Anchoring Energy Measurements at the Aqueous Phase/Liquid Crystal Interface with Cationic Surfactants Using Magnetic Freedericksz Transition

Supporting Information Fatma Yesil, Masayori Suwa, Satoshi Tsukahara.

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- IV. Determination of the threshold magnetic field from the oscillation of the transmission intensity

I. Pendant drop method and Estimation of the interfacial concentration

The surface tension measurements were done in the same condition as the anchoring energy measurements. We prepared a salt solution containing 0.1 mol L-1 of lithium sulfate and 0.01 mol L⁻¹ of sulfuric acid. The stocks solutions of surfactants were prepared by dissolving alkyltrimethylammonium bromides into the above salt solution. The concentrations were adjusted to 50 mmol L⁻¹ for C₁₂TAB and 5 mmol L⁻¹ for C₁₄AB. 10 mL of the salt solution was poured in a square shaped glass tank. We placed 5CB in a glass syringe attached to a glass capillary tube with an internal diameter of $291\mu m$. The outlet of the capillary was put in the salt solution, and then a droplet of 5CB was formed at the edge of the capillary tube by adjusting the syringe. Because no dependence of the surface tension on the droplet size was observed [S1] we adjusted the drop size manually. The shape of the droplet was observed with a CCD camera (Neptune 100, watec). The concentration of surfactant was increased by adding its stock solution and mixing immediately with a magnetic stirrer. After 5 min of every addition, we took the image of 5CB droplet. By analyzing these images, we measured the maximum horizontal diameter of the 5CB droplet, d_e , and the width of the droplet at d_e from the bottom of the droplet, d_s . We calculated the surface tension, γ by substituting d_e and d_s into the Young-Laplace equation ^[16], which can be written as

$$\gamma = \frac{\Delta \rho g d_e}{H} \tag{S1}$$

where *H* stand for the mean curvature, which is a function of d_e and d_s , and $\Delta \rho$ is the density difference between the aqueous solution and 5CB ^[S1] and *g* the gravitational acceleration constant. The obtained Gibbs isotherm was shown in figure S1. In the case of the surfactant with longer alkyl chain, the surface tension decreases in lower concentration, this is a usual trend observed for homologous series; described by Traube ^{[15][S4]}. Moreover we know from Traube's rule that each addition of a methyl group in the alkyl chain will induce an increase of the molecule surface active about 3.2 times. Thus the obtained surface activities fro Figure S1 could confirm that Traube's rule was respected so we can testify that our measurement method was a suitable measurement. Figure S1 permitted us to determine the critical micellar concentration (CMC); 6×10^{-3} mol L⁻¹ for C₁₂TAB and 0.8 × 10⁻³ mol L⁻¹ for C₁₄TAB. We saw that the CMC are in the same sequence as the CMC reported on table 1 but the values are lower because due to an increase of the electrolyte concentration [^{S2}].



Figure S1. Obtained Gibbs isotherms for C₁₂TAB and C₁₄TAB.

The relationship between the surface tension and the surfactant concentration in bulk can be expressed by the Syzszkowski equation as follows;

$$\gamma = \gamma_0 \left[1 - b \ln\left(1 + \frac{C}{a}\right) \right]$$
(S2)

We fitted this equation to the experimental data with non-linear least square method and obtained the parameter *a* and *b*. In this fitting, the tension of pure water/LC interface, γ_0 , was fixed to the literature value of 26mN/m ^[S3]. Afterward we substituted *a* and *b* into the following equation to obtain the interfacial excess of surfactant, Γ ,

$$\Gamma = -\frac{C}{RT}\frac{\partial\gamma}{\partial C} = \frac{b\gamma_0}{RT}\frac{C}{a} / \left(1 + \frac{C}{a}\right)$$
(S3)

Figure S2 shows the evolution of Γ with the surfactant concentration in the aqueous phase. The longer alkyl chain the surfactant has, the more surfactant adsorbed to the water/LC interface.



