MBBA and substrates with various surfactants

(a) In_2O_3 evaporated glass substrate.

	Surfactants	Concentration (mol/l)	Solvent	With drawing speed (mm/s)	Temperature ($^\circ\text{C}$)	Θ (deg)	B_{θ} ($\times 10^{-3}$ erg/cm 2)
cationic	FS-150 [3]	6.9×10^{-4}	water	~ 300	23.0 ~ 23.5	0	10 ± 2
	DMOAP [3]	2.0×10^{-3}	—	—	21.5 ~ 23.5	0	11 ± 4
	$\text{C}_{18}\text{H}_{37}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	3.0×10^{-3}	ethanol	~ 1	21.5 ~ 24.5	0	2.7 ± 0.3
	$\text{C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	—	—	~ 300	22.5	0	7.6
	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	—	—	~ 1	24.5 ~ 25.0	0	2.7 ± 1.2
	$\text{C}_{10}\text{H}_{21}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$	—	—	—	21.5 ~ 24.0	0	2.1 ± 0.7
	$\text{C}_{14}\text{H}_{29}\text{N}^+(\text{CH}_3)_3\text{Br}^-$	—	—	—	24.0	0	9
	$\text{C}_{12}\text{H}_{25}\text{N}^+(\text{CH}_3)_3\text{Br}^-$	—	—	—	23.5 ~ 24.5	0	7
	$\text{C}_{10}\text{H}_{21}\text{N}^+(\text{CH}_3)_3\text{Br}^-$	—	—	—	24.0	~ 0	4.4 ± 0.7
	$\text{C}_8\text{H}_{17}\text{N}^+(\text{CH}_3)_3\text{Br}^-$	—	—	—	22.5	~ 75	< 1
	$\text{C}_6\text{H}_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^-$	—	—	—	22.5	~ 75	< 1
	nonionic	$\text{C}_{18}\text{H}_{37}\text{NH}_2$	3.0×10^{-2}	—	~ 300	22.0 ~ 24.0	0
$\text{C}_{16}\text{H}_{33}\text{NH}_2$		—	—	—	23.0	0	3.5 ± 1.2
$\text{C}_{14}\text{H}_{29}\text{NH}_2$		—	—	—	23.0 ~ 24.0	0	4.0 ± 0.7
$\text{C}_{12}\text{H}_{25}\text{NH}_2$		—	—	—	22.5 ~ 23.5	~ 3	> 1.5
$\text{C}_{10}\text{H}_{21}\text{NH}_2$		—	—	—	23.0	~ 3	> 1.9
$\text{C}_8\text{H}_{17}\text{NH}_2$		—	—	—	23.5	~ 12	~ 0.32
$\text{C}_6\text{H}_{13}\text{NH}_2$		—	—	—	23.0	~ 24	~ 0.22
amphoteric	$\text{C}_{16}\text{H}_{33}\text{OH}$	4.1×10^{-3}	—	—	23.0	0	4.8
	Lecithin	(0.1 wt %)	n-hexane	—	22.5 ~ 23.0	0	5.9 ± 1.3
	Cepharin	—	—	—	24.0	~ 5	~ 6.3

(b) Glass substrate [3].

	Surfactants	Concentration (mol/l)	Solvent	With drawing speed (mm/s)	Temperature ($^\circ\text{C}$)	Θ (deg)	B_{θ} ($\times 10^{-3}$ erg/cm 2)
	FS-150	6.9×10^{-4}	water	~ 300	24.5 ~ 25.5	0	6.4
	DMOAP	2.0×10^{-3}	—	—	24.5 ~ 25.5	0	6.1
	$\text{C}_{16}\text{H}_{33}\text{NH}_2$	3.0×10^{-2}	ethanol	—	23.0	0	2.6
	Lecithin	(0.1 wt %)	n-hexane	—	24.5 ~ 25.5	0	3.1

rigorously derived by neglecting the φ -dependent term. The results indicate that B_θ depends on the surfactants chain length. B_θ -vs- n relationships are given in figure 2. Figure 2 shows that B_θ depends

