Sticking Probabilities in Adsorption from Liquid Solutions: Alkylthiols on Gold

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The sticking probability, defined as the rate of adsorption per molecular collision with the surface, directly expresses the difficulty encountered by a molecule in scaling the barrier to adsorption. Its prior use has been restricted to adsorption of gases. A method extending this concept to adsorption from liquid solutions is applied to transient measurements of alkylthiol adsorption onto gold from ethanol solutions. The initial sticking probability increases from $\sim 10^{-8}$ to $\sim 10^{-6}$ with alkyl chain length, implying a stabilization of the transition state by ~ 0.65 kJ/mol per CH_2. Since their sticking probabilities in the gas phase are ~ 1.0, the solvent increases the activation free energy by ~ 40 kJ/mol.

PACS numbers: 68.45.Da, 68.10.Jy, 82.65.–i

The most fundamental way to express an adsorption rate constant is in terms of a sticking probability (S). It is defined as the probability that the molecule adsorbs upon its collision with the surface, and is just the rate of adsorption per unit area (R_{ads}) divided by the collision frequency with the surface (J_s, the number of molecules which collide with the surface per second per unit area): $S = R_{ads}/J_s$. Measurements of sticking probabilities versus coverage, temperature, and internal energy have allowed surface scientists to extract many details about the kinetics, activation energy, mechanism, and dynamics of adsorption processes from the gas phase. Yet sticking probability is rarely mentioned in studies which address the kinetics of adsorption from liquid solutions.

To obtain a sticking probability, one must properly calculate the collision frequency J_s of a liquid-phase solute with a surface. In gas-phase adsorption, J_s is simply derived from the kinetic theory of gases [1]: $J_s = n^*[k_B T/(2\pi m)]^{1/2}$, where k_B is Boltzmann's constant, T is the temperature, m is the mass of the adsorbate molecule, and n^* is the number of adsorbate molecules per unit volume in the gas phase above the surface. To our knowledge, no one has described how to calculate the collision frequency in liquids, even for simple cases where no concentration gradient exists. Since there is no characteristic step length in diffusion through liquids [2], random-walk models would not easily provide this.

The collision frequency or flux of a solute onto the surface of a solid from a liquid solution is given by $J_s = C_s v_T$, where C_s is the concentration of the solute in that liquid nearest to the surface and v_T is the mean thermal velocity of the solute molecules relative to the solid surface (i.e., the component of the molecule's velocity perpendicular to the surface, instantaneously averaged over that half of the molecules which are moving with some velocity component toward, rather than away from, the surface). We assume that the solute exhibits a classical Maxwell-Boltzmann velocity distribution in its motion in the solvent, as is true for all but tiny adsorbates. This thermal velocity then can be calculated as a special case of a formula derived by Schurr [3] for the average relative velocity

of two spherical molecules in a solvent, which he used to estimate their collision frequencies in analyzing bimolecular reaction kinetics in solution. If we take one molecule to have mass m (representing the adsorbing solute) and the other "molecule" to be infinitely heavy and thus have infinite radius (representing the flat surface of the solid), then his formula reduces to $v_T = [k_B T/(2\pi m)]^{1/2}$. The collision frequency is then just $J_s = C_s[k_B T/(2\pi m)]^{1/2}$. Interestingly, this is the same as the expression above for gas-phase adsorption, since both are derived from the same classical velocity distributions. One can then determine the sticking probability even in liquids by simply dividing the measured adsorption rate by this collision frequency. A similar expression was used by Marcus [4] to calculate the maximum rate at which a solute can experience electron transfer near an electrode surface, which is just its forward flux through an imaginary plane near the surface.

Since diffusion is slow in liquids, the solute concentration in that solvent nearest to the surface, C_s, is often significantly depleted (relative to the bulk) due to adsorption. If the diffusion constant for the solute, D, is known, one can determine C_s versus time since there is only one set of concentrations versus distance from the surface and time which are consistent with (1) the initial conditions, (2) the observed adsorption rate versus time, and (3) Fick's law of diffusion.

We present here transient rate measurements of the adsorption of a series of alkylthiols onto gold from ethanol solution by surface plasmon resonance (SPR) spectroscopy. The measured rates and values of C_s calculated in this way are used to determine sticking probabilities versus coverage and alkylthiol chain length. To our knowledge, this is the first time accurate sticking probabilities have been determined for adsorption from liquid solutions. The adsorption of alkylthiols on gold has been studied actively. The resulting stable films of chemisorbed alkylthiolates provide self-assembled monolayers (SAMs) which form the basis for many recipes for the organo- and biofunctionalization of gold surfaces [5–10]. Numerous studies have addressed the kinetics of their adsorption

from liquid solutions [5,7,11–23], yet none have reported sticking probabilities.

