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Hydrogen-bond control of structure and conductivity of Langmuir films

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Lateral conductivity and a high proton mobility at the water-Langmuir film interface appears when the monolayer is compressed below a critical area. For a fatty acid monolayer, this critical area lies between 35 and 40 Å^2, and it was thought to correspond to the formation of a H-bonded network between the monolayer headgroups and the water molecules. In this work, the mobility and lateral conductivity are successfully explained using a simple geometric model, hydrogen bond data, and a unidimensional model for proton transfer (PT) in hydrogen bonds. According to the model, hydrogen bonds and PT effectively occur when the distance between oxygens is $R<2.8$ Å. It is shown that the critical value for a fatty acid monolayer corresponds to a distance of 7 Å between polar heads, which leads to $R=2.8$ Å. This represents a theoretical justification for the hypothesis of proton conduction via a hop and turn mechanism. Furthermore, the strong hydrogen bonds below the critical area are responsible for the monolayer structuring, which causes the surface potential to increase sharply at this area. [S1063-651X(98)01806-6]

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I. INTRODUCTION

Recent developments in the characterization of Langmuir monolayers have shown that an important critical packing density exists below which a number of monolayer properties are changed. For instance, upon compressing Langmuir monolayers, the surface potential ΔV rises sharply when a critical area is reached [1–9]. This has been observed for various compounds, including simple aliphatic materials, such as phospholipids [2], fatty acids, and fatty alcohols [7], as well as materials made from macromolecules such as conducting polymers [8] and lignins [9]. For some of these materials, the presence of a critical area has also been observed in data from *in situ* ellipsometry [10,11], UV reflection [12], Maxwell displacement current [13,14], and lateral conductance measurements [15,16]. Of particular relevance is the lateral conductance, which is attributed to an enhanced protonic conductance along the monolayer [15]. This conduction has been postulated [16] as arising from proton transfer via a hop and turn mechanism in a H-bonded network involving water molecules from the subphase and the headgroups of the monolayer-forming material. Electronic as well as ionic conduction processes have been discarded, since the materials employed in some experiments are neutral and do not possess either free or delocalized electrons. Furthermore, the protonic conductance would be very similar to that already reported in phospholipid bulk samples.

In spite of the plausibility of the proton conductance hypothesis, no explanation has been offered for the existence of a critical area, let alone the conductance value observed experimentally. Albeit in a different context, Iwamoto and Mizutani [17] also addressed the problem of a critical packing density by proposing a theoretical model in which the critical area denotes a phase transition associated with the chain orientation. However, their model cannot be applied to long chain aliphatic compounds, as the critical area predicted would be far larger than the area actually measured. Here we show that the value for the critical area can be explained within the hypothesis of a H-bonded network, and therefore this area is dependent on the monolayer headgroup rather than on chain orientation. It is shown that, in a stearic acid, monolayer proton transfer can only take place when the distance between oxygen atoms from two neighboring carboxylic groups (proton donor and acceptor) is below a typical value for the hydrogen bonds length. This leads to a predicted value for the critical area below which an enhanced conductance due to the monolayer should be observed, which agrees with the measured critical area. Furthermore, the theoretical model predicts that for the donor-acceptor distances prevailing in condensed Langmuir monolayers, one goes from a two-state system to a non-two-state system, which facilitates proton transfer with a resulting proton mobility that is likely to be considerably higher than that in bulk water or even in ice. This refutes a statement by Shapovalov and Il'ichev [18], in that Langmuir monolayers are too thin to allow an enhanced proton conductance to be measured, as will be commented upon below.

II. EXPERIMENTAL RESULTS

Figure 1 shows lateral conductance, surface potential, and surface pressure curves for stearic acid. While the surface pressure has no special feature, simply being indicative of the formation of a condensed monolayer of a typical one-chain aliphatic compound, the other curves display a critical area—the same within experimental dispersion—at which both signals start to rise. Stearic acid was chosen because its monolayer characteristics, including packing, are well known. Subsidiary experiments were carried out with stearoyl alcohol and several phospholipids [19], all of them displaying a lateral conductance of the order of 10^{-8} S and critical areas which depended upon the compound. In all cases the critical area for conductance coincided within experimental error with the onset of the surface potential, similarly to the curves shown in Fig. 1 for stearic acid. The shape of the surface potential curve was explained [1] using the Demchak-Fort model [20], in which a monolayer is consid-

