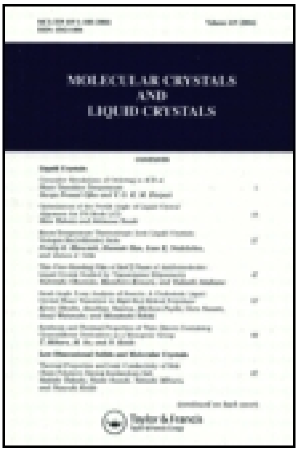

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Orientational Ordering in Langmuir Monolayer of Liquid Crystal on a Water Surface

Akihiko Sugimura [a] , Mitsumasa Iwamoto [b] & Ou-Yang Zhong-can [c]

[a] Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1, Nakagaito, Daito-shi, Osaka, 574, Japan

[b] Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152, Japan

[c] Institute of Theoretical Physics, Academia Sinica, P.O. Box 2735, Beijing, 100080, China

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ORIENTATIONAL ORDERING IN LANGMUIR MONOLAYER OF LIQUID CRYSTAL ON A WATER SURFACE

AKIHIKO SUGIMURA, †MITSUMASA IWAMOTO, AND
‡OU-YANG ZHONG-CAN

Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1, Nakagaito, Daito-shi, Osaka 574, Japan

†Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152, Japan

‡Institute of Theoretical Physics, Academia Sinica, P.O. Box 2735, Beijing 100080, China

Abstract The phase transition of an 8CB monolayer on a water surface was investigated experimentally and theoretically. A weak first-order phase transition of the nematic molecules from isotropic to polar orientation was clearly detected by compressing the film in the range of immeasurably low surface pressure by means of Maxwell-displacement-current-measuring techniques. On the basis of the interaction of dipolar molecules with a liquid surface, the thermodynamics of the molecular orientation and related mechanical and electric effects for Langmuir monolayers of molecules were also studied theoretically to elucidate the experimental results. It was shown that the compression of the molecular area should lead to a weak first-order phase transition of the orientation of molecules from the isotropic phase to the polar one. It was also predicted theoretically that a Maxwell displacement current with a sharp pulse shape is generated at the onset of the transition.

INTRODUCTION

Monolayers formed on a water surface exhibit very interesting physico-chemical properties as two-dimensional and interfacial systems. Recently, the phase behavior of liquid crystal systems on a water surface has received much attention from both a scientific and technological point of view. Most theoretical studies on the molecular orientation of monolayers have considered only the nematic ordering,[1] which is represented as the order parameter $< (3\cos^2\theta - 1)/2 >$; θ is the tilt angle of hydrocarbon chains away from the normal to the monolayer, $< >$ denotes a thermodynamics average. However these studies give no detailed information on the polar orientational order defined as $S =< \cos\theta >$. The polar ordering may be of major importance in Langmuir monolayers. Water-insoluble molecules are terminated by both the hydrophilic group and hydrophobic group (usually one or two long hydrocarbon chins). Due to the amphiphilic nature of the molecules, a polar alignment must be induced in the monolayer.[2]

In this paper the phase transition of the nematic phase of octyl cyanobiphenyl (8CB) film on a water surface was investigated experimentally by means of surface-balance and Maxwell-displacement-current-measuring techniques.[3] A weak first-order phase transition of the nematic molecules from isotropic to polar orientation was clearly detected by compressing the film in the range of immeasurably low surface pressure. On the basis of the interaction of dipolar molecules with a liquid surface, which is briefly introduced in the previous report[4] by the same authors, the thermodynamics of the molecular orientation and related mechanical and electric effects for Langmuir monolayers of molecules were also studied theoretically to elucidate the experimental results.

EXPERIMENTAL

Figure 1 shows the Langmuir-trough used in the present study. It was the same as that previously used.[5] Briefly, the trough has a rectangular shape and its area is 1,050 cm^2. Above the water surface at the center of the trough, electrode 1 is placed parallel to the surface. The working area of the electrode is 44.2 cm^2, and the distance between electrode 1 and the water surface is 1 ± 0.05 mm. The liquid crystal used here is 4'-n-octyl-4-cyanobiphenyl (8CB). An 8CB molecule, which could be considered a small rod like particle, is composed of a hydrophilic polar (cyano) head group and a hydrophobic alkyl tail group. Using a microsyringe the monolayer of