Figure S2. Interfacial concentration as a function of surfactant's the solution concentration.

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- [S2] E. Fuguet. C. Rafols, M. Roses, E. Bosch, Analytica Chimica Acta, 2005, 548, 95-100
- [S3] J. Proust, E. Perez, L. Ter-Minassian-Saraga, Colloid & Polymer Sci., 1978, 256, 666-681
- [S4] J. Traube, Justus Liebigs Ann. Chem., 1891, 265, 27-55

II. Derivation of equation 1: definition are taken from [4]

In our study the Freedericksz transition is studied at simultaneously weak and strong anchored interface. This is a new concept so we have to settle the equation. For this we had to determine the coordinate of the studied system, figure S3.



Figure S3: Definition of the system studied

The distortion energy is defined as follow,

$$f_d = \frac{1}{2}K_1(\nabla \cdot n)^2 + \frac{1}{2}K_2\{n \cdot (\nabla \times n)\}^2 + \frac{1}{2}K_3\{n \times (\nabla \times n)\}^2$$
(S4)

Where n is a director vector with the coordinate $(\sin\theta, 0, \cos\theta)$, K_1 , K_2 and K_3 are the elastic constant respectively for splay, twist and bent deformation. This is the fundamental formula of the continuum theory for nematics. Applaying the present coordinate condition and in the case of very small θ we observe,

$$f_d = \frac{1}{2} K_3 \cos^2 \theta \left(\frac{d\theta}{dz}\right)^2$$
 (S5)

In the presence of magnetic field and by taking in to account the magnetic field direction we can derivate the free energy as shown in equation S6,

$$f_{mag} = -\frac{1}{2}\mu_0^{-1}\Delta\chi B^2 sin^2\theta \quad (S6)$$

where μ_0 is the vacuum permeability and $\Delta \chi$ is the magnetic anisotropy.

Substitution of the equation S5 and S6 into the Euler-Lagrange equation gives S7;

$$\frac{d^2\theta}{dz^2} + \frac{1}{\xi^2} \sin\theta \cos\theta = 0 \quad (S7)$$

Where the ξ is the coherence length. The coherence length definition is $\xi = \frac{1}{B} \sqrt{\frac{K_3}{\mu_0^{-1} \Delta \chi}}$ where

B is the magnetic field.

At the critical field and in the case of **strong anchoring**, as it is the case for the OTS/LC interface it is known that ξ_c is equal to d/π because K3/W_{OTS} is about 0.1 µm, which is much smaller than d (25 µm) in the present system. Based in this we can calculate the B_c , the threshold magnetic field.

$$B_c = \frac{\pi}{d} \sqrt{\frac{K_3}{\mu_0^{-1} \Delta \chi}} \,(\mathrm{S8})$$

In the case of liquid interface, a **weak anchoring** is expected so the LC at the interface can incline. A weak anchoring implies the boundary condition so we introduced in this section a new parameter called the extrapolation length, d_e . We schematically imaged the d_e on the figure S4. One side of the liquid crystal is supported by the OTS-glass, so the other side is in contact with an aqueous solution. The aqueous solution interface is a weak so $\theta(0) \neq 0$; so we assumed that the LC layer is extended by d_e .



Figure S4: schematic presentation of the LC layer thickness

The free energy of LC interface at z=0 and *d* can respectively be expressed as;

$$F_s(0) = 0$$
 (S9)
 $F_s(d) = \frac{1}{2}W\theta(d)^2$ (S10)

