Notes

Orientation Effects for Quaternized Poly-4-vinylpyridine Adsorption onto an Oxidized Silicon Surface

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Introduction

Adsorption of ligands onto surfaces is an active area of study in many fields. Of interest in the present paper is the study by Sukhishvili and Granick[1] on the adsorption of the quaternized poly-4-vinylpyridine cation (P^+, following their notation for this organic cation) onto a flat silicon crystalline surface in the presence of a variety of inorganic cations. The purpose of their study was to provide some insight into the mode adsorption of poly(vinylpyridine) (PVP) with polystyrene latices,[2,3] DNA,[4] and silicon oxide[5] by examination of the monomeric unit association with a homogeneous surface. Data were obtained by Fourier transform infrared with attenuated total reflection (FTIR-ATR), and the tilt of the P^+ was determined from the ratio of the absorption in the p- and s-polarization directions, viz., the dichroic ratio D. The resulting isotherms exhibited a "two-step" adsorption profile. Sukhishvili and Granick[1] suggested that the two-step process reflected a *single-layer coverage* with *two orientation states of the ligand*. That is, under conditions of low coverage the plane of the P^+ cations was oriented parallel to the surface whereas at higher coverage the plane of the molecules was more perpendicular to the adsorption surface. We show herein that the exact one-dimensional nearest-neighbor model in which site exclusion effects are lost at higher coverage may account for their observations.

Theory

Since there is an increase in the amount of P^+ in going from the parallel to perpendicular orientations of the bound ligand,[1] we adapt the mathematical model we proposed for the interpretation of ligand binding to linear biomolecules in which the ligands covered more than one available site.[6] In that study the adsorption of a ligand excluded q contiguous sites upon binding to the linear lattice.

To modify the matrix generation method as described[6] for the present system, we take advantage of the fact that the mode of interaction of the P^+ ligand is electrostatic. Therefore, we partition the P^+ cation into two regions: the charged portion of the cation is indicated by the number "1" and the neutral part by the number "2". Thus, the single molecule is represented as (1−2). For the electrostatic adsorption to occur the "1" portion of each cation *must* be in contact with the surface. The orientation of the molecule onto the surface is thus contained in the neutral part of the cation. If the ring of the cation is parallel to the surface, then the "2" portion of the molecule is also "attached" to the surface and excludes the site following the electrostatically bound site. However, if the cation is oriented with its ring perpendicular to the surface, then the "2" portion of the molecule does not exclude binding to the adjacent site. An unbound site is represented by the number "0", the point of electrostatic attachment by "1", and the excluded site by "2". Hence, the sequence of sites of the linear lattice contains a series of "0", "1", and "2" with the constraints that a "2" cannot follow a "0" or another "2". Using this notation, the linear sequence of four sites (0)(1)(1)(2) is interpreted as having one unbound site [the (0)] followed by a P^+ oriented perpendicular to the surface [the (1)] which is followed by a P^+ bound parallel to the surface [the (1)(2), which occupies two lattice sites and thus excludes the adsorption of a different ligand at the fourth site]. The statistical weighting factors for the three types of site association are 1 for the unbound site (the reference state), $m_f B$ for the perpendicular orientation, and $m_f B R_{||}$ for the parallel orientation, where the factor $R_{||}$ accounts for the difference in the free energy of adsorption due to the orientation of the P^+. We next take into consideration the electrostatic interaction between the nearest-neighbor bound ligands. To this end we adopt the notation for the remote-neighbor interaction, where the weighting factor W_1 is the pair interaction for the configuration (1)(1) and W_2 for the configuration (1−2)(1). The electrostatic interaction between two adjacent site with perpendicular−perpendicular orientations is distinguished from the interaction for parallel−perpendicular orientations through the weighting factors W_1 and W_2, respectively. The generation matrix for the grand partition function is obtained from a two-dimensional grid of (0), (1), and (2) states for the jth and $(j + 1)$th sites. The generation of the grand partition function is effected by matrix multiplication,[6]

$$\Xi = (1, m_f B, 0)\cdot\mathbf{M}^{N-1}\cdot\begin{pmatrix}1\\1\\1\end{pmatrix}$$

$$= (1, m_f B, 0)\cdot\begin{bmatrix}1 & m_f B & 0\\ 1 & m_f B W_1 & R_{||}\\ 1 & m_f B W_2 & 0\end{bmatrix}^{N-1}\cdot\begin{pmatrix}1\\1\\1\end{pmatrix} \quad (1)$$