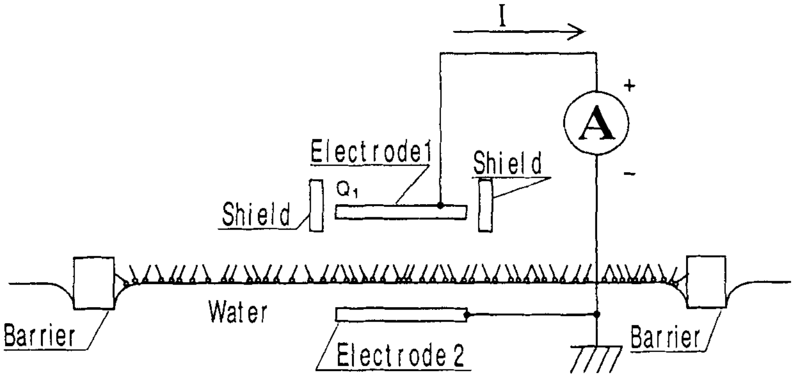

FIGURE 1 Schematic diagram of the experimental set up used for the present study.

of 8CB is formed spreading 8CB from a chlorohorm solution on the surface of water in the Langmuir-trough. The monolayer formed on a water is compressed from both sides of the trough with aid of two moving barriers at room temperature. The two barriers move simultaneously in opposite directions. The monolayer between the two barriers is compressed with constant velocity. As a result, a displacement current I is generated from the monolayer. During the compression of the monolayer a displacement-current-molecular-area ($I - A$) isotherm is monitored in conjunction with the surface pressure-molecular area ($\Pi - A$) isotherm. Figure 2 shows a typical example of the displacement current generated from 8CB molecules during the compression with a constant barrier velocity of 40.0 mm/min from $A = 230$ Å^2 to 50 Å^2, before the initial rise of the surface pressure. The surface-pressure-area isotherm is also shown in the figure. Although the surface pressure change is not detectable by means of the surface balance in this range, initial flow of the displacement current is, however, found to occur at $A = 100$ Å^2.

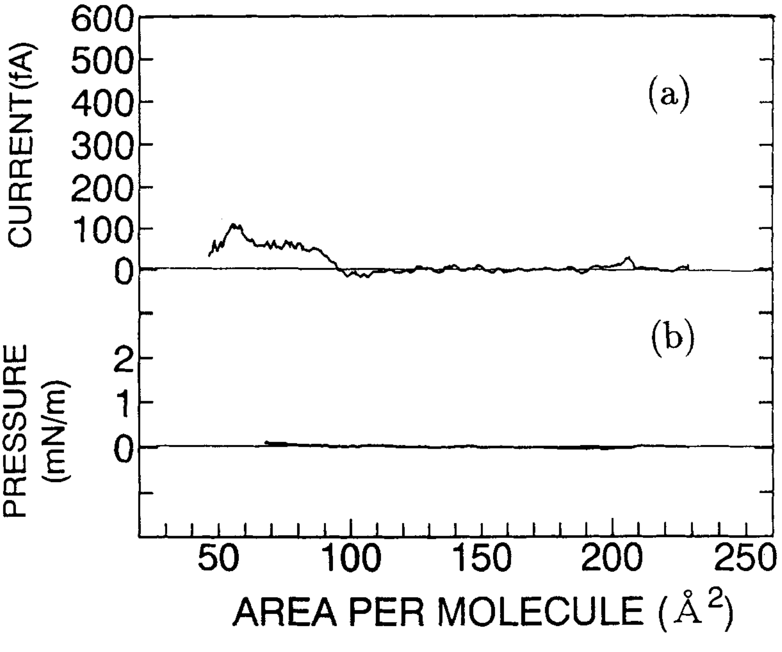

FIGURE 2 Experimental area dependencies of (a) the displacement current and (b) surface pressure.

THEORY

We discuss a monolayer on an air-water interface. The polar interaction for one molecule on the surface monolayer can be obtained by assuming the intuitive structure illustrated in Fig.3, where each molecule occupies a mean area A on the water surface. The critical area A_o is defined as $\pi\ell^2$, in which ℓ is the partial length of the molecules along their long axis above the liquid surface. A_o can be obtained from the $\Pi - A$ isotherms in a Langmuir-trough or from the experimental measurement of a Maxwell displacement current ($I - A$ isotherms). We assume that the dipoles have terminal charges $\pm q$ a distance ℓ apart, i.e., the dipole moment being $p = q\ell$ and that the orientational distribution of the molecules in the azimuthal plane is random (i.e., C_∞ symmetry). The effect of the interaction between the dipolar molecules is considered by introducing a dielectric constant ϵ_m for the monolayer. Now the contribution of the tilt angle to the interaction is only that of the terminal charge q at a distance $d = \ell\cos\theta$ from the interface. However, it is well known that such a charge experiences a force as if there were an image charge of strength $-q(\epsilon_w - \epsilon_m)/(\epsilon_w + \epsilon_m)$ at the same distance d on the other water side of the interface, where ϵ_w is the dielectric constant of the water. This force corresponds to an interaction energy $W(\theta)$ which is given by