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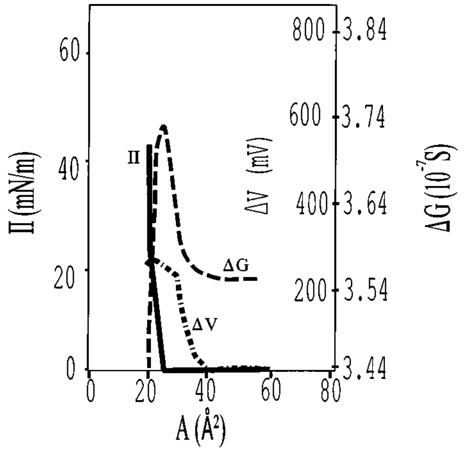

FIG. 1. Surface pressure Π, surface potential ΔV, and lateral conductance isotherms ΔG as functions of area per molecule A for a stearic acid monolayer (from Ref. [15]). Stearic acid was purchased from Sigma and used as received. Langmuir monolayers were spread from a 1-mg/mL chloroform solution of stearic acid onto an ultrapure water subphase ($p\mathrm{H}=5.8$). Experiments were carried out using a Langmuir trough mounted on an antivibration table, and housed in a temperature-controlled 10.000 class clean room. Experiments were carried out at room temperature (21 °C). Ultrapure water was supplied by a Millipore system comprising a RO cartridge coupled to a Milli-Q purification system. The surface potential was measured with a Kelvin probe to an accuracy of 110 mV. Lateral conductance was measured with two bright platinum plates immersed into the subphase, through which a current flows by applying a 1.0-V dc voltage. The current is measured using a Keithley electrometer.

ered as a three-layer capacitor with distinct dielectric constants. Taylor and co-workers [21,22] also showed that the measured ΔV can be related to group dipole moments for a number of aliphatic compounds. The sharp increase in potential was attributed [1] to a drastic decrease in the dielectric constant at the water-monolayer interface. Because at the measured critical area there is very little space for molecular reorientation, the change in dielectric constant appeared to be the only factor that could cause the increase in potential. As we shall discuss later, this hypothesis is completely consistent with the formation of the H-bonded network inherent in the proton transfer model used here.

With regard to the lateral conductance measurements, it is interesting to discuss the controversy over the possibility of detecting an enhanced conductance due to the monolayer presence. The first attempts to detect protonic conduction along Langmuir monolayers showed a lateral conductance of 10^{-8} S for various phospholipid and fatty acid monolayers spread onto an ultrapure surface, and using 2-cm-wide platinum electrodes which were partially immersed into the Langmuir trough [15,16]. Other research groups failed to replicate these experiments [18,23], therefore casting doubt on whether an enhanced lateral conductance was indeed a genuine, real effect. Based on our experience with the experimental setup, we may say that this failure was not surprising in view of a number of experimental difficulties for detecting the monolayer conductance. There are three major difficulties: (i) it is very hard to obtain a blank measurement (with no monolayer) in which the conductance does not vary upon compression of the barriers; (ii) because the monolayer is ultrathin, the enhancement in conductance is only a few percent of the bulk conductance, even when ultrapure water is employed; (iii) when the surface pressure starts to rise, the meniscus between the monolayer-water interface and the platinum electrodes is moved downwards (the so-called meniscus effect), thus decreasing the contact area and consequently the measured conductance. The first difficulty can only be eliminated if adequately purified water is employed, and also if very stringent precautions are taken for carrying out the experiments. The Langmuir trough must be inside a temperature-controlled clean room, the chemical products must be of adequate purity, and stringent procedures must be adopted for film fabrication. As one may see in Fig. 1, the meniscus effect is responsible for a large decrease in the conductance. Such a difficulty has been eliminated while measuring other Langmuir monolayers by almost fully immersing the platinum electrodes into the subphase, so that a meniscus is practically absent [24]. The experimental setup can also be improved if a differential system is employed [24], which allows for the subtraction of the subphase conductance, thus increasing the accuracy with which the monolayer conductance can be measured.

The lateral conductance measured for an insulating material cannot be purely ionic because a conductance is also detected for noncharged phospholipids such as dipalmitoyl phosphatidyl choline [16]. Nor can it be attributed to polarization effects, since dc and ac conductance curves are the same [24]. The conductance has been attributed to a proton conduction along the monolayer according to a hop and turn mechanism [25], which only becomes efficient below a given critical area per molecule. However, no attempt has been made to explain the value of the critical area.