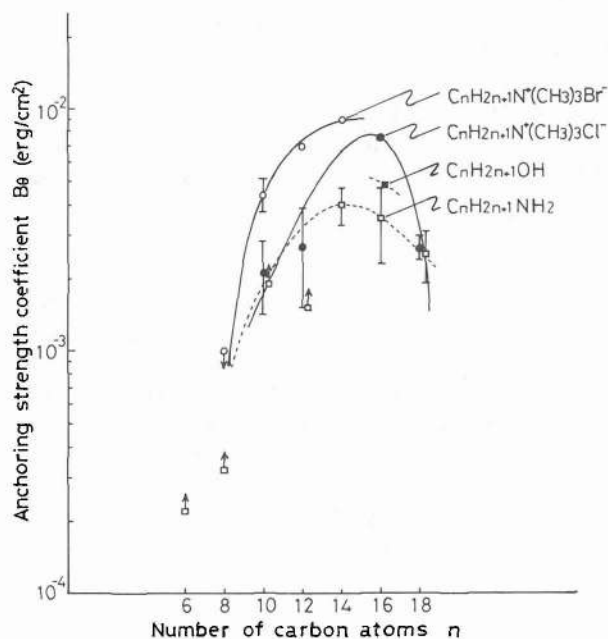


FIG. 2. — Relations between anchoring strength coefficient B_θ and number of carbon atoms n in surfactant alkyl chain.

also on the polar groups of the surfactants. Larger values of B_θ were obtained for cationic surfactants than for nonionic surfactants of the same chain length. Besides, B_θ 's for the insulating glass substrates are smaller than those for the In_2O_3 evaporated conductive substrates. In case of $n = 8$ or 6 , Θ is larger and therefore φ -dependent interaction term takes part in molecular orienting forces. This brings about a conical configuration (Fig. 3). This configuration is strongly affected by the LC molecules flow. Polarized microscopic observation gives a director distribution drawing as shown in figure 3. Parallel dark lines in the LC flow direction (x -axis) indicate $\partial\varphi/\partial x \approx 0$. Their darkness becomes maximum under the cross-nicols condition, that means $\partial\varphi/\partial z = 0$. $\partial\varphi/\partial y = 2\pi/cl$ (c is a constant) is obtained by the observation for a wedge cell. In case of larger l values, $\partial\varphi/\partial y$ becomes nearly equal to zero and the configuration is something like a planar structure. Thermal treatment breaks the conical configuration. If the cell is heated above the nematic-isotropic transition temperature and then cooled slowly under a magnetic field perpendicular to the substrates, a different configuration is obtained. In this configuration, several regions of different φ 's are divided by surface disclination lines and Néel type walls. $\theta = \Theta$ is assumed in a large part of the cell except in the vicinity of those defects, and Θ can be estimated by capacitance measurements. $\Theta = 75^\circ$ was obtained for n -alkyl trimethyl ammonium bromides ($n = 6, 8$). In

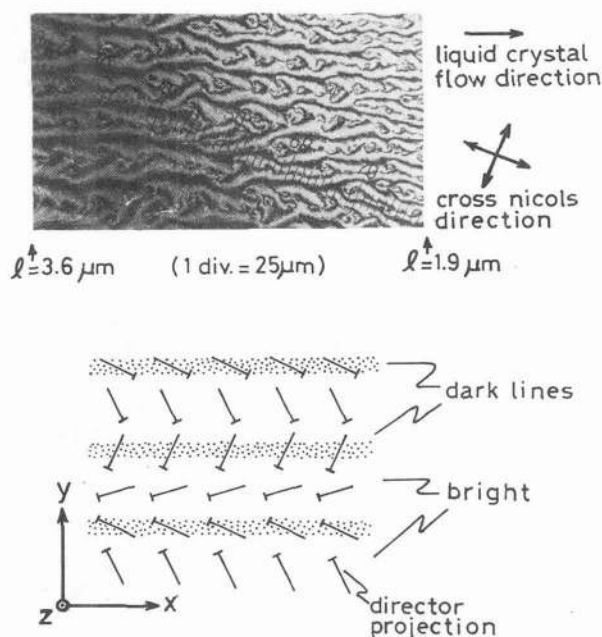


FIG. 3. — Polarized microscopic observation of conical configuration (wedge cell, n -hexyl trimethyl ammonium bromide).

