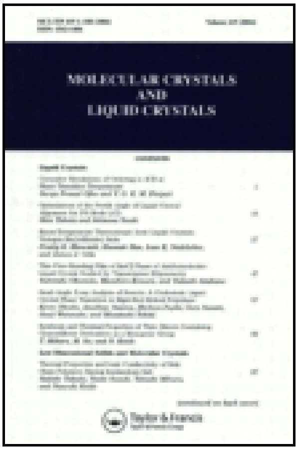

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Discrimination of Chiral and Racemic Phospholipid Monolayers by Maxwell-Displacement-Current Measurement Technique

Mitsumasa Iwamoto [a] & Chen-Xu Wu [a]

[a] Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguroku, Tokyo, 152-8552, Japan

Version of record first published: 24 Sep 2006

To cite this article: Mitsumasa Iwamoto & Chen-Xu Wu (2000): Discrimination of Chiral and Racemic Phospholipid Monolayers by Maxwell-Displacement-Current Measurement Technique, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 141-146

To link to this article: http://dx.doi.org/10.1080/10587250008024885

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 141-146
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Discrimination of Chiral and Racemic Phospholipid Monolayers by Maxwell-Displacement-Current Measurement Technique

MITSUMASA IWAMOTO and CHEN-XU WU

Department of Physical Electronics, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguroku, Tokyo 152-8552, Japan

The Maxwell-displacement-current measurement (MDC) and surface pressure of chiral and racemic phospholipid [α-phosphatidylcholine dipalmitoyl (DPPC)] monolayers at the air-water interface by monolayer compression were performed. It was found that some critical MDC peaks were generated with different amplitude and sign depending on the chirality of the phospholipids in the plateau region. This anomalous MDC generation is theoretically interpreted as the molecular twist-conformation transition induced by monolayer compression.

INTRODUCTION

Usually phospholipid [α-phosphatidylcholine dipalmitoyl (DPPC)] molecules are referred to as chiral due to the lack of the mirror plane symmetry. They can show a variety of structures in the bulk of aqueous solutions, and their thermodynamics and intra-aggregate forces in bulk of solutions have been extensively investigated. Lunquist[1] found that for monolayers of 2-alkanos and certain derivative racemates, pure enantiomers form different crystal-like phases. However, the role of the chirality of the amphiphiles in the structure multilicity has not been studied clearly. Since monolayers at the air-water interface show some different phases during monolayer compression and can reveal more information on the molecular conformation than in bulk, it is possible to examine the physico-chemical properties and the molecular conformation of chiral and racemic compounds in the monolayer state by monolayer compression using Maxwell-displacement-current measurement technique.[2]

EXPERIMENT

Figure 1 shows the schematic of our experimental setup, which is similar to that used

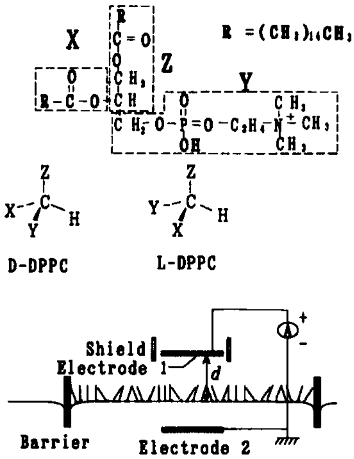

FIGURE 1 Schematic diagram for molecule DPPC (above) and experimental setup (below).

in our previous study.[2] The monolayers of DPPC formed on the water surface were compressed with two floating barriers at a constant barrier velocity of 40 mm/min. Figure 2 shows the typical experimental results of the measurement for four samples. As shown in Fig. 2, the $\pi - A$ isotherms of these four samples are almost the same function of molecular area A containing nearly the same pressure plateau in the range of 65 to 85 Å^2 of molecular area at a temperature of 20°C. The latter was usually referred to two-dimensional (2D) phase transition region from the expanded monolayer to condensed one. From the present $\pi - A$ measurement it seems that the mentioned phase transitions are obviously independent of the chirality of the molecules composed in the monolayers. However, the result of measurement in MDC shown in Fig. 2 above reveals that although the main shapes of the MDC viewed as a function

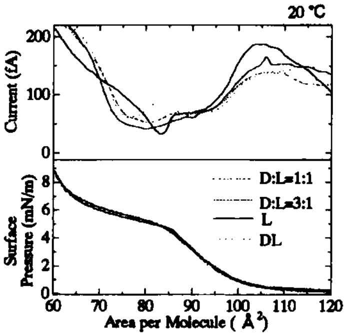

FIGURE 2 $\pi - A$ isotherms (below) and corresponding Maxwell displacement currents (above) measured in four DPPC monolayers composed of pure L-DPPC, PL-DPPC, and mixtures with molar ratios of D-:L-DPPC=1:1, 3:1, respectively.