The SPR instrument used here to measure the volume of adsorbed thiolates is described in [24]. The gold-coated glass slides were prepared as in [24] and mounted on the 80 μl SPR flow cell. A syringe pump and two valves allow rapid switching of the flow cell contents between pure solvent and solvent plus thiol. After a steady baseline is established in pure solvent, the thiol was injected from the sample loop into this flow cell to initiate adsorption in a stop-flow manner. Control experiments proved the system time response to be ~0.8 s [25]. The observed changes in the wavelength of the reflectance minimum (SPR resonance) were converted into coverages (thiols/cm^2) using a formalism for quantitative SPR described elsewhere [24], the known refractive indices of solvent and adsorbates [24], and calibration of the SPR sensitivity to changes in bulk refractive index (without adsorption).

Figure 1 shows measurements of the SPR wavelength versus time for the adsorption of a series of alkylthiols onto the gold surface at room temperature from ethanol solutions. For the very thin layers produced here, the relative coverage of each thiol is equal to its shift in SPR wavelength normalized by its saturation shift [24]. Therefore, the curves in Fig. 1 directly give the relative coverages of each thiol versus time. For all the thiols, saturation appeared to be reached by ~600 s, the longest time measured. Only the first 40 s are shown since they reached ~80% of saturation in this most important period. After converting their saturation SPR responses to absolute coverages, all the alkylthiols showed about the same saturation coverage of $(4.8 \pm 0.2) \times 10^{14}$ molecules/cm^2. This
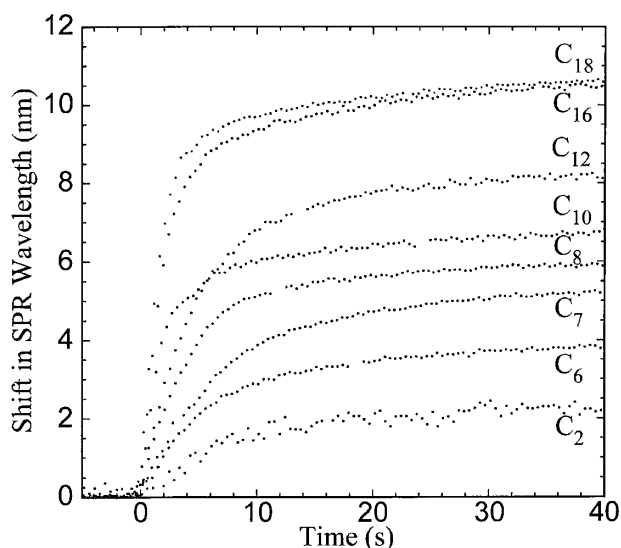

FIG. 1. The SPR response versus time upon adsorption of a series of alkylthiols from ethanol solution onto Au at room temperature. The adsorption transients were initiated by switching the thiol solution into the ethanol-filled SPR flow cell at time 0. The solution concentrations used here were all 0.5 mM except with C$_{16}$ (0.25 mM) and C$_{18}$ (0.2 mM). "C$_n$" is a thiol with n carbons.

saturation packing density is consistent with prior results [5], which were explained as due to closest packing of the alkyl chains [26]. The rate of adsorption was determined by the instantaneous slope of coverage versus time.

A finite-difference numerical method was used to calculate the concentration of these thiols versus distance from the surface and time, using these observed transient rates as a boundary condition. Briefly, the flow cell volume is divided up into a series of thin layers parallel to the (infinite area) surface. At time 0, each layer is assigned the known initial bulk concentration. As the adsorbate then sticks to the surface in the first incremental time step, the solution layer nearest the surface is accordingly depleted, resulting in a concentration gradient between it and the next layer. Fick's law is then used to calculate the resulting diffusive flux between these two layers in the next time step. This is iteratively extended in subsequent time steps to each successive incremental layer, with the boundary condition that the irreversible flux out of the zeroth layer (to the surface) equals the measured rate of adsorption at that time. The diffusion constant D for the thiols in ethanol were taken as 9.5×10^{-6} to 5.7×10^{-6} cm^2/s for HSCH$_2$CH$_3$ to HS(CH$_2$)$_{17}$CH$_3$, respectively, based on the reported value of D for allyl alcohol in ethanol [27], adjusting for each thiol's volume. This adjustment used the Stokes-Einstein equation [1] to relate D to the effective hydrodynamic radius, estimated by assuming spherical molecules with densities as reported for the pure thiol [27]. Finite difference methods were often applied to fit adsorption transients to simulations of the adsorption kinetic equation, taking into account diffusion and concentration gradients [28–30]. Our current treatment differs in that the intrinsic adsorption rate constant versus coverage is *directly* extracted from the adsorption transient data, whereas in those earlier studies it was necessary to assume some form of the intrinsic rate law (i.e., to assume how the intrinsic rate constant varies with coverage).