In Sec. III the experimental results for both the surface potential and lateral conductance are explained using a simple geometric model, hydrogen bond data, and a unidimensional model for proton transfer (PT) in hydrogen bonds [26]. We suggest that the polar groups and the water form strong hydrogen bonds below a critical area. Strong hydrogen bonds create a highly structured media, and allow for a much faster proton transfer along the hydrogen bond network. The conductance happens via a ''hop and turn'' mechanism [25] with proton transfer through the hydrogen bonds.

III. HYDROGEN BOND DATA AND PROTON TRANSFER THEORY APPLIED TO LANGMUIR MONOLAYERS

Important information on the expected parameters of Langmuir films can be obtained from typical hydrogen bond data, assuming that these bonds play a role in controlling the structure of the films. Such structuring is reflected on surface potential and lateral conductance measurements, which are explained here for a fatty acid monolayer using Kiefer's simple model for PT in hydrogen bonds [26]. The simplicity of this unidimensional model has great appeal, since it helps to create a simple physical picture for the phenomena involved, even though the hydrogen bond data can be found through other theoretical approaches. This model was meant to be a tool for addressing the electronic contribution to PT. In this work we shall restrict our attention to its consequences related to the hydrogen bond length R in which the

PT can effectively occur, since it is crucial to explain our experimental data.

The model considers the energetics and dynamics of a simplified unidimensional proton coordinate under the presence of an effective potential. In PT reactions, a shift of electron density also accompanies the nuclear transfer. A localized part of the electronic density which mainly corresponds to the bond with the proton is shifted from one nucleus to another [27]. The theory of PT is based on the assumption that the nuclei move on a much slower time scale than electrons, i.e., on Born-Oppenheimer (BO) surfaces [28–30]. The model consists of two BO surfaces, corresponding to different electronic states seen by the proton. They are associated with the reaction

$$A-H\cdots B\Leftrightarrow A\cdots H-B,$$

where state A has an electron density localized between nucleus A and the proton (called the donor), and state B has density between the proton and nucleus B (called the acceptor).

This simple model describes PT reactions based on phenomenological parameters that are physically meaningful. The electronic contribution is redefined into few simple coordinates that can be handled without attempting to solve a many body problem. The electronic part is effectively reduced to two components: one which moves with the proton transfer, and one which remains stationary. The effective Hamiltonian for the system fixing A and B and neglecting solvent interaction is as follows:

$$H=T_x+T_r+V_2(r:R)+V_{eA}(x;r)+V_{eB}(x;r;R)$$

where r is the A-H separation, R is the A-B separation, and the coordinate x describes the effective electronic coordinate. T_x and T_r are the kinetic energy terms for the electrons and proton, respectively. $V_2(r,R)$ is a van der Waals-like nonbonding potential with each of the two oxygens, which was assumed to be a Morse-like potential. V_{eB} and V_{eA} are interactions designed to localize the electron density on the A and B sides of the proton, respectively. For example, in an AH-B system, V_{eA} localizes the electron density to form a bond between the proton and the A nucleus. The potentials V_2, V_{eA}, and V_{eB} were chosen such that they give reasonable properties for the AH and $AH\cdots B$ systems. The potentials are characterized by five parameters which are obtained by five relations associated with the physical properties of the H bonds. The solutions were found by manually probing the parameter phase space. Using the Born-Oppenheimer approximation, the electronic contributions $T_x+V_{eA}(x,r)$ and $T_x+V_{eB}(x,r,R)$ were replaced by the donor and acceptor eigenenergies [$E_A(r)$ and $E_B(r)$], respectively. They were assumed to follow an exponential behavior with the distance between the proton and the atom it is bounded to. The two electronic states can be represented through two Born-Oppenheimer surfaces. For simplicity a linear symmetric O_A-$H\cdots O_B$ system was considered. The exact quantum one-dimensional wave functions were calculated using a discrete variable representation basis [31].

