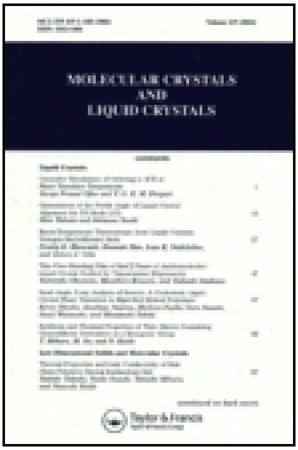

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

A Study on the Dielectric Relaxation Time of Arachidic Acid Monolayers by MDC Measurement

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Version of record first published: 24 Sep 2006

To cite this article: Su-Young Cho, Kyung-Sup Lee, Jin-Won Song, Young-Keun Kim, Young-Il Choi, Yichun Liu & Mitsumasa Iwamoto (2000): A Study on the Dielectric Relaxation Time of Arachidic Acid Monolayers by MDC Measurement, Molecular

Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 191-194

To link to this article: http://dx.doi.org/10.1080/10587250008024897

Mol. Cryst. Liq. Cryst., 2000, Vol. 349, pp. 191-194
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A Study on the Dielectric Relaxation Time of Arachidic Acid Monolayers by MDC Measurement

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Maxwell displacement current (MDC) measurement has been employed to study the dielectric property of Langmuir-films, A method for determining the dielectric relaxation time of floating monolayers on the water surface is presented. MDC flowing across the monolayers is analyzed using a rod-like molecular model. It is revealed that the dielectric relaxation time of monolayer in the isotropic polar orientational phase is determined using a linear relationship between the monolayer compression speed and the molecular area A_m. Compression speed α was about 30, 40, 50mm/min.

Keywords: dielectric relaxation; arachidic acid; organic

INTRODUCTION

MDC measurement has been employed to study the dielectric property of Langmuir-films. Using this technique, we have studied the piezoelectric property of Langmuir-films, the phase transition of monolayers and so on. We experimentally investigated the dielectric relaxation phenomenon of a liquid crystal monolayer by the MDC measurement. It is essential to develop a method for determining the dielectric relaxation time $\tau$of monolayer, because the relaxation time carries one of the basic physicochemical properties. In this paper, we examine the dielectric relaxation time of organic monolayers by MDC measurement.[1-4]

ANALYSIS

Figure 1 shows a model of floating monolayer on a water surface. For simplicity, we confine our discussion to monolayers in the isotropic polar orientational phase. Briefly, the monolayer consists of rodlike polar molecules with a length l. Each molecule has a permanent electric dipole moment μ in the direction along the molecular long axis, and it stands at a tilt angle θ away from the normal direction to the water surface. The motion of rodlike polar molecules is restricted within $0<\theta<\theta_A$, where $\theta_A = \sin^{-1}\sqrt{A/A_0}$ $(A_0 = \pi l^2)$. Here A is the molecular area and A_0 is the critical molecular area. The monolayer film is sandwiched between Electrodes 1 and 2.

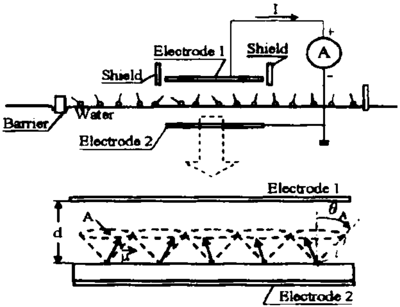

FIGURE 1. Molecular model on the water surface.

Electrode 1 is suspended in the air parallel to and at a distance *d* from the water surface. The orientational order parameter *S (t)* of the organic monolayers on Electrode 2 is given by

$$S(t) = \int_0^{\theta_A} \cos\theta f(\cos\theta, t)\sin\theta d\theta . \qquad (1)$$

Here $f(\cos\theta, t)$ denotes the orientational distribution function at t=t. Assuming that the orientational motion of molecules satisfies the Debye-Brownian motion equation, we obtain the following rate equation.

$$\frac{d}{dt}(S(t)-S_{eq}) = -\frac{S(t)-S_{eq}}{\tau} + \frac{1-<\cos^2\theta>}{\xi}RU(t) \qquad (2)$$

Here τ is the dielectric relaxation time of monolayer films, and given by

$$\tau = \frac{\xi}{kT}\frac{<(\cos\theta - <\cos\theta>)^2>}{1-<\cos^2\theta>} \qquad (3)$$

Where < > represents the thermal average, k is the Boltzmann constant, ξ is the frictional constant of monolayer, R is the external stimulation, and *U(t)* is a step function.