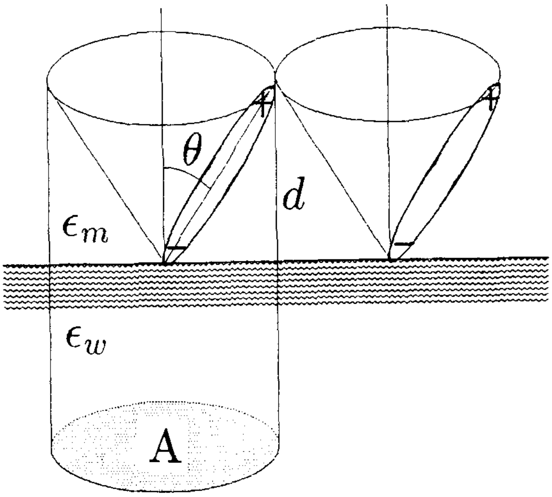

FIGURE 3 The geometry of the monolayer at the air-water interface.

$$W(\theta) = -\frac{q^2}{4(4\pi\epsilon_\circ\epsilon_m)d}\left(\frac{\epsilon_w - \epsilon_m}{\epsilon_w + \epsilon_m}\right) = -\frac{p^2}{16\pi\epsilon_\circ\epsilon_m\ell^3\cos\theta}\left(\frac{\epsilon_w - \epsilon_m}{\epsilon_w + \epsilon_m}\right) , \qquad (1)$$

where $\epsilon_\circ$ is the permittivity of free space. From Eq.(1) and $\epsilon_w > \epsilon_m$, it is clear that for the molecular area $A > A_\circ = \pi\ell^2$, the dipolar molecules should lie on the interface plane ($\theta = 90°$). On the other hand, when the area is compressed to $A < \pi\ell^2$, the molecule can align in the range of $0 \leq \theta \leq \theta(A)$, where $\theta(A) = \arcsin(\sqrt{A/A_\circ})$ with the orientational distribution function

$$f(\cos\theta) = \exp\left[-W(\theta)/kT\right]/Z , \qquad (2)$$

where Z is the single-particle partition written as

$$\begin{aligned} \mathrm{Z} &= \int_0^{\theta(A)} e^{-W(\theta)/kT}\sin\theta \mathrm{d}\theta = \int_0^{\theta(A)} e^{x/\cos\theta}\sin\theta \mathrm{d}\theta \\ &= e^x - \cos\theta(A)e^{x/\cos\theta(A)} + x\left[\mathrm{Ei}\left(\frac{x}{\cos\theta(A)}\right) - \mathrm{Ei}(x)\right] , \end{aligned} \qquad (3)$$

where $\mathrm{Ei}(x) \equiv \int (e^x/x)\,\mathrm{d}x$ and $\cos\theta(A) = \sqrt{1 - A/A_\circ}$. In Eq.(3) we introduced the parameter x defined by

$$x = \frac{p^2}{16\pi\epsilon_\circ\epsilon_m\ell^3}\left(\frac{\epsilon_w - \epsilon_m}{\epsilon_w + \epsilon_m}\right)/kT , \qquad (4)$$

Parameter x describes the relative strength of the polar interaction with respect to kT. Using the expressions of Eqs.(1)-(4), the character of the transformation from the isotropic phase to the polar one of the monolayer may be revealed. For a complete treatment the dielectric constant ϵ_m has to be a function of area A. However, as a first approximation, we shall assume it to be constant. The area dependence of the polar order parameter is given by

$$\begin{aligned} S &= \int_0^{\theta(A)} \cos\theta f(\cos\theta)\sin\theta \mathrm{d}\theta = \frac{1}{\mathrm{Z}}\int_0^{\theta(A)} e^{x/\cos\theta}\cos\theta\sin\theta \mathrm{d}\theta \\ &= \frac{1}{2}\left\{x + \frac{e^x - \cos^2\theta(A)e^{x/\cos\theta(A)}}{e^x - \cos\theta(A)e^{x/\cos\theta(A)} + x\left[\mathrm{Ei}(x/\cos\theta(A)) - \mathrm{Ei}(x)\right]}\right\} . \end{aligned} \qquad (5)$$

