



Cooperative effect in electron transfer between metal substrate and organized organic layers

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Abstract

A model is given that shows that the electronic properties of close packed organized organic layers, adsorbed on conductive substrate, may be very different from the properties of the single adsorbed molecule. The difference arises from a cooperative effect that results in electron transfer between the substrate and the layer. It is induced when molecules having dipole moment and low polarizability are organized so that their dipole moment is perpendicular to the surface. The thermodynamics of the problem is described. The model provides a possible rationalization to recent observed new experimental properties of adsorbed organized organic layers.

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1. Introduction

The structure of organized close packed films is known to be controlled, among others things, by the electrostatic interaction between the molecules. For example, McConnell and coworker (see e.g. [1]) and Möhwald [2] explained the structure of phospholipids on water as resulting from the balance between the molecules dipole–dipole interaction and the line energy (tension). Minimizing the free energy of the layer results in different shapes of the domains and in certain domain sizes.

It is also known that this interaction may affect the structure of Langmuir Blodgett films [4]. In all these studies the dipole moment of the molecules in the layer was assumed to be constant and the interaction with the substrate (water in most cases) was assumed to include the image charge.

In the present work we introduce another possibility for reducing the free energy of an organized layer. This channel for reduction in free energy is valid in the case where molecules have large dipole moments in the direction orthogonal to the surface and when the substrate has either a low work function or a high electron affinity. In these cases, charge transfer between the layer and the substrate may occur, which can alter dramatically the electronic properties of the layer [5,6].

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Here we discuss the conditions under which this charge transfer takes place and provide thermodynamic framework for the process. In the case that the length of the dipole moment of the molecules exceeds the distance between them, one can idealize the monolayer of dielectric molecules with electric built-in dipole moment P as a uniform dielectric layer of dielectric permeability ϵ , thickness, which is approximately the effective length of a molecule, and having the surface charge density, σ , on the top and $-\sigma$, on the bottom of the layer. The density σ is evaluated as $\sigma = P/(La^2)$, and may be either positive or negative. Here a^2 is the area per molecule and L is the length of the dipole. The distance from the metal to the nearest dielectric surface is H (Fig. 1).

In the case of large σ , this system has huge electrostatic energy with the surface density $W = 2\pi L\sigma^2/\epsilon$, see below Eq. (2). This electrostatic energy can cause charge redistribution within the molecules, due to the Stark effect [3]. Another way by which the electrostatic energy can be decreased is by electron (or hole) transfer from the substrate to this ‘capacitor’. When the molecules have very low lying electronic states, like in highly conju-

gated systems, intramolecular electron rearrangement is most probable. This amounts to the system having high polarizability and hence the layer has large dielectric permeability ϵ . However, when the molecules are saturated hydrocarbons, the energetically more favorable process is charge transfer with the substrate. The price to pay for the transfer of one electron is the difference, A , between the work function of the metal and the electron affinity (or ionization potential) of the dielectric. This difference may be positive or negative. In general, the induced charge may be distributed somehow within the capacitor. For simplicity we assume that this charge is located at some distance x from the top of the layer, which may be found from the minimization of the energy. It will be shown that our simplification does not effect the final results.

The resulting simple model of the dielectric layer is shown in Fig. 1. A charged layer with a surface density $-\Delta\sigma$ will have an image charge (in the case of high dielectric substrate) with density $+\Delta\sigma$. The value of induced charge $\Delta\sigma$ and the position x can be determined by minimization of the total energy of the system with respect to the adjustable parameters of the model, x and $\Delta\sigma$.

The electric displacement vectors D_i and electric fields E_i in the three regions will be directed as shown in Fig. 1 and can be found using Gauss’ law

$$\begin{aligned} D_1 &= 4\pi\sigma, & E_1 &= 4\pi\sigma/\epsilon, \\ D_2 &= 4\pi(\sigma - \Delta\sigma), & E_2 &= 4\pi(\sigma - \Delta\sigma)/\epsilon, \\ D_3 &= 4\pi\Delta\sigma, & E_3 &= 4\pi\Delta\sigma. \end{aligned} \quad (1)$$

Note that the field E_1 is the same as in the absence of screening ($\Delta\sigma \equiv 0$). So the only possible way of decreasing the electrostatic energy in the layer is by decreasing the field in region 2. This can be achieved if σ and $\Delta\sigma$ both have the same sign. In the following we will assume $\sigma > 0$, $\Delta\sigma \geq 0$. It is also clear that $|\Delta\sigma| \leq |\sigma|$, hence we have a possible range for $\Delta\sigma$: $\sigma \geq \Delta\sigma \geq 0$.

In order to remove one electron from the substrate, we need to perform the work A . So, the energy of the system has, besides the electrostatic energy, contributions from work function $A\Delta\sigma/e$ (per unit area).