case of n -alkyl amines, Θ is about 12° for $n = 8$ and about 24° for $n = 6$. In this configuration, B_θ 's are estimated by the topological observation used in reference [1]. They are of the order of 10^{-4} erg/cm².

5. Discussion. — The results presented in section 4 are summarized: Θ is zero (homeotropic alignment) for the long-chain surfactants and increases as chain length decreases. B_θ depends on both the hydrophobic chain and the hydrophilic group of the surfactants. That is, decreasing the chain length makes B_θ smaller, and B_θ 's for cationic surfactants are larger than those for nonionic surfactants of the same chain length. Also, substrate materials influence B_θ . That is, for cationic surfactants, glass substrates reduce B_θ values by almost half, compared with In_2O_3 evaporated glass substrates. These results help in considering mechanisms of LC molecular orientation on substrates.

5.1 STERIC CONSIDERATION. — The relations between Θ and n are interpreted as a result of steric effects. It is known that LC molecules align homeotropically when the alkyl chains of surfactants are perpendicular on the substrate, and align parallel when they are parallel on the substrate [4]. Therefore, it is considered that surfactant alkyl chains tend to align perpendicular if they are long enough. LC molecules lie parallel to the chains because of dispersive forces. Actually the long alkyl chains of surfactants were found to be orienting perpendicular on the substrate. Figure 4 shows reflective electron diffraction patterns for In_2O_3 evaporated substrates without surfactants (a) and with n -tetradecyl trimethyl

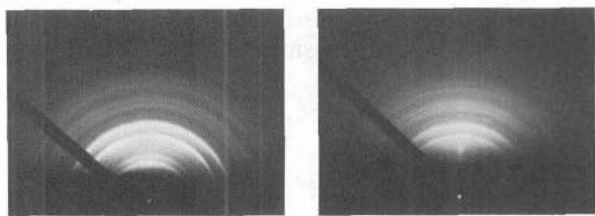


FIG. 4. — Reflective electron diffraction patterns. (a) In_2O_3 evaporated glass surface. (b) n-tetradecyl trimethyl ammonium bromide layer on In_2O_3 evaporated glass.

ammonium bromide layer (b). Figure 4b shows a vertical line of spots, which suggests a perpendicular orientation of alkyl chains on the substrate. Decreasing of B_θ for rather short-chain surfactants is considered to be the result of the dispersive force n -dependence.

5.2 ELECTROSTATIC CONSIDERATION. — The effects of the polar group of surfactants and the substrate materials on B_θ values suggest that polar interactions play several roles in the molecular orienting forces. According to J. E. Proust *et al.* [5], dipole-dipole interactions are dominant in the LC molecular alignment at a humid glass surface. The dipole-dipole interaction acts to orient MBBA molecules parallel on such a glass substrate. Actual alignment of MBBA on the surfactant layer with alkyl chains is, therefore, determined by a balance between polar and nonpolar (dispersive) forces. Dispersive forces are dominant in the interfacial interactions between LC molecules and the long-chain surfactant layer, and promote homeotropic alignment in cooperation with steric effects. Even in case of homeotropic alignment, polar interactions have latent effects on B_θ values.