In the MDC measurement, monolayers are compressed at a monolayer compression speed of α from the molecular area $A = A_i$. Electronic charges are induced on Electrode 1 due to the presence of polar molecules on the water surface, and the magnitude of these electronic charges by monolayer compression. As a result, MDC flows through an ammeter. MDC is expressed as

$$MDC = I = -K\frac{d}{dA}\left(\frac{S}{A} - \frac{S_{eq}}{A_i}\right) \tag{4}$$

with $K = \frac{\alpha\mu}{d}B$. Here B is the working area of electrode 1.

Therefore the following relation is easily obtained by integrating the MDC with respect to the molecular area

$$\frac{S}{A} - \frac{S_{eq}}{A_i} = -\frac{1}{K}\int_{A_i}^{A} IdA \tag{5}$$

Substituting Eq. (5) into Eq. (4), the following equation is obtained

$$I = \frac{1}{\tau\alpha}\int_{A_i}^{A} IdA + K\frac{S_f}{\tau\alpha} - \frac{1}{A}\int_{A_i}^{A} IdA \tag{6}$$

assuming $S_{eq}(A_i) = 0$. It should be noted here that rod-like polar molecules lie on water surface at the molecular area $A > A_0$, due to the Coulomb attractive force working between polar molecules and the water surface. That is $S_{eq}(A_i) = 0$ for $A > A_0$. Usually in the MDC measurement, the monolayer compression starts at $A = A_i > A_0$.

At the molecular area $A = A_m$ MDC reaches maximum, therefore $dI/dA = 0$ at $A = A_m$. The dielectric relaxation time τ (A) of monolayers can be determined as a function of the molecular area.[3]

EXPERIMENT

Monolayers of arachidic acid were spread from dilute chloroform solutions (0.5 *mmol*) onto the surface of pure water.

The working area of Electrode 1 was 45.6 cm^2. The distance *d* between Electrode 1 and the water surface was 1 mm. The displacement current *I* was measured by an electrometer (Keithley 6517).

Arachidic acid was spread on pure water(pH 6.0, 18.2 MΩ cm) and maintained at 20 ℃. After a monolayer was rested for 5 minutes, the monolayer was compressed at a compression speed of 30, 40, 50 mm/min. MDCs were measured during monolayer compression.

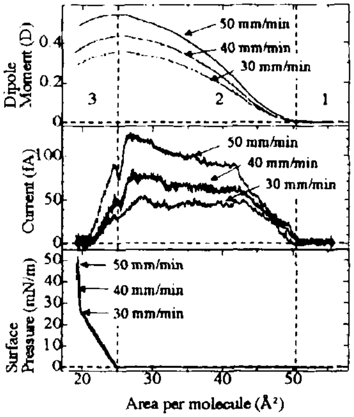

FIGURE 2. π -A, I-A, D-A of barrier compress

RESULTS AND DISCUSSION

Figure 2 shows a typical example of MDCs, where MDCs were initiated to flow at the molecular area $A=A_0$, due to the phase transition from the isotropic planar alignment phase on water surface (Range 1) to the polar orientational isotropic phase (Range 2). MDC peaks appear in the range of molecular area A between 51 Å^2 and 25 Å^2 (Range 2) by monolayer compression. We plotted the vertical component $m_z(=\mu S)$ of the dipole moment of monolayers determined by Eq. (5), assuming $S_{eq}(A_i)=0$. Figure shows the relationship between a and A_m. A linear relationship between α and A_m is obtained.(Figure 3)

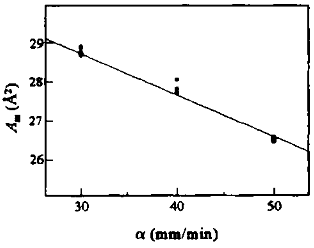

FIGURE 3. Relationship between a and A_m

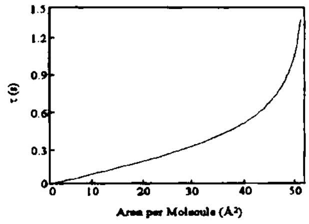

FIGURE 4. Dielectric relaxation time

From this liner relationship between α and A_m in Figure 3, the frictional constant ξ is calculated as 0.68×10^{-19} Js. After that, we calculated the dielectric relaxation time of monolayers from Eq. (3). The results were plotted in Figure 4. It is found that the dielectric relaxation times are a few seconds, depending on the molecular area A.

CONCLUSION

We presented a method for determining the dielectric relaxation time τ of floating monolayers on the water surface using MDC across monolayers. It is revealed that the dielectric relaxation time τ of monolayers in the isotropic polar orientational phase gives a liner relationship between the monolayer compression speed a and the molecular area A_m.

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