A three stage model for adsorption of nonionic surfactants

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A three stage model for the adsorption of nonionic surfactants is proposed which makes use of existing theory from studies of random sequential adsorption. The model is simulated and the adsorption curves are found. The theory of random sequential adsorption is used to calculate the coverage exactly at the end of each of the three stages.

I. INTRODUCTION

The adsorption of nonionic surfactants onto both hydrophilic and hydrophobic surfaces has been extensively researched from the point of view of physical chemistry.[1,2] In these studies nonionic surfactants were assumed to interact with both the surface and each other. The resultant adsorption isotherms were then explained in terms of interaction strength and surfactant orientation.

A five stage model for adsorption has been postulated[1,3] in which interaction was favored with the surface by a specific part of the molecule (see Fig. 1). This model contains three different adsorption sequences, denoted by A, B, and C. The adsorption sequence is determined by the surfactant's interactions with the surface. In sequences A and C a vertically orientated monolayer is formed in stage V, but sequence B halts at stage III. The processes corresponding to these stages are as follows.

(I) The molecule is adsorbed onto a surface mainly due to van der Waal's interaction. Some other interaction may be present, but this will be surfactant/surface dependent. The molecule lies flat on the surface as a result of positive adsorption along its length. This may be caused by van der Waal's forces or hydrophobic/hydrophilic interactions with the surface.

(II) More surfactants are adsorbed onto the surface and are held flat against the surface until a horizontal monolayer is built up.

(III A) If the hydrophilic group is only weakly adsorbed it may be displaced from the surface by the alkyl chains of adjacent molecules.

(III B) If there is no favored type of displacement for the molecules then the adsorbate remains flat on the surface. This may be due to low concentration levels which do not give rise to significant surfactant–solute interactions.

(III C) If there is a strong interaction between the hydrophilic group and the surface the alkyl chains are displaced and surfactant–solute interactions become significant.

(IV A) and (IV C) As the surfactant concentration in the bulk solution approaches the critical micelle concentration the molecules on the surface change orientation, becoming vertically orientated and reveal more vacant sites on the surface. This results in a significant increase in the adsorption rate.

(V A) and (V C) Virtually all sites are full and a saturation limit is reached. After (V C) micelle production may take place on the surface.

In stages III and IV, for cases A and C in Fig. 1, the change in surfactant orientation from horizontal to vertical is fundamental to the explanation of the isotherm profile. Without it the secondary adsorption process cannot be explained in terms of the number of sites onto which adsorption can take place.

The isotherms corresponding to each of the three adsorption sequences is given in Fig. 2. The different stages are marked on the graphs. Note that the graphs are of surfactant adsorbed against concentration.

In this paper we propose a new three stage model based upon the process of random sequential adsorption. This is the process by which particles are placed on a surface or line in an irreversible, random manner. At each time step a random position and orientation is chosen for the particle. If a particle can be placed in this position without overlapping with any previously placed particle then it is deposited onto the line or surface. This subject is much studied, the review by Bartelt and Privman[4] provides an up to date list of references. Most problems have been solved exactly in one dimension either on the lattice, where k-mers are deposited,[5,6] or in the continuum, where lines of length 1 are deposited.[7] In the continuum the problem is better known as the random car parking problem.

In two dimensions various numerical studies have been performed.[4] In all these models the surface becomes covered with particles as time evolves. When the surface is full, in the $t = \infty$ limit, no further deposition is possible and the surface is said to be jammed. The proportion of the surface covered in this limit is called the jamming coverage.