Then we add the total free energy equation, $F = \int_0^d f(\theta, \frac{d\theta}{dz}) dz$ and we imposed a small variation,

$$F'' = \int_0^d f\left(\theta + \delta\theta, \frac{d(\theta + \delta\theta)}{ds}\right) dz + \frac{1}{2}W\theta(d)^2 + W\theta(d)\delta\theta(d)$$
$$= \int_0^d f \, dz + \frac{1}{2}W\theta(d)^2 + \int_0^d \left(\frac{\partial f}{\partial \theta} - \frac{d}{dz}\frac{\partial}{\partial\left(\frac{d\theta}{dz}\right)}\right)\delta\theta + \left[\frac{\partial f}{\partial\left(\frac{d\theta}{dz}\right)}\right]_{z=d} + W\theta(d)\delta\theta(d)$$
(S11)

To minimize the total free energy, additional boundary condition appears. It is important to note that if $\delta\theta(d)$ is negative F"<F; so the following equation S12 is not satisfied and yields to the equation S13

$$\frac{\frac{\partial f}{\partial (\frac{d\theta}{dz})}}{K_3 \frac{\partial f}{\partial dz}}\Big|_{z=d} + W\theta(d) = 0$$
(S12)
$$K_3 \frac{\frac{\partial f}{\partial dz}}{K_3 \frac{\partial f}{\partial dz}}\Big|_{z=d} = -W\theta(d)$$
(S13)

S7 can also be written as; S14 where C is a constant. Then we substituted $\theta((d + d_e)/2) = \theta_m$. We also derived $C = -\left(\frac{1}{2}\right) sin^2 \theta_m$ because θ_m is the maximum value. Later we assume $sin \ \theta_m \approx \theta_m$ we finally obtained the equation S12 where ξ_c indicates the coherence length at the threshold magnetic field value which is by definition equal to $\xi_c = \frac{1}{B_c} \sqrt{\frac{K_3}{\mu_0^{-1} \Delta \chi}}$.

$$\frac{1}{2}\xi^{2}\left(\frac{d\theta}{dz}\right)^{2} + \frac{1}{2}\sin^{2}\theta = C \quad (S14)$$
$$\xi_{c}\left(\frac{d\theta}{dz}\right) = \pm\sqrt{\sin^{2}\theta_{m}\sin^{2}\theta} = \pm\sqrt{\theta_{m}^{2} + \theta^{2}} \Leftrightarrow \pm\frac{d\theta}{\sqrt{\theta_{m}^{2} + \theta^{2}}} = \frac{dz}{d\xi_{c}} \quad (S15)$$

integrating both side of S15 from z=0 to $(d + d_e)/2$ gives S16; we also integrated S15 from $(d + d_e)/2$ to d and obtain equation S17. Then we substituted the equation S13 into the equation S18 and obtained S19. S18 was obtained by S15

$$d + d_e = \pi \xi_c \text{ (S16)}$$

$$\frac{d - d_e}{2\xi_c} = \frac{\pi}{2} - \sin^{-1} \left(\frac{\theta(d)}{\theta_m}\right) \approx \frac{\pi}{2} - \frac{\theta(d)}{\theta_m} \text{ (S17)}$$

$$\xi_c \left. \frac{d\theta}{dz} \right|_{z=d} = -\sqrt{\theta_m^2 - \theta(d)^2} \text{ (S18)}$$

$$\frac{\theta(d)}{\theta_m} = \left[1 + \left(\frac{\xi_c W}{K_3}\right)^2 \right]^{-1/2} \approx \frac{K_3}{\xi_c W} \text{ (S19)}$$

if $\theta(d)/\theta_m \ll 1$; equation S19 is added into S17 and we obtain

$$d - d_e \approx \pi \xi_c - \frac{\kappa_3}{W} (S20)$$

From S16 and S20 we can understand that $d_e = K_3/W$, and from this last equation we can finally find out the equation 1; equation of the threshold magnetic field value from the Freedericksz transition, equation used in our experiment:

$$B_c = \frac{\pi}{d + \frac{K_3}{W}} \sqrt{\frac{K_3}{\mu_0^{-1} \Delta \chi}}$$
(1)

III. Measurement of the thickness of 5CB [22]

As mentioned in the manuscript, we should measure the precise thickness of 5CB film in order to estimate the anchoring energy from Freedericksz transition. The thickness was determined from the reflection spectrum. The condition was shown in Fig. S5c. The electric field of light reflected bottom interface (5CB/glass) can be written as

$$E_{\text{bottom}} = \alpha_{\text{bottom}} E_0 \exp[-i\omega t]$$
(S21).