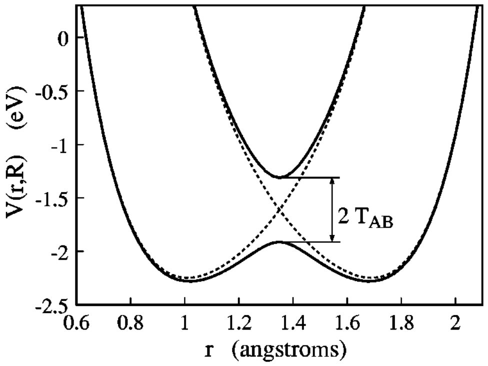

FIG. 2. Effective proton potentials $V(r,R)$ for electronic states A and B at a fixed separation $A\cdots B$. r is the proton coordinate, and T_{AB} is the electronic coupling between states A and B. Dashed lines are states A and B. Solid lines are the diagonalized upper and lower surfaces.

For the PT to take place, an electronic coupling is now included, and a full diagonalization of the system yields upper and lower surfaces. The splitting between the two surfaces is dependent on the strength of the coupling. A typical PT reaction assumes a large enough electronic coupling T_{AB} (adiabatic limit), such that only the lower surface is needed. In Fig. 2, the effective potential (lower surface) is shown as a function of r. The effective potential barrier height increases as R increases (Fig. 3). This feature has been confirmed by many other theoretical studies [32–37]. Also seen by theoretical studies is a transition from a double well system to that of a single well [33,35,37,38] as R is decreased. The decrease in barrier height increases the splitting of the two lowest proton energy states. Some authors [28,32,39–41] assumed that the splitting between the two lowest lying proton states behaves as an exponential decay with an exponent linear in R [$\Delta E\propto\exp(-\lambda R)$, $\lambda\approx 25-35\ \text{Å}^{-1}$], similar to the result obtained by the Kiefer model. The splitting is the best parameter to infer the strength of the H bond. The OH$\cdots$O hydrogen bond lengths in carboxylic acids and their hydrates exhibit a wide range, from very short (2.5 Å), to relatively weak bonds with $R\sim 2.9$ Å [42]. According to our model, PT can effectively occur when R is smaller than ≈ 2.8 Å. We point out that, in this first analysis, we just want to draw reasonable numbers to understand the experimental results.

The polar part of amphiphilic molecules in the films is arranged in a bidimensional triangular lattice. We assume that between the polar groups there are water molecules,

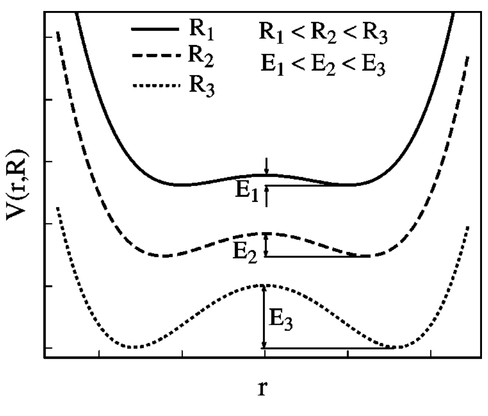

FIG. 3. Qualitative behavior of the effective potential $V(r,R)$ as function of proton coordinate r for different R.

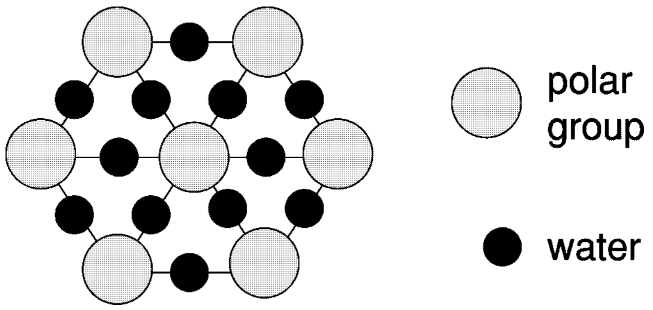

FIG. 4. Bidimensional arrangement of hydrophilic part at the monolayer-water interface.