of the molecular area A are roughly similar for the four samples of DPPC, there exist some essential differences between them: The most striking characteristic is the generation of MDC peak which appears in the beginning of the pressure-plateau, A = 85 Å^2, with different amplitude and sign for the four examples. From the view point of molecular level, the four examples of the DPPC monolayers differ only from their chirality: DL-DPPC is racemic, L-DPPC and D-DPPC both are chiral with different optical activity. Therefore, the mentioned MDC peak should reveal some molecular conformation change relating to the molecular chirality.This anomalous MDC generation may be of significant help to understand the chiral discrimination from molecular conformation level.

CALCULATION AND DISCUSSION

As chiral PCL molecules must be lack of the mirror plane symmetry, the dipole $\vec{P}$ is not located in the molecular long axis but it is in a cylindrical surface (Fig. 3), i.e., describing in the molecular frame as

$$\vec{r_0} = (x_\mu, y_\mu, z_\mu) = (a, 0, h), \tag{1}$$

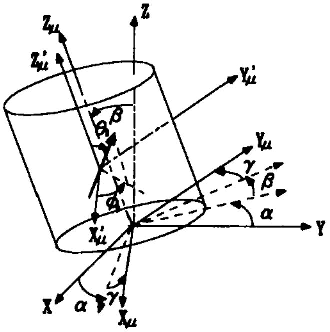

FIGURE 3 Sketch of rodlike molecular model for PCL monolayers at the air-water surface. The cylinder represents the molecular long-axis and the side dipole flanking the cylinder with polar angle θ_D and twist angle ϕ_D. The latter serves to describe the chirality of the molecules: $\phi_D = 0$ and π for racemic, otherwise for chiral.

where z_μ is along the molecular long axis. Besides an angle θ_D $(0 \leq \theta_D \leq \pi)$ away from $\vec{z_\mu}$, it is assumed that the dipole is not in the plane of $y_\mu = 0$, but with a tilted angle ϕ_D to it $(0 \leq \phi \leq 2\pi)$, i.e., in the molecular frame

$$\vec{P}/P = (\sin\theta_D \cos\phi_D, \sin\theta_D \sin\phi_D, \cos\theta_D) \tag{2}$$

It is easy to check that $\phi_D \neq 0$ represents the chirality and $\phi_D = 0$ and π mean racemic states with biaxiality ordering.[3] In the case of $\theta_D = 0$ and $\theta_D = \pi$, Eq. (2) reduces to the simplest uniaxial symmetry.[3] Other geometry of the monolayer composed of the dipolar molecules is the same as that in Ref. 3, as illustrated in Fig. 3: The average orientation direction of the molecular long axis is upright to the water surface and referred to z-direction of the laboratory frame. It is then obvious that the molecular orientation is confined in the range of $0 \leq \beta \leq \theta(A) = \arcsin\sqrt{A/A_0}$ (see Fig. 3) due to the effect of hard-core intermolecular repulsive force working among molecules, where β is the angle between $\vec{z}$ and the molecular long axis, $A_0 = \pi l^2$, l is the partial length of the molecules along their long axis above the water surface, and A is the mean molecular area. Besides the repulsive force, the distribution of

β is also affected by the attractive Coulomb force working from the image of the molecular dipole in the bulk water, i.e., the interaction energy is[4]

$$W(\beta) = -P^2 \left(\frac{\epsilon_w - \epsilon_m}{\epsilon_w + \epsilon_m}\right) \frac{1 + \cos^2 \theta_L}{32\pi\epsilon_0 (r_0 \cos\theta')^3}, \tag{3}$$

where ϵ_m and ϵ_w are the dielectric constants of monolayer and the water, respectively, ϵ_0 is the permittivity of free space, θ_L is the angle of the dipole direction from $\vec{z}$, and $d = r_0 \cos\theta'$ is the distance of the dipole above the water surface, hence, $r_0 = |\vec{r_0}| = \sqrt{a^2 + h^2}$ and θ' is the angle between $\vec{z}$ and the direction of the position vector of the dipole $\vec{r_0}$.