II. THE THREE STAGE MODEL

When intermolecular interactions are considered to be negligible it is possible to model adsorption processes using k-mers. Each k-mer has a preferred end for adsorption onto the surface. The end is predetermined at random. In this paper we introduce a three stage model for the adsorption of nonionic surfactants in which the first and last stages can be described by the random sequential adsorption of these k-mers. The second stage is a change in ori-
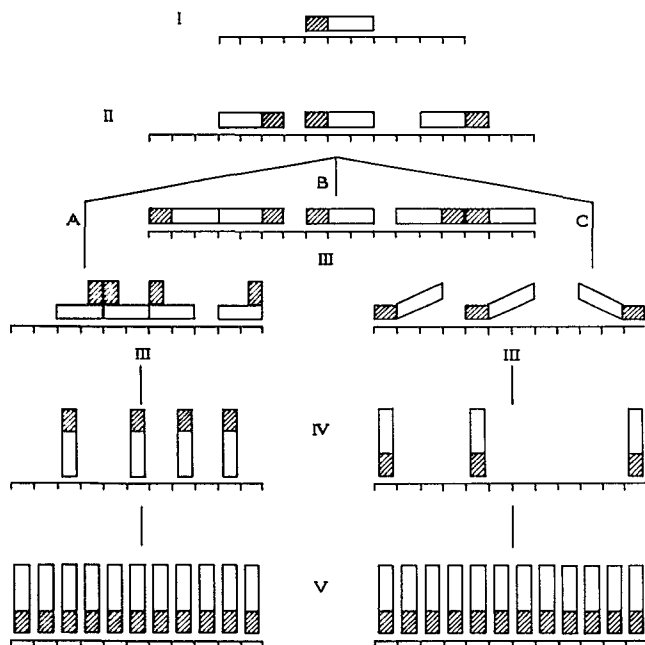
FIG. 1. The five stage adsorption sequence postulated by Ref. 1.
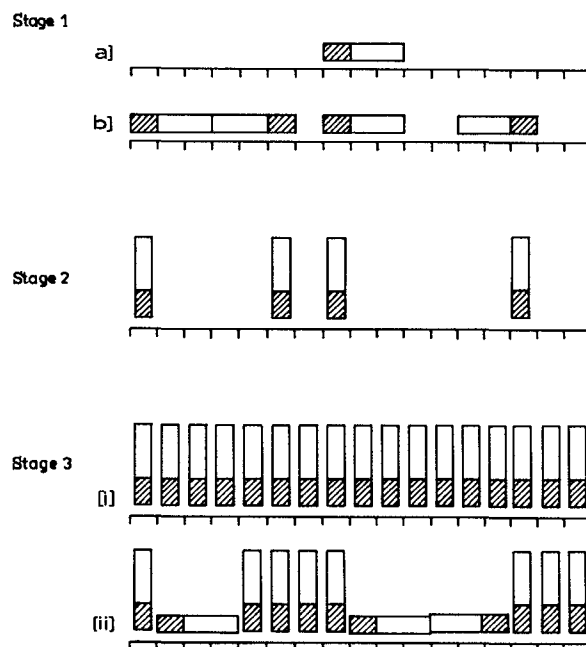

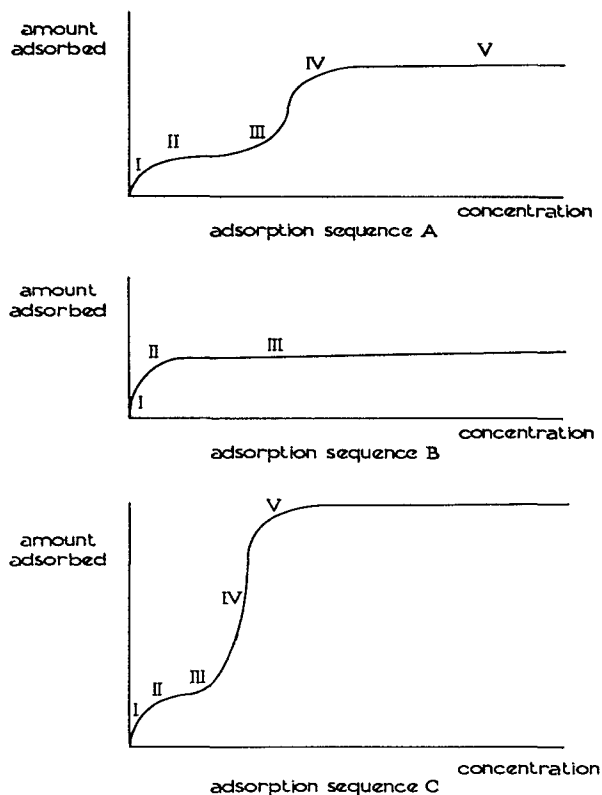FIG. 3. The three stage model for the adsorption of nonionic surfactants.

FIG. 2. The isotherm corresponding to each of the sequences in the five stage model.

entation of the k-mers from horizontal to vertical. The preferred end is the one that remains in contact with the surface.

We now consider each stage of this three stage model, shown in Fig. 3, in detail.

A. Stage 1

The molecule is adsorbed onto a surface which has very few other molecules adsorbed. The molecule lies horizontally due to the weak van der Waal's interaction with the surface along the length of the molecule.

As more molecules are adsorbed onto the surface a randomly orientated monolayer is formed. Such monolayers have known dynamics and calculable coverage.[4,5]

B. Stage 2

It is assumed that the jamming limit is reached in stage 1 before stage 2 begins. During stage 2 the adsorbed molecules lift up preferentially to become vertically orientated, thus exposing more vacant sites. A k-mer will lift up to reveal $k-1$ sites. The preferred end of the k-mer remains in contact with the surface. This process takes place much faster than both the previous and subsequent adsorption mechanisms and is simulated as an almost instantaneous event. In this way there is no gradual lifting of the monolayer but a distinct transition from one state to another.