The bulk concentrations used for these measurements were large, so that the extent of depletion near the surface resulting from adsorption in these calculations was usually a relatively minor correction to the bulk concentrations (<20% for most; 60% for worst case: C$_{18}$). Thus, our final sticking probabilities are insensitive to the details of these calculations and the exact values of the diffusion coefficients used.

Each rate curve from Fig. 1 was converted into sticking probability versus time as follows: (1) the finite-difference solution to Fick's law described above was used to solve for the concentration nearest the surface versus time, (2) this concentration and the mass of the thiol molecule (uncorrected for any solvation shell) were used as above to calculate a collision frequency versus time, and (3) the rate at each time was divided by this collision frequency to give the sticking probability.

The resulting sticking probabilities, when plotted versus coverage instead of time, decayed nearly linearly for every thiol, as expected for a first-order Langmuir adsorption

mechanism [1]: $S = S_0(1 - \theta/\theta_{max})$. Here S_0 is the initial sticking probability and θ/θ_{max} is the coverage relative to one monolayer. "Monolayer" in this case does not refer to true saturation, but to that coverage (θ_{max}) at which this linear decrease in sticking probability extrapolates to zero. This extrapolation gave a monolayer coverage of $\sim(4.0 \pm 0.4) \times 10^{14}$ molecules/cm^2 for each thiol, which is $\sim20\%$ below the true saturation reached at very much longer times. This suggests that another process controls the adsorption kinetics in this last 20%, which is possibly rate limited by some reorganization or crystallization in the adlayer as suggested in other studies [14,22,31,32].

The initial sticking probability S_0 was determined for each alkylthiol by fitting its sticking probability versus coverage data to $S_0(1 - \theta/\theta_{max})$, treating S_0 and θ as fitting parameters. The resulting values of S_0 are plotted (in log format) versus chain length in Fig. 2. We will present elsewhere [33] a more complete account of these fits and the observed deviations from Langmuir kinetics at high coverages. As seen, S_0 increases by a factor of ~65 with chain length. The solid line shows the linear best fit to these data, which corresponds to $S_0 = P_0 \exp(bN_{CH2})$, where N_{CH2} is the number of methylene groups in the alkyl chain (not counting the terminal CH$_3$), and P_0 and b are constants whose best-fit values are 1.24×10^{-8} and 0.26 per methylene group, respectively. This exponential behavior is easily understood on the basis of energetic effects on the stability (i.e., Gibb's free energy) of the transition state for adsorption. Within this picture, the slope $b = 0.26$ corresponds to the transition-state stabilization energy per methylene group, in units of RT (at $T = 298$ K). This gives a decrease in the activation free energy

for adsorption by 0.65 kJ/mol per methylene group. That is, one can express the straight line of Fig. 2 as $S_0 = v \exp\{-[\Delta G_0 - (0.65 \text{ kJ/mol})N_{CH2}]/RT\}$, where ΔG_0 is the activation Gibb's free energy for an alkylthiol with no methylene groups in the alkyl chain (i.e., HSCH$_3$) and v is the prefactor. Note that $P_0 = v \exp[-(\Delta G_0/RT)]$, so that ΔG_0 is ~45 kJ/mol if v is near unity.

Figure 2 shows that the adsorption rate increases with alkylthiol chain length. Just the opposite trend was seen in the desorption rates of these same thiolate species by Bain *et al.* [7], who concluded that their activation energy for desorption into hexadecane solvent increases by ~0.8 kJ/mol per methylene group. They attributed this to attractive interactions of the adsorbed thiolate to coadsorbed thiolates and the gold, which get stronger with each CH$_2$. If we assume that this variation in the activation energy for desorption in hexadecane also applies in our solvent (ethanol), then by summing the effects of chain length on the desorption and adsorption activation free energies (0.8 and 0.65 kJ/mol per methylene, respectively), the stabilization of the adsorbed state results: 1.45 kJ/mol per methylene group. Thus, the energy of the transition state changes by $\sim50\%$ of the relative energy changes of the product, suggesting a structure for the transition state midway between reactants and product. The activation barrier is thus associated to some extent with the displacement of adsorbed solvent molecule(s) from the gold, but also with the loss of solvent molecules from the solvation shell of the dissolved thiol.