The value of S tends to unity at $A/A_\circ = 0$ and this represents the perfect polar phase, i.e., all molecules align with the direction normal to the monolayer surface. The order parameter in the case of weak or nonpolar molecules, i.e., $x = 0$ is derived from the limit of S for $x \to 0$, i.e.,

$$S_\circ = \frac{1}{2}\left[1 + \cos\theta(A)\right] . \qquad (6)$$

In order to compare with the usual isotropic-nematic phase transition, we also calculate the nematic order parameter. Using Eq.(2) $< \cos^2\theta(A) >$ can be calculated as

$$< \cos^2\theta(A) > = \frac{1}{3}\left\{Sx + \frac{(2S - x)\left[e^x - \cos^3\theta(A)e^{x/\cos\theta(A)}\right]}{e^x - \cos^2\theta(A)e^{x/\cos\theta(A)}}\right\} . \qquad (7)$$

Substituting Eq.(7) in the expression of

$$< \mathrm{P}_2 >= \frac{1}{2}\left[3 < \cos^2\theta(A) > -1\right] , \tag{8}$$

we obtain the nematic order parameter.

In the limit $x \to 0$, Eqs.(7)(8) lead to the following relation

$$< \mathrm{P}_2 >_\circ = \frac{1}{2}\left[\cos\theta(A) + \cos^2\theta(A)\right] . \tag{9}$$

The relative standard deviation of the polar order parameter, $\delta S/S = \sqrt{< \cos^2\theta > - S^2}/S$, can be estimated using Eqs.(5)(7). The relative standard deviation in the limit $x \to 0$ can be obtained using Eqs.(6)-(9) as

$$\left(\frac{\delta S}{S}\right)_\circ = \sqrt{\frac{1}{3}}\left[\frac{1-\cos\theta(A)}{1+\cos\theta(A)}\right] = \sqrt{\frac{1}{3}}\left[\frac{1-\sqrt{1-A/A_\circ}}{1+\sqrt{1-A/A_\circ}}\right] . \tag{10}$$

It is clear that $\delta S/S$ increases with the increase of x, and in the case of $x = 0$, $\delta S/S = 0$ in the limit $A/A_\circ \to 0$ and $\delta S/S = \sqrt{1/3}$ in the limit $A/A_\circ \to 1$.

To reveal the effects of the polar order phase transition in the $(\Pi - A)$ isotherm, we calculate the additional surface pressure from the thermodynamic relation

$$\delta\Pi = kT\frac{\partial}{\partial A}\ln \mathrm{Z} , \tag{11}$$

and Eqs.(1)-(3). This results in the following simple form

$$\begin{aligned} A\frac{\delta\Pi}{kT} &= \frac{A}{\mathrm{Z}}\frac{\partial}{\partial A}\int_0^{\theta(A)} e^{x/\cos\theta}\sin\theta d\theta \\ &= \frac{(S - x/2)\tan^2\theta(A)\cos\theta(A)}{e^{x[1-1/\cos\theta(A)]} - \cos^2\theta(A)} . \end{aligned} \tag{12}$$

In the case of weak or nonpolar molecules ($x = 0$) Eq.(11) leads to the value

$$A\frac{\delta\Pi}{kT} = \frac{1+\cos\theta(A)}{2\cos\theta(A)} . \tag{13}$$

This equation shows that $A\delta\Pi/kT$ has a peak at the transition in the case of $x = 0$.

DISCUSSION

Our most promising attempt is to answer the question of how one can probe the true property of the polar order S at the transition region in an experiment. The mechanical balance method used to measure $\Pi - A$ isotherms is not suitable. In order to detect the fast change of S at the critical area $A_\circ$, it is essential to use an electric measurement, in which the fast orientational change of polar molecules in monolayers on a water-air interface can be probed by measuring the Maxwell-displacement current generated from the change. The variation of the Maxwell-displacement current I with the compression of the monolayer is given by[5]

$$I = \frac{B\gamma_o}{d_1}\left(\frac{m}{A} - \frac{\mathrm{d}m}{\mathrm{d}A}\right) , \tag{14}$$

where B is the working area of the electrode, $\gamma_o = -(1/A)(\mathrm{d}A/\mathrm{d}t)$ is the constant compression ratio, m is the average vertical component of the dipole moment of one molecule, and d_1 is the distance between the above electrode and the water surface. With polar ordering $S =< \cos\theta(A) >$ and $m = Sp$, Eq.(14) may be written as

$$I = \frac{pB\gamma_o}{d_1 A}\left(S - A\frac{\mathrm{d}S}{\mathrm{d}A}\right) . \tag{15}$$