C. Stage 3

Molecules are adsorbed onto the surface in the vacant sites revealed by stage 2. The orientation of the molecules adsorbed in stage 3 strongly affects the total number of molecules placed on the surface at saturation. Thus adsorption in stage 3 can be modeled as being either: (i) by

the deposition of molecules with a vertical orientation only, resulting in a vertically orientated monolayer (see Fig. 3); or (ii) by the deposition of a mixture of horizontal and vertical molecules.

III. THEORY

In this section the various stages are described theoretically. The quantities given are for the deposition of dimers although they are easily generalized to k-mers.

A. Stage 1

Stage 1 is just the random sequential adsorption of k-mers onto an empty line. Thus for dimers $(k=2)$ the coverage at time t (Refs. 4 and 5) is

$$\theta(t) = 1 - \exp\{-2[1 - \exp(-t)]\} \tag{1}$$

and once the jamming limit has been reached the final coverage is simply

$$\theta(t=\infty) = 1 - \exp(-2). \tag{2}$$

The probability of a single site being vacant on the surface, $P_1(1)$, is

$$P_1(1) = \exp(-2), \tag{3}$$

where $P_r(n)$ is defined as the probability that a site is part of a section of n or more empty sites at the end of stage r. The coverage at the end of the rth stage can be easily obtained from these probabilities; it is just $1 - P_r(1)$.

B. Stage 2

In stage 2 the k-mers lift up to reveal more vacant sites while keeping their preferred end in contact with the surface. For dimers no more than three adjacent sites will be vacant once they have become vertically orientated. Consequently, $P_2(n)$, the probability of n or more adjacent sites being vacant after stage 2, will be nonzero for $n=1, 2$, and 3 only. It is simple to show that they are given by

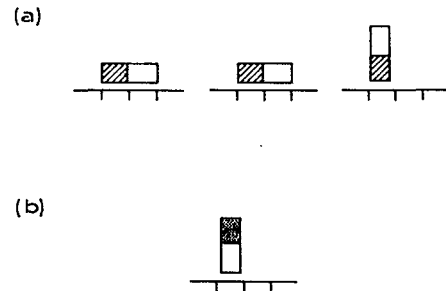$$P_2(3) = \frac{1}{4} P_1(1) = \frac{\exp(-2)}{4}, \tag{4}$$

FIG. 4. (a) The permitted orientations of dimers in the third stage of sequence (ii) (b) and the orientation not allowed.

$$P_2(2) = \frac{1}{4} P_1(0) + \frac{1}{2} P_1(1) + 2P_2(3)$$

$$= \frac{1 - 5\exp(-2)}{8}, \tag{5}$$

$$P_2(1) = \frac{1}{2} P_1(0) + \frac{1}{4} P_1(1) + 3P_2(3)$$

$$- 2[P_2(2) - 2P_2(3)]$$

$$= \frac{1 - \exp(-2)}{2}. \tag{6}$$

The probabilities $Q(n)$ of exactly n adjacent vacant sites are

$$Q(3) = P_2(3), \tag{7}$$

$$Q(2) = P_2(2) - 2P_2(3), \tag{8}$$

$$Q(1) = P_2(1) + 3P_2(3) - 2[P_2(2) - 2P_2(3)], \tag{9}$$

with the fraction of vacant sites, T, being given by

$$T = Q(1) + 2Q(2) + 3Q(3). \tag{10}$$

This quantity can be used to check that the sum of the fractions of occupied and vacant sites is one.

C. Stage 3

The line is not empty at the onset of stage 3 so it is not possible to use the initial condition, $P(s,0) = 1$ for all s, used in the solution of the dynamics in stage 1. On completion of stage 2 there are only gaps of lengths 1, 2, and 3 so $P(s,0)$ is nonzero for $s=1$, 2, and 3 only. Now the equations cannot be solved exactly and and we iterate them numerically using, for dimers, (4,5,6) as initial conditions.

(i) If stage 3 is the adsorption of vertically orientated k-mers only, i.e., monomers, the rate equations are[4,5]

$$-\frac{dP(s,t)}{dt} = \begin{cases} (k-s+1)P(k,t) + 2\sum_{j=1}^{s-1} P(k+j,t) & s \leqslant k \\ (s-k+1)P(s,t) + 2\sum_{j=1}^{s-1} P(s+j,t) & s \geqslant k \end{cases} \tag{11}$$

For $k=1$, these equations give

$$-\frac{dP(s,t)}{dt}=sP(s,t) \tag{12}$$

and hence an exponential destruction of the gaps.

