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THE CALCULATION OF BIAXIAL MOLECULES AT THE AIR-LIQUID INTERFACE

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Abstract The molecular orientational order and the Maxwell displacement current (MDC) of biaxial molecules are calculated with a thermostatistical approach in the range of molecular area of immeasurably low surface pressure.

INTRODUCTION

In the year of 1994, Sugimura *et al.* considered the monolayer of amphiphile as half of a membrane and studied the orientational order of monopolar molecule monolayers at the air-liquid interface,[1] using the order parameter represented as an average of first order Legendre polynomial $S = \langle P_1(\cos\theta)\rangle = \langle\cos\theta\rangle$,[1,2] where $\langle\ \rangle$ denotes a thermodynamic average, and θ is the tilt angle of the molecule long-axis away from the normal direction of the monolayer surface.[2] For biaxial molecules like cyclohexanecarboxylate-type molecule (DON), we take the following definition:

$$S = (P_{\parallel}\langle\cos\theta_{\parallel}\rangle + P_{\perp}\langle\cos\theta_{\perp}\rangle)/\sqrt{P_{\parallel}^2 + P_{\perp}^2}, \tag{1}$$

where $P_{\parallel}$ and $P_{\perp}$ are the permanent dipoles in the direction parallel and perpendicular to the molecule long-axis respectively, $\theta_{\parallel}$ and $\theta_{\perp}$ are their corresponding tilt angles (see Figure 1).

CALCULATION

As a model, we consider a biaxial monolayer film with a permanent dipole not parallel to the molecule-axis (e.g. DON) on an air-water surface as shown in Figure 1. The biaxial molecule is simplified as a rod-like axis with a length l. The rotation

angular displacement φ round the molecular axis and tilt angle $\theta_{\parallel}$, $\theta_{\perp}$ at an arbitrary position as shown in Figure 1(b), satisfy $\cos\theta_{\perp} = \cos\varphi\sin\theta$ and $\theta_{\parallel} = \theta$. The critical molecular area A_0 is again estimated to be πl^2. By introducing an image dipole at

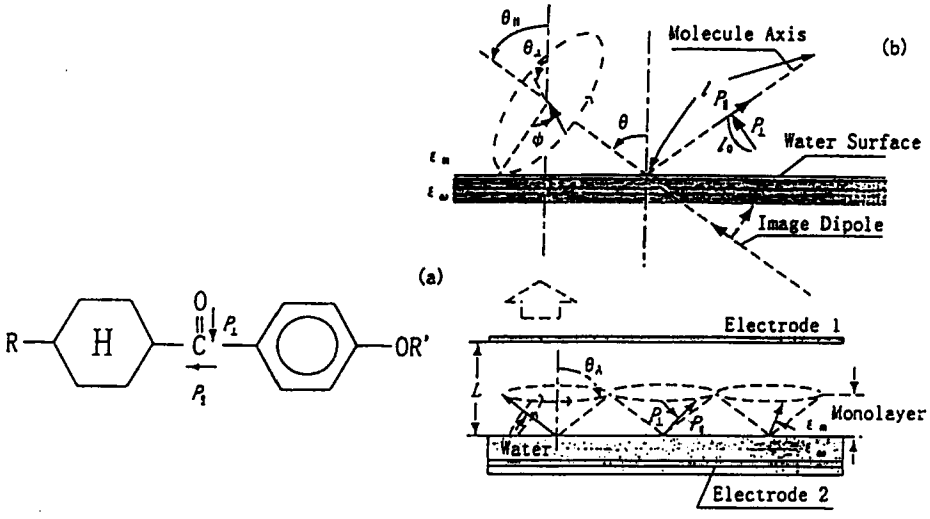

FIGURE 1 (a) Molecular structure of DON and (b) sketch of the model for the biaxial molecule monolayer at an air-liquid interface.

a mirror position with respect to the water surface (see Figure 1), the interface interactions working between $P_{\perp}$ and $P_{\parallel}$ and water surface are given by[3,4]

$$W_{\perp}(\theta) = -\frac{P_{\perp}(\cos^2\theta_{\perp}+1)}{64\pi\epsilon_0 d^3}\frac{\epsilon_w - 1}{\epsilon_w + 1}$$
$$\approx -\chi_{\perp}kT\frac{\sin^2\theta\cos^2\varphi + 1}{\cos^3\theta}(1 + 3\frac{l_0}{l}\tan\theta\cos\varphi) \quad (2)$$
$$W_{\parallel}(\theta) = -\chi_{\parallel}kT\frac{\cos^2\theta + 1}{\cos^3\theta}, \quad (3)$$