Here, E_0 and ω are respectively the amplitude of the electric field and the angular frequency of the incident light, *t* is time, and α_{bottom} is the amplitude reflectance of 5CB/Glass surface. Assuming that the light is irradiated normal to the interface and the 5CB is homeotropically aligned against the interfaces that is the light propagates along the optic axis of 5CB, the reflected light at the top interface (water/5CB) can be expressed as follows;

$$E_{\rm top} = \alpha_{\rm top} E_0 \exp\left[-i(\omega t + 4\pi n_{\rm 5CB} d/\lambda)\right]$$
(S22)

taking into account the optical path difference $2n_{5CB}d$, where n_{5CB} is a refractive index of 5CB for ordinary ray ^[S5], λ is the wavelength of the light and α is the amplitude reflectance at the water/5CB interfaces. These reflected lights interfere with each other, and then the total electric field, *E*, was expressed by the simple summation of S21 and S22 ($E = E_{bottom} + E_{top}$). The intensity of reflected light, I_{R} , can be written as

$$I_{\rm R} = EE^* = (\alpha_{\rm bottom}^2 + \alpha_{\rm top}^2 + 2\alpha_{\rm bottom}\alpha_{\rm top}\cos[4\pi n_{\rm 5CB}d/\lambda])E_0^2$$
(S23),

where *E** represents the complex conjugation of *E*. Therefore, an interference pattern can be observed in the reflectance spectrum. The transverse axis was converted to the wavenumber in 5CB, $\tilde{\nu} = n_{5CB} / \lambda$. The wavelength dispersion of n_{5CB} was from from the literature value.[ref] After that the following Fourier transformation was conducted:

$$\hat{I}_{\rm R}(2d) = \int I_{\rm R}(\widetilde{\nu}) \exp(-2\pi i \,\widetilde{\nu} \cdot 2d) \mathrm{d}\,\widetilde{\nu} \qquad (S24).$$

Then, from the power spectrum density, $P(2d) = |\hat{I}_R(2d)|^2$, the thickness of 5CB can be determined.

The setup for the measurement of the reflection spectrum is depicted in Fig. S5a. The microscope for the observation of Freedericksz transition was used. We quenched the magnetic field and removed the analyzer while the thickness measurement was conducted. To avoid to heat the Cu grid, the light from 575 nm to 750 nm in wavelength was irradiated by epi-illumination configuration. The interfered reflected light was collected into a optical fiber, which guided the light to the spectrophotometer, with the same objective and the tube lens. As the core of the fiber was 400 μ m in diameter and the magnification of the objective was 4×, the measurement area of the reflection spectrum was 100 μ m in diameter on the object plane as shown in Fig.S5b. Therefore, we were able to measure the thickness of the 5CB in each compartment separately. Figure S6a shows a typical reflection spectrum with an

interference pattern. Fourier transformation of the reflection spectrum yields the power spectrum. We estimated the thickness from the weighted average of the power spectrum density.



Figure S5 The illustration of the setup for the thickness measurement (a), the region of the measurement of the thickness (b) and a schematic diagram of the interference of the reflected lights at 5CB/OTS glass and water/5CB interface(c).



Figure S6 A typical reflection spectrum (a) and its power spectrum obtained by Fourier transformation of the reflection spectrum (b).

[S5] L. Jun, W. Chien-Hui, S. Gauza, R. Lu, W. Shin-Tson, J. Disp. Technol. 2005, 1, 51-61.

IV. Determination of the threshold magnetic field from the oscillation of the transmission intensity



Figure S7 Comparison of the $B_c \times d$ measured using the peaks and valleys method and the direct reading