This involvement of solvent molecules in determining the relative free energy of the transition state is highlighted by realizing that these same alkylthiols have an initial sticking probability near unity when adsorbing from the gas phase onto clean gold in ultrahigh vacuum at room temperature [32]. The ethanol solvent decreases the sticking probability of decanethiol by a factor of $\sim10^7$. This corresponds to a destabilization of the transition state by ~40 kJ/mol (relative to the free solution-phase thiol). Conversely, this can be viewed as the solvent stabilizing the free solution-phase thiol relative to its transition state for adsorption from solvent. Since the solvent does stabilize a dissolved alkylthiol relative to its energy in vacuum (i.e., through van der Waals attractions), some of that stabilization may be lost in the transition state simply because its proximity to the gold will not allow as many nearest-neighbor solvent molecules. The transition state energy may be high partially because those solvent molecules must be shed from the adsorbing thiol before it can establish much bond strength to the gold, as it proceeds along the reaction coordinate.

The increase in the rate with alkylthiol chain length agrees qualitatively with previous results [6,7,12,18,31]. In contrast, Dannenberger *et al.* [23] reported the opposite trend, probably because their rates are at much lower concentrations and are therefore diffusion limited.

Some adsorption kinetics from liquids have been analyzed within a diffusion-limited Langmuir model [22,34,
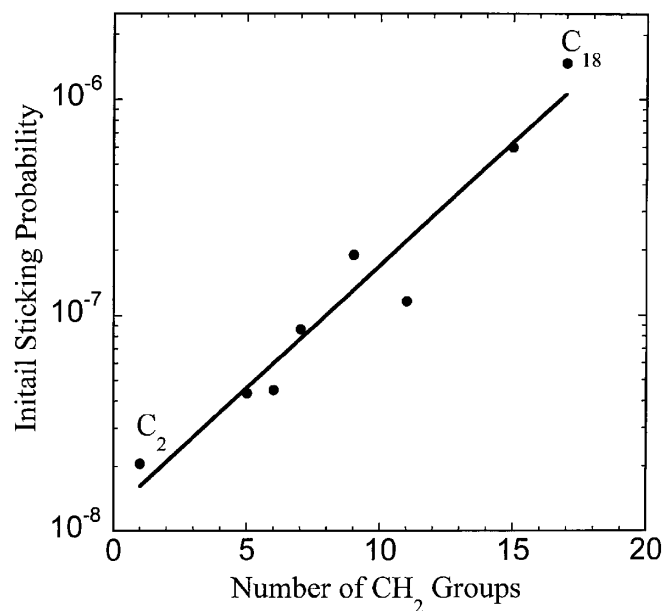
FIG. 2.   The logarithm of the initial sticking probability (S_0) versus chain length for alkylthiols adsorbing onto gold from ethanol solution, and the best-fit straight line.

35], but it is applicable only if the sticking probability is always unity and the desorption rate is so fast that the saturation (equilibrium) coverage θ_{sat} is tiny. Others have assumed purely diffusion-controlled, irreversible adsorption with unit sticking probability [28,36,37], which gives a never-ending growth of coverage (θ) versus time (t) as $\theta = C_{bulk}(Dt/2)^{1/2}$, where C_{bulk} is the adsorbate concentration in the bulk of the solvent. Still others [38–40] have assumed that a nonunit sticking probability would simply factor into this expression as $\theta = S C_{bulk}(Dt/2)^{1/2}$, and they used this to estimate initial sticking probabilities. When our initial adsorption rate data were fitted to this equation, S_0 values resulted that were $\sim 10^6$-fold greater than the true values of Fig. 2.

In conclusion, the initial sticking probabilities (S_0) for alkylthiols adsorbing onto gold from ethanol solution increase with alkyl chain length from $\sim 10^{-8}$ to $\sim 10^{-6}$, implying that the transition state for adsorption is strongly destabilized in solvent, but stabilized by 0.65 kJ/mol with each added CH_2. First-order Langmuir adsorption kinetics are followed up to a coverage of 4×10^{14} molecules/cm^2, after which another 20% adsorbs at a much slower rate.