where $d(= l\cos\theta/2 - l_0\cos\varphi\sin\theta/2)$ is the distance of $P_{\perp}$ from the water surface, $\chi_{\perp} = \frac{{P_{\perp}}^2}{8\pi\epsilon_0 l^3 kT}\frac{\epsilon_w - 1}{\epsilon_w + 1}$ and $\chi_{\parallel} = \frac{P_{\parallel}^2}{8\pi\epsilon_0 l^3 kT}\frac{\epsilon_w - 1}{\epsilon_w + 1}$. We selected $P_{\perp} = 2.5$ D, $P_{\parallel} = 0.8$ D, $l = 2.0$ nm,[5], $l_0 = P_{\perp}/e$ =0.05 nm, $\chi_{\perp} = 9.2\times10^{-3}$ and $\chi_{\parallel} = 1.0\times10^{-3}$ for DON. The calculation based on Equation (2) is believable within the region $[0°, 76°]$ with a deviation under 10%. The orientational order parameter S is defined as

$$S = \int_0^{2\pi} d\varphi \int_0^{\theta_A} \cos\theta\frac{e^{-W/kT}}{Z}\sin\theta d\theta, \quad (4)$$

where $W = W_\perp + W_\parallel$ and Z is the single-particle partition function given by

$$Z = 2\pi[(1-\cos\theta_A)+(\frac{\ln\cos\theta_A}{2}-\frac{3\cos^2\theta_A-1}{4\cos^2\theta_A})\chi_\perp+(-\ln\cos(\theta_A)+\frac{1-\cos^2\theta_A}{2\cos^2\theta_A})\chi_\parallel], \quad (5)$$

as $W_\perp/kT << 1$ and $W_\parallel/kT << 1$ in the region $[0°, 76°]$. With Boltzmann distribution Equation (4), the orientational order of $P_\perp$ and $P_\parallel$ are given by

$$\begin{aligned} S_\perp &= \frac{1}{Z}\frac{3\pi\chi_\perp l_0}{4l}(\frac{32}{3}+\frac{7}{3\cos^3\theta_A}-\frac{10}{\cos\theta_A}-3\cos\theta_A) \\ S_\parallel &= \frac{\pi[(1-\cos^2\theta_A)+(\cos\theta_A-\frac{1}{\cos\theta_A})(2\chi_\parallel+\chi_\perp)]}{Z}. \end{aligned} \quad (6)$$

The total MDC I (Figure 2) generated by monolayer compression with constant

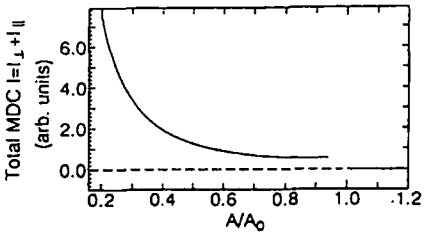

FIGURE 2 The theoretical total MDC I

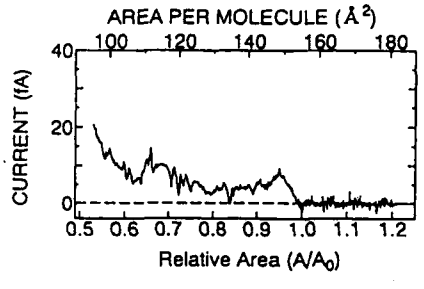

FIGURE 3 Displacement current of DON103 monolayer with a constant compression speed γ of 40mm/min.

speed $\gamma = -dA/dt$ is given by

$$I = I_\perp + I_\parallel = \frac{B\gamma}{L}(\frac{P_\perp S_\perp + P_\parallel S_\parallel}{A^2} - \frac{d(P_\perp S_\perp + P_\parallel S_\parallel)}{AdA}). \quad (7)$$

Here B is the working area of the electrode, and L is the distance between water surface and the upper electrode. Figure 2 shows the experimental result in Figure 3.

DISCUSSION AND CONCLUSION

For better comparison between $P_\perp$ and $P_\parallel$ in the contribution of MDC, we designate a ratio $\alpha_I = I_\perp/I_\parallel$, which are shown in Figure 4. Figure 4 demonstrates that the total MDC of biaxial molecules are mainly created due to the dipole moment $P_\parallel$ parallel to the molecule long-axis despite of its much smaller dipole moment in

comparison with the dipole moment $P_\perp$ perpendicular to the molecule long-axis, as

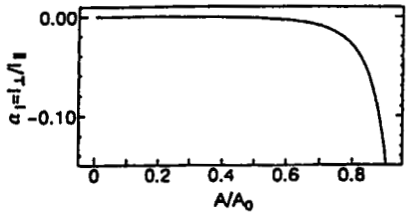

FIGURE 4 Ratio α_I shows the opposite MDC direction and the great contribution discrepancy between $P_\perp$ and $P_\parallel$.

the monolayer is compressed. Figure 4 also reveals that the direction of MDC created by $P_\perp$ and $P_\parallel$ is different. It should be noted here that the present model is useful only in the range of low surface pressure, just after the phase transition at the molecular area A_0 from the planar alignment phase to the polar one, because the intermolecular interaction becomes important as the monolayer is further compressed.

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