To describe the apparent relations of both θ_L and θ' with the geometry given in Fig. 3, we introduce the relationship between the molecular frame $\vec{r_\mu} = (x_\mu, y_\mu, z_\mu)$ and the laboratory one $\vec{r} = (x, y, z)$ with Euler angles (α, β, γ) defined as the convention in[4]

$$\vec{r} = R(\alpha, \beta, \gamma) \cdot \vec{r_\mu} \tag{4}$$

where 3×3 matrix $R(\alpha, \beta, \gamma)$ is the usual Euler rotation matrix (see Eq. (3) in Ref. [10b]). From Eq. (4) we have in the molecular frame

$$\vec{z}/z = (-\sin\beta\sin\gamma, -\sin\beta\cos\gamma, \cos\beta) \tag{5}$$

and obtain from Eqs. (1), (2), and (5)

$$\begin{aligned} \cos\theta_L &= (\vec{z}/z)\cdot(\vec{P}/P) = -\sin\theta_D \sin\beta \sin(\gamma + \phi_D) + \cos\theta_D \cos\beta && (6) \\ r_0 \cos\theta' &= \vec{r_0} \cdot (\vec{z}/z) = -a \sin\beta \sin\gamma + h \cos\beta. && (7) \end{aligned}$$

Substituting Eqs. (6) and (7) into Eq. (3) yields the apparent expression for interaction energy, and using the Onsager approximation[5]

$$e^{-W(\beta,\gamma)/kT} = 1 - W(\beta, \gamma)/kT, \tag{8}$$

we can calculate the average molecular dipolar moment in $\vec{z}$ direction

$$\begin{aligned} \langle P_z \rangle &= \frac{P}{Z} \int_0^{2\pi} d\gamma \int_0^{\theta(A)} \cos\theta_L \left(1 - \frac{W}{kT}\right) \sin\beta d\beta, \\ &= \frac{\pi P}{Z} \cos\theta_D \sin^2\theta(A) + \frac{\pi P \eta}{Z r_0^3} \{\cos\theta_D [(2 - 3\cos^2\psi)(\cos^{-1}\theta_A \sin^{-1}\alpha - \sin^{-1}\psi) \\ &\quad - \sin^2\psi \cos^2\psi (\sin^{-3}\psi - \cos^{-3}\theta_A \sin^{-3}\alpha)] \\ &\quad + \tan\psi \cos^2\psi \sin\theta_D \cos\phi_D (3\cos^{-1}\theta_A \sin^{-1}\alpha - 2\sin^{-1}\psi \\ &\quad - \sin^2\psi \cos^{-3}\theta_A \sin^{-3}\alpha)\}, && (9) \end{aligned}$$

where k is the Boltzmann constant, T is the temperature, $\eta = P^2[(\epsilon_w - \epsilon_m)/(\epsilon_w + \epsilon_m)]/32\pi\epsilon_0 r_0^3 kT$, $\tan\psi = h/a$, and $\cos\alpha = \cos\psi/\cos\theta(A)$. It is now clear that the molecular twist-conformation transitions of ϕ_D $(0 < \phi_D \leq \pi/2)$ to $\pi - \phi_D$ or ϕ_D $(3\pi/2 \leq \phi_D < 2\pi)$ to $\phi_D - \pi$ have to induce the great change of $\langle P_z \rangle$, hence the MDC peak occurs at the critical area independent of the racemic or chiral examples. This is in good agreement with experiment as shown in Fig. 2 above.

On the other hand, for certain examples the values of both ϕ_D have to be determined by their chirality, so the anomalous MDC peaks have different amplitude and sign. Roughly speaking, the amplitude of the MDC peak for the transition between both racemic states of $\phi_D = 0,\ \pi$ should be the largest due to $\mid \delta \cos\phi_D \mid = 2$ being maximal for the change of $\mid \delta \cos\phi_D \mid$. This is also confirmed by the MDC peak of the DL-DPPC monolayer given in experiment (Fig. 2 above). Briefly, we can estimate that the MDC change flowing through the circuit due to the molecular twist-conformation transition is approximately related to $\eta \sin\theta_D$, from the chiral effect on $\langle P_z \rangle$ explicitly expressed in factor $\cos\phi_D$ [the last term in Eq. (9)]. This reveals that the larger the interaction (which is proportional to η) is, the more striking the molecular twist-conformation transition will be.

CONCLUSION

From the above discussion, we show that the generation of the MDC from racemic and chiral monolayers can reveal the molecular twist-conformation transition. The transition-induced MDC peak can serve to estimation of the molecular structures. This may have significance in biology, chemistry, and physics.

References

[1] M. Lundquist, *Arkiv. Kem. 17,* 183 (1960).

[2] X. Xu and M. Iwamoto, *Jpn. J. Appl. Phys. 36,* 237 (1997).

[3] A. Sugimura, M. Iwamoto, and Z. C. Ou-Yang, *Phys. Rev. E 50,* 614 (1994) ; ibid. *54,* 6537 (1996).

[4] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 1985).

[5] L. Onsager, *Ann. N. Y. Acad. Sci. 51,* 627 (1949).