5.3 PHYSICOCHEMICAL CONSIDERATION. — Here alignment on a longchain surfactant layer is considered, where dispersive forces are dominant. In this case, the interfacial interaction energy is considered to be

$$W_s = \gamma_s^d + \gamma_L^d(\theta) - W_a^d(\theta), \quad (3)$$

where γ_s^d and $\gamma_L^d(\theta)$ represent dispersive terms for substrate and liquid crystal surface tension, respectively. Also, $W_a^d(\theta)$ represents the dispersive term of adhesion energy. According to F. M. Fowkes [6], we can write

$$W_a^d(\theta) = 2 \sqrt{\gamma_s^d \cdot \gamma_L^d(\theta)}, \quad (4)$$

$$\gamma_s^d \cong \gamma_c, \quad (5)$$

where γ_c is the critical surface tension of a substrate. In case of $\Theta = 0^\circ$, by inserting eq.'s (1), (4) and (5) into eq. (3), we can get

$$\frac{A}{2} + \frac{B_\theta}{2} \sin^2 \theta = \gamma_c + \gamma_L^d(\theta) - 2 \sqrt{\gamma_c \cdot \gamma_L^d(\theta)}, \quad (6)$$

that is,

$$\frac{B_\theta}{2} = \gamma_L^d\left(\frac{\pi}{2}\right) - \gamma_L^d(0) - 2 \sqrt{\gamma_c} \left(\sqrt{\gamma_L^d\left(\frac{\pi}{2}\right)} - \sqrt{\gamma_L^d(0)} \right). \quad (7)$$

Measured γ_c values for substrates with n-alkyl trimethyl ammonium bromide layers by the contact angle method are shown in figure 5. Using the assumption of $\gamma_L^d(0) < \gamma_L^d(\theta) < \gamma_L^d(\pi/2)$, $\Theta = 0^\circ$ is obtained in case of $\gamma_c < \gamma_L^d(0)$ [1]. Therefore, it is possible that an approximate value $\gamma_L^d(0) \cong 26$ dyn/cm can be attained, from figure 5. By using B_θ and γ_c of n-alkyl

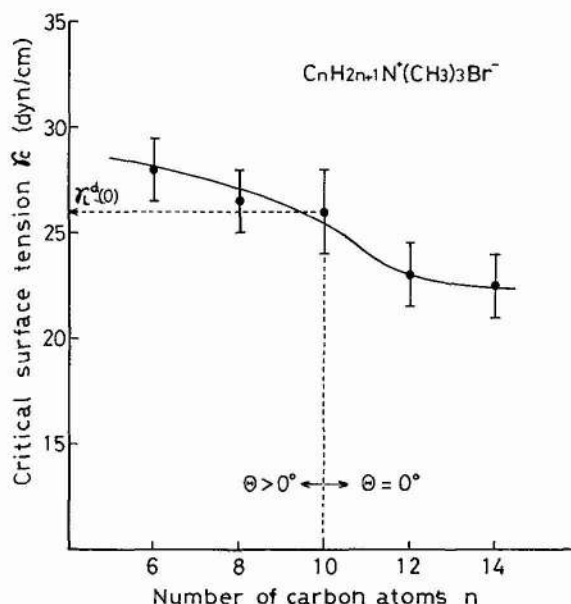


FIG. 5. — Critical surface tension for substrates with n-alkyl trimethyl ammonium bromide layers.

trimethyl ammonium bromide layers ($n = 12, 14$). a $\gamma_L^d(\pi/2)$ value is obtained from eq. (7) which gives the MBBA surface tension anisotropy

$$\gamma_L^d\left(\frac{\pi}{2}\right) - \gamma_L^d(0) = (4.5 \pm 1.3) 10^{-2} \text{ dyn/cm}.$$

Despite rough measurements of γ_c values, the surface tension anisotropy of liquid crystals is very small [7].

As a summary, Θ -vs- n relationships and electron diffraction observation suggest steric effects in mechanisms for molecular orientation. n -dependences of B_θ indicate that dispersive interactions play several roles in molecular orienting forces, and also polar interactions contribution is suggested by the results that B_θ is affected by both surfactant polar groups and substrate materials. The anisotropic anchoring strength of the surfactant layer with n-alkyl chain was found to be not so strong. Also, the surface tension anisotropy of MBBA was estimated to be rather small.

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