(ii) If the adsorption in stage 3 is a mixture of horizontal and vertical k-mers the rate equations can be obtained from those for the deposition of two k-mer sizes k_1, k_2 with $k_2 \leqslant k_1$. These have been shown to be of the form[8]

$$-\frac{dP(s)}{dt}=\begin{cases} \alpha(k_1-s+1)P(k_1)+(1-\alpha)(k_2-s+1)P(k_2)+2\sum_{j=1}^{s-1}[\alpha P(k_1+j)+(1-\alpha)P(k_2+j)] & s\leqslant k_2\leqslant k_1 \\[2mm] \alpha(k_1-s+1)P(k_1)+(1-\alpha)(s-k_2+1)P(s)+2\alpha\sum_{j=1}^{s-1}P(k_1+j)+2(1-\alpha)\sum_{j=1}^{k_2-1}P(s+j) & k_2\leqslant s\leqslant k_1 \\[2mm] \alpha(s-k_1+1)P(s)+(1-\alpha)(s-k_2+1)P(s)+2\alpha\sum_{j=1}^{k_1-1}P(s+j)+2(1-\alpha)\sum_{j=1}^{k_2-1}P(s+j) & k_2\leqslant k_1\leqslant s \end{cases} \tag{13}$$

where α, $1-\alpha$ are the probabilities of depositing a k-mer of length k_1, k_2, respectively. We are interested in $k_1=k$ and $k_2=1$.

It can be argued that the probability of adsorption of a horizontal dimer is twice that of a vertical dimer since in the model considered the surface interacts preferentially with one end of the dimer. It is assumed that it is the shaded part of the dimer in Fig. 4(a) which interacts with the surface preferentially and remains in contact even after a change in orientation. For $k>2$ we also assumed that the probability of a horizontal deposition was twice that of a vertical one i.e., $\alpha=2/3$. Other assumptions are possible, particularly a k dependent α. We found that this had no qualitative effect on the results for the relatively small values of k that we considered. Thus to summarize, stage 3 using sequence (ii) can be described for k-mers using Eq. (13) with $k_1=k$, $k_2=1$, and $\alpha=2/3$. The initial conditions for dimers are given in Eqs. (4), (5), (6).

IV. MODEL SIMULATION RESULTS

Figure 5 shows a plot of the number of k-mers placed against time, for molecules of lengths $k=2$, 5, 10, and 20 on a lattice of 100 000 sites. In this simulation only vertical molecules are adsorbed in stage 3. Figure 6 shows the same plot in which both horizontal and vertical molecules are adsorbed in stage 3. Figure 7 shows a comparison between adsorption mechanisms used in Figs. 5 and 6 for k-mers of lengths $k=2$ and 10.
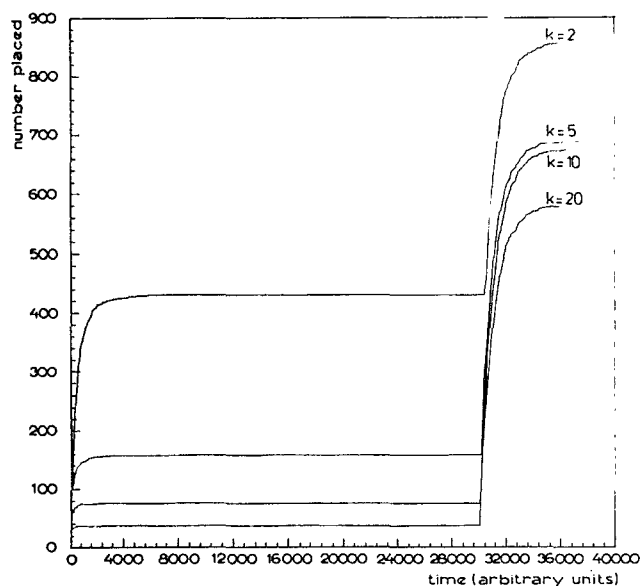