In Eq.(15) the term $-A\mathrm{d}S/\mathrm{d}A$ represents the fast varying component of the current. To consider the displacement current generated from a monolayer during the compression, we can derive theoretically the component $-A\mathrm{d}S/\mathrm{d}A$ using Eqs.(1)-(3) as

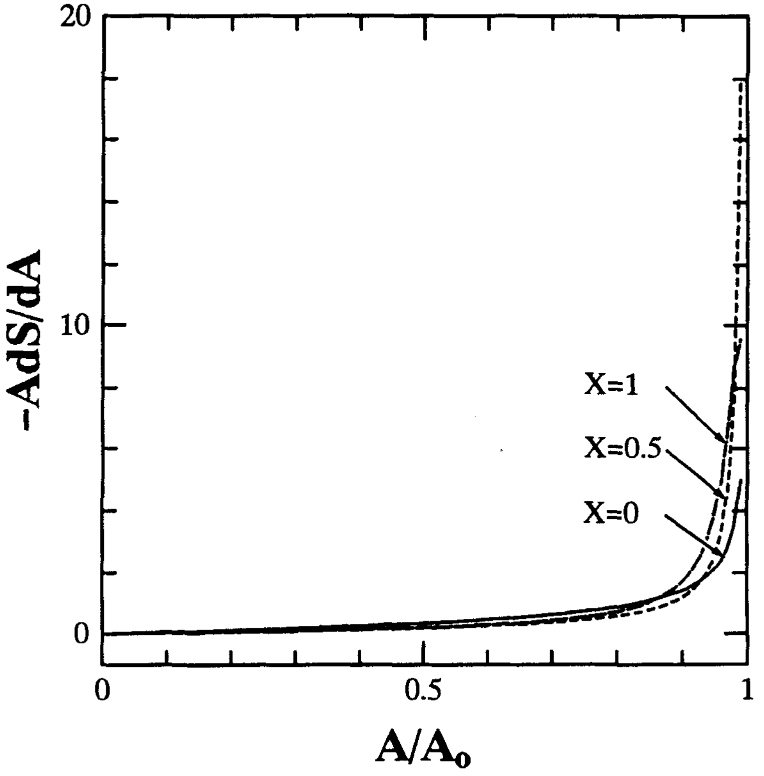

FIGURE 4 Theoretical area dependence of the relative compression ratio of the polar order, $-A\mathrm{d}S/\mathrm{d}A$.

$$\begin{aligned}-A\frac{\mathrm{d}S}{\mathrm{d}A} &= -A\frac{\mathrm{d}\theta}{\mathrm{d}A}\frac{\mathrm{d}S}{\mathrm{d}\theta} \\ &= \left[\frac{\tan\theta(A)}{2}\right]\left\{\frac{\sin\theta(A)\,[S-\cos\theta(A)]\,(2S-x)}{e^{x[1-1/\cos\theta(A)]}-\cos^2\theta(A)}\right\} \\ &= \frac{\sin\theta(A)\tan\theta(A)\,[S-\cos\theta(A)]\,(2S-x)}{2\left\{e^{x[1-1/\cos\theta(A)]}-\cos^2\theta(A)\right\}}\,. \end{aligned} \qquad (16)$$

Figure 4 shows the numerical result of Eq.(16), which displays a clear sharp peak at $A = A_o$. Evidently the experiment in 8CB monolayer measures such a current peak at A=100 Åas shown in Fig.2 (a). However the experimental data of $\Pi - A$ shown in Fig.2 (b) does not show a similar sharp change at this transition. It is possible that in the $\Pi - A$ curve, the sharpness of the peak pulse is reduced due to the viscosity of the monolayer and the inertia of the mechanical measurement system. The theoretical results show good agreement with the experimental results for 8CB in the Maxwell-displacement current measurement. Similar good agreement was also found in the recent experiment on a monolayer of 5CB (4-pentyl- 4'-cyano-bipheneyl) on an air-water interface.

CONCLUSION

The present theory predicts that a sharply increasing peak pulse of pressure Π or current I should occur at $A = A_o$ with the area compression. For the $I - A$ isotherms, such a peak-pulse can be found in its transition. In the $\Pi - A$ curve, however, no such peak pulse is observed due possibly to the viscosity of the monolayer and the inertia of the mechanical measurement system. These predictions offer a better understanding of the process of the monolayer compression or expansion and the associated effects. The good agreement with previous and recent experiments confirms our theoretical proposal. It is clear that, although the main source of the phase transition may not be the polar interactions, the polar nature of the molecules offers a good way of monitoring the phase transition. Of course, this model is in its early stages and a more exact and complete development of the model is still needed for future study.

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