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[1] I. N. Levine, *Physical Chemistry* (McGraw-Hill, New York, 1995).
[2] S. Nir and W. D. Stein, J. Chem. Phys. **55**, 1598 (1971).
[3] J. M. Schurr, Biophys. J. **10**, 700 (1970).
[4] R. A. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1964).
[5] R. G. Nuzzo, B. R. Zegarski, and L. H. Dubois, J. Am. Chem. Soc. **109**, 733 (1987).
[6] C. D. Bain and G. M. Whitesides, Science **240**, 62 (1988).
[7] C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, J. Am. Chem. Soc. **111**, 321 (1989).
[8] K. L. Prime and G. M. Whitesides, J. Am. Chem. Soc. **115**, 10 714 (1993).
[9] J. Spinke, M. Liley, F. J. Schmitt, H. J. Guder, L. Angermaier, and W. Knoll, J. Chem. Phys. **9**, 7012 (1993).
[10] A. L. Plant, Langmuir **9**, 2764 (1993).
[11] C. D. Bain and G. M. Whitesides, J. Am. Chem. Soc. **111**, 7164 (1989).
[12] C. D. Bain, J. Evall, and G. M. Whitesides, J. Am. Chem. Soc. **111**, 7155 (1989).
[13] H. A. Biebuyck, C. D. Bain, and G. M. Whitesides, Langmuir **10**, 1825 (1994).
[14] Y. Zhang, R. H. Terrill, and P. W. Bohn, J. Am. Chem. Soc. **120**, 9969 (1998).
[15] Y. Zhang, R. H. Terrill, and P. W. Bohn, Anal. Chem. **71**, 119 (1999).
[16] H. J. Kim, S. Kwak, Y. S. Kim, B. I. Seo, E. R. Kim, and H. Lee, Thin Solid Films **327–329**, 191 (1998).
[17] H. M. Schessler, D. S. Karpovich, and G. J. Blanchard, J. Am. Chem. Soc. **118**, 9645 (1996).
[18] S. Xu, S. Cruchon-Dupeyrat, J. C. Garno, G.-Y. Liu, G. K. Jennings, T.-H. Yong, and P. E. Laibinis, J. Chem. Phys. **108**, 1 (1998).
[19] R. F. DeBono, G. D. Loucks, D. D. Mann, and U. J. Krull, Can. J. Chem. **74**, 677 (1996).
[20] D. S. Karpovich and G. J. Blanchard, Langmuir **20**, 3315 (1994).
[21] W. Pan, C. J. Durning, and N. J. Turro, Langmuir **12**, 4469 (1996).
[22] K. A. Peterlinz and R. Georgiadis, Langmuir **12**, 4731 (1996).
[23] O. Dannenberger, M. Buck, and M. Grunze, J. Phys. Chem. B **103**, 2202 (1999).
[24] L. S. Jung, C. T. Campbell, T. M. Chinowsky, M. N. Mar, and S. S. Yee, Langmuir **14**, 5636 (1998).
[25] L. S. Jung, K. E. Nelson, C. T. Campbell, P. S. Stayton, S. S. Yee, V. Perez-Luna, and G. P. Lopez, Sens. Actuators, B **54**, 137 (1999).
[26] L. H. Dubois and R. G. Nuzzo, Annu. Rev. Phys. Chem. **43**, 437 (1992).
[27] D. R. Lide, *Handbook of Chemistry and Physics* (CRC Press, Boston, 1990), 71st ed.
[28] A. F. H. Ward and L. Tordai, J. Chem. Phys. **14**, 453 (1946).
[29] S. W. Feldberg, in *Electrochemistry: Calculations, Simulations and Instrumentation,* edited by J. S. Mattson, J. H. B. Mark, and H. C. MacDonald (Dekker, New York, 1972).
[30] J. D. Andrade and V. Hlady, Adv. Polym. Sci. **79**, 1 (1986).
[31] A. Ulman, Chem. Rev. **96**, 1533 (1996).
[32] P. Schwartz, F. Schreiber, P. Eisenberger, and G. Scoles, Surface Sci. **423**, 208 (1999).
[33] L. S. Jung and C. T. Campbell (to be published).
[34] W. N. Bond and H. O. Puls, Philos. Mag. **7**, 864 (1937).
[35] J. R. Rahn and R. B. Hallock, Langmuir **11**, 650 (1995).
[36] H. Motschmann and M. Stamm, Macromolecules **24**, 3681 (1991).
[37] J. B. Schlenoff, M. Li, and H. Ly, J. Am. Chem. Soc. **117**, 12 528 (1995).
[38] K. Park, H. Park, and R. M. Albrecht, in *Colloidal Gold Principle, Methods and Applications,* edited by M. A. Hayat (Academic Press, San Diego, 1989), Vol. 1, Chap. 18.
[39] K. Park, S. R. Simmons, and R. M. Albrecht, Scanning Microsc. **1**, 339 (1987).
[40] K. C. Grabar, P. C. Smith, M. D. Musick, J. A. Davis, D. G. Walter, M. A. Jackson, A. P. Guthrie, and M. J. Natan, J. Am. Chem. Soc. **118**, 1148 (1996).