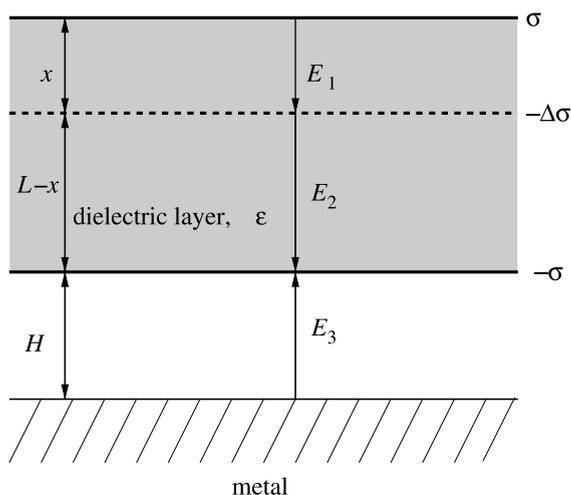


Fig. 1. A model of the dielectric layer. The H and L are distance between the metal to the nearest dielectric surface and the thickness of the layer, respectively. We displayed positions of the surface charge densities $\pm\sigma$, $\pm\Delta\sigma$, and denoted electric fields E_n in the regions $n = 1, 2$ and 3.

The total energy per unit area is therefore

$$\begin{aligned}
 W(x, \Delta\sigma) &= \frac{1}{8\pi} (E_1 D_1 x + E_2 D_2 (L - x) \\
 &\quad + E_3 D_3 H) + \frac{A\Delta\sigma}{e} \\
 &= \frac{2\pi}{\epsilon} \{x [\sigma^2 - (\sigma - \Delta\sigma)^2] \\
 &\quad + L(\sigma - \Delta\sigma)^2 + \Delta\sigma^2 H\} + \frac{A\Delta\sigma}{e}. \quad (2)
 \end{aligned}$$

x and $\Delta\sigma$ are free parameters that are determined from the condition of the minimum of the energy $W(x, \Delta\sigma)$. Because $\sigma^2 - (\sigma - \Delta\sigma)^2 \geq 0$, the free energy is an increasing function of the coordinate x , minimization of W requires $x = 0$. This means that charge is transferred between the substrate and the layer.

By requiring that $dW(0, \Delta\sigma)/d\Delta\sigma = 0$, we obtain the condition on $\Delta\sigma$:

$$(\epsilon H + L)\Delta\sigma - \sigma L / + \epsilon A / 4\pi e = 0. \quad (3)$$

So we find

$$\Delta\sigma = \frac{1}{L + \epsilon H} \left(\sigma L - \frac{\epsilon A}{4\pi e} \right). \quad (4)$$

The induced charge transfer per one adsorbed molecule, Δq , is given by

$$\begin{aligned}
 \Delta q &= \Delta\sigma a^2 = \frac{1}{L + \epsilon H} \left(\sigma L a^2 - \frac{\epsilon A a^2}{4\pi e} \right) \\
 &= \frac{1}{L + \epsilon H} \left(P - \frac{\epsilon A a^2}{4\pi e} \right). \quad (5)
 \end{aligned}$$

Let us make a rough estimation of Δq . We will assume that the effective charge separation in the molecule is equal to the charge of an electron e . Then $\sigma = e/a^2$, and

$$\Delta q = \frac{L}{L + \epsilon H} \left(e - \frac{\epsilon A a^2}{4\pi e L} \right). \quad (6)$$

We will also assume that $L \gg \epsilon H$, and express the work function A in Rydberg units

$$A = \kappa \frac{e^2}{2a_0},$$

where $a_0 \simeq 0.53 \text{ \AA}$ is the Bohr radius, and κ is the dimensionless constant of order unity (for work

function $A \simeq 4.3 \text{ eV (Au)}$ $\kappa \simeq 0.32$). Then for Δq one obtains the estimate

$$\frac{\Delta q}{e} = 1 - \frac{\epsilon \kappa a^2}{8\pi a_0 L}. \quad (7)$$

Using values $a^2 \simeq 20 \text{ \AA}^2$, $L \simeq 20 \text{ \AA}$, $\epsilon \simeq 10$ we have

$$\frac{\Delta q}{e} = 1 - 0.24 = 0.76.$$

This estimation lies within reasonable range $0 \leq \Delta q/e \leq 1$.

We can also account for finite value of H . If $H \simeq 0.1L$ and $\epsilon \simeq 10$ then $L/(L + \epsilon H) = 1/2$, and Δq decreases by a factor of two.

The results presented above indicate that when molecules have relatively large dipole moment, namely dipole moment that exceeds $1.6 \times 10^{-3} v \text{ D/\AA}^3$ [7], where v is the volume of the molecules in cubic angstroms, charge transfer may occur between the substrate and the layer. This value of dipole moment density is common for most self-assembled or Langmuir–Blodgett made films and therefore the phenomenon described may be more widespread than realized. Clearly, charge transfer is more favorable when the substrate is metallic, since the work function for metal is relatively low (rarely exceeding 5 eV), and the electron affinity is also large. In addition, while for a dipole layer, no image charge exists since there is no electric field outside the layer, after the charge transfer the image charge contributes to the stabilization of the layer. Hence, the mechanism described here of organization induced charge transfer is expected to occur mainly for conducting substrates, either solids or solutions. Interestingly, in order to reduce the dipole moment, the charge transfer occurs so as to cancel the charge on the pole farther away from the substrate. In the model it appears through the minimization of free energy for $x = 0$. This means that upon charge transfer, the surface dipole flips sign, as indeed was observed recently [8].

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