The adsorption isotherms were obtained by the standard finite difference expression for an infinitely long lattice using only the largest eigenvalue of the generation matrix, denoted by λ_L. The fraction of bound sites θ_b is calculated from the finite difference expression,

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$$\theta_b = \frac{\log[\lambda_L(m_f + \delta m_f)] - \log[\lambda_L(m_f - \delta m_f)]}{\log[m_f + \delta m_f] - \log[m_f - \delta m_f]} \quad (2)$$

where $\delta m_f = 0.001 m_f$ is the increment change in the molality of the counterion concentration used in the calculations presented herein.

All programs used in this study were written with *Mathematica*, a system for doing mathematics on a computer. Since the objective of this paper is to show that orientation of the bound ligands may account for the two-step adsorption isotherm of P^+ onto silica, we select a set of parameters to achieve this goal without going into a detailed description of the origin of these values. Thus, we are making a qualitative assessment of the steepness and location of the transitions in the experimental isotherm. We found the following parameters adequate for this comparison: $B = \exp(7)$, $R_{||} = \exp(4)$; $W_1 = \exp(5)$; and $W_2 = \exp(4)$. The results are shown in Figure 1.

We point out that in order to attain the "sharp" steps as exhibited in Figure 1 and the experimental data, it is necessary that *all* of the interactions in the proposed model be *attractive*, i.e., that the respective Boltzmann weighting factors be greater than unity. The fact that $R_{||} > 1$ indicates the preference of the parallel configuration over the perpendicular configuration, which may be accounted for in terms of the closer proximity of the charged group to the surface sites for the former relative to the latter mode of adsorption. The observation that $W_1 > 1$ and $W_2 > 1$ means that the interaction between neighboring sites is also attractive. At first glance this may seem contradictory to electrostatic theory since the neighboring bound ligands are of the same charge. However, one must take into consideration that the adsorption of a ligand next to the bound site involves the interaction between not only the adjacent ligands but also the neighboring sites. That is, a ligand binding to the $j + 1$ site interacts with not only the ligand at the jth site but also the *surface* sites j and $j + 2$. It has been shown that for monovalent ligands the sign of the pairwise interaction with neighboring ligand and adjacent site may indeed be "attractive" if the sites are sufficiently close.[7] The observation that $W_2 < W_1$ indicates that the orientation stearic effect has a greater "effective" repulsion than purely electrostatic effects.

The parallel−perpendicular orientation transition has also been discussed by Sellami, Hamraoui, Privat, and Olier[8] for 2,5-dimethylpyridine onto a silica surface. Within the context of their study, the transition from parallel to perpendicular orientation of P^+ is a surface phase transition that is governed by the solution concentration of the ligand. Our simulations clearly indicate that the sharpness of this transition requires an attraction between nearest neighbors.

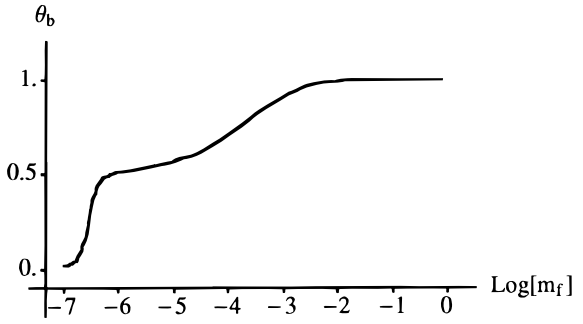

Figure 1. Adsorption isotherm for the orientation model. The above isotherm was generated from eqs 1 and 2 using the parameters $B = \exp(7)$, $R_{||} = \exp(4)$; $W_1 = \exp(5)$; and $W_2 = \exp(4)$.

We conclude that the proposed interpretation of Sukhishvili and Granick[1] of monolayer adsorption with significant contributions of stearic hindrance to adsorption has a sound theoretical basis.

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