through which a net of H bonds is formed (Fig. 4). Also assumed is a simple geometric model for the configuration of these molecules, as illustrated in Fig. 5. The critical area for fatty acids corresponds to a distance of 7.1 Å between polar heads (38 Å^2/molecule). This distance corresponds to a distance R between donor and acceptor oxygens of 2.8 Å. Below this distance a net with strong H bonds is formed. As explained above, the H-bond strength and PT increase exponentially with decreasing R. This suggests that the dramatic increase in the conductance below the critical area is due to a PT in a ‘‘hop-and-turn’’ mechanism. It must be stressed that the proton conductivity (i.e., mobility) must be considerably higher for a Langmuir monolayer than in bulk water. Otherwise, because the monolayer is extremely thin, it would not be possible to detect the enhancement in conductance due to the monolayer. This point was actually raised by Shapovalov and Il’ichev [18], who were skeptical about the possibility of ever detecting monolayer conductance. Their skepticism was based on an estimate of monolayer conductance in which the maximum proton mobility was taken to be that of ice. However, it is clear from the PT calculations that the barrier heights depend exponentially on the distance between donor and acceptor oxygens. This distance dependence explains the high proton mobility in condensed monolayers for which R is smaller than in bulk water or in ice (R is 2.76 Å for ice I [43]).

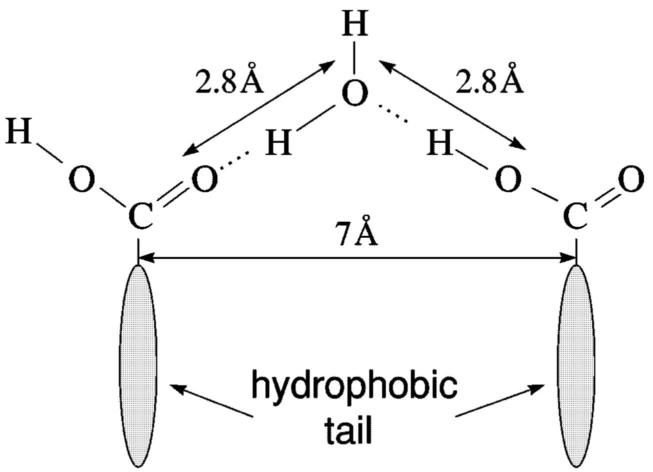

FIG. 5. Geometrical arrangement necessary for the proton transfer to take place. The C—O distance is around 1.36 Å and the C═O distance 1.24 Å. We use the average value of 1.3 Å for these distances, and assume the angle between O—C═O 120° symmetrically oriented around the hydrophobic tail axis.

These strong H bonds also explain the abrupt increase, below the critical area, in the surface potential. It is associated with a drastic decrease in the dielectric constant at the film-water interface caused by structuring the monolayer. Furthermore, if one varies R from 2.9 to 2.5 Å, keeping all the other parameters fixed, the area per molecule A decreases from ~40 to ~32 Å^2, which roughly corresponds, in Fig. 1, to the interval where there is a more drastic increase in the surface potential ΔV. When the strong H bonds are already formed, there is no reason for a further large decrease in the dielectric constant and this result was actually obtained in the fitting of surface potential data for a stearic acid monolayer [1]. Interestingly, formation of H bonds between water and filmforming molecules was suggested by Tachibana, Yoshizumi, and Hori while investigating monolayers of 12-hydroxyoctadedecanoic acids [44].

IV. CONCLUSION

This work has suggested a simple mechanism for the control of the structure and conductivity of Langmuir films, which is based on hydrogen bond data and a simple model for proton transfer. In particular, an explanation has been given for the appearance of lateral conductivity and changes in surface potential when the monolayer is compressed below a critical area. According to our model, the critical area corresponds to the formation of a strong H-bonded network between the monolayer headgroups and the water molecules. These hydrogen bonds below the critical area are responsible for the monolayer structuring which causes the surface potential to increase sharply. At the critical area, PT also effectively occurs, which happens when the distance between oxygens is $R < 2.8$ Å. It is shown that the critical value for a fatty acid monolayer corresponds to a distance of 7 Å. This represents a theoretical justification for the hypothesis of proton conduction via a hop and turn mechanism. Obviously, this model is only applicable to the monolayers where the formation of a H-bonded network plays a dominant role.

This is the simplest first order approach to model the monolayer structuring via H bonds. There are a number of other important factors that should be included in a detailed description. The oxygens were considered chemically equivalent, yielding symmetric potentials. The oxygens from water molecules and from the polar headgroups are not chemically equivalent, so the asymmetry should be included in a more detailed study. In this case solvent effects are expected to directly control the PT reactions [45]. The hydration of the polar heads as well as the steric effects between water molecules are also expected to play an important role. These are the issues that must be addressed if more complicated cases of amphiphilic molecules are to be treated.

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