FIG. 5. Number of k-mers placed against time from sequence (i) of the three stage model. The graphs are for $k=2$, 5, 10, and 20.
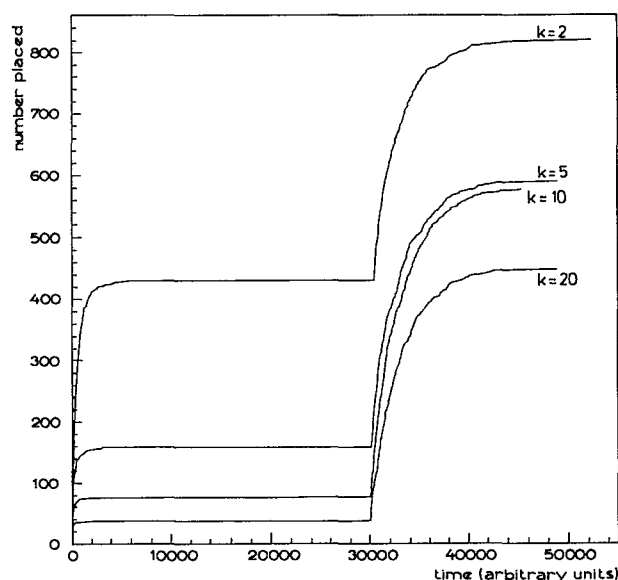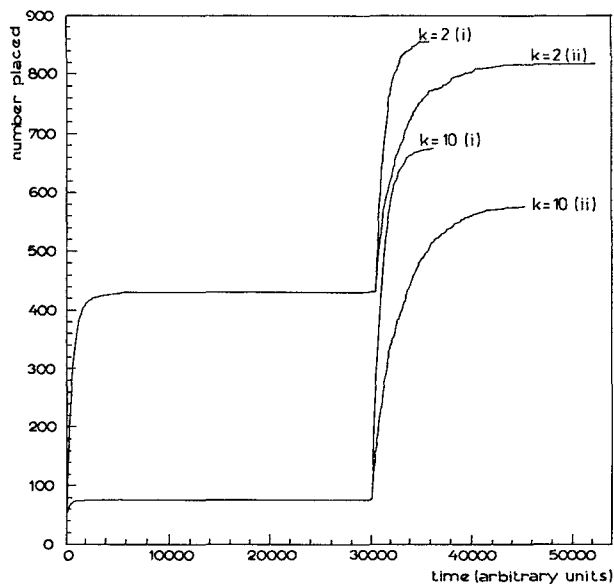

FIG. 6. Same as Fig. 5 for sequence (ii).

FIG. 7. A comparison between adsorption sequences (i) and (ii) for
$k=2$ and 10.

FIG. 9. Same as Fig. 8 but for sequence (ii).

Figure 8 shows the probability per site of finding a gap of length 1, 2, and 3 during stage 3 with only vertical dimers are adsorbed. Figure 9 shows the same quantities if both vertical and horizontal dimers are being deposited. A comparison between the probabilities shown in Figs. 8 and 9 is shown in Fig. 10. It can be seen that deposition of only vertical dimers in stage 3 leads to a faster rate of destruction compared to that obtained by deposition of both horizontal and vertical dimers.

The curves in Figs. 5, 6, and 7 can be understood as follows. The initial rise and plateau is stage 1, the vertical rise is stage 2, and the eventual saturation is stage 3. All
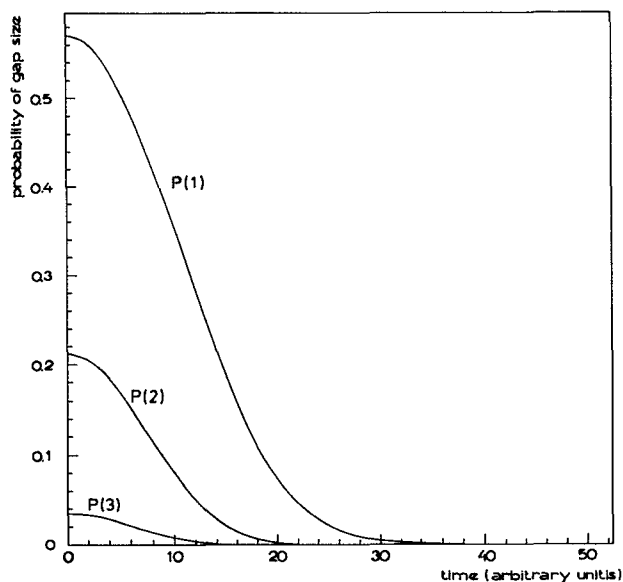
these curves are similar to the adsorption curves in Fig. 2. The curves can been made to look more like the experimental curves by shortening the time allowed for stage 1.

V. CONCLUSIONS

A simple three stage model for the deposition of nonionic surfactants based on the deposition of k-mers was introduced. The deposition of k-mers was modeled in two ways: depositing molecules in stage 3 which are vertical and both vertical and horizontal.

FIG. 8. Probability per site of gaps of length 1, 2, and 3 during sequence (i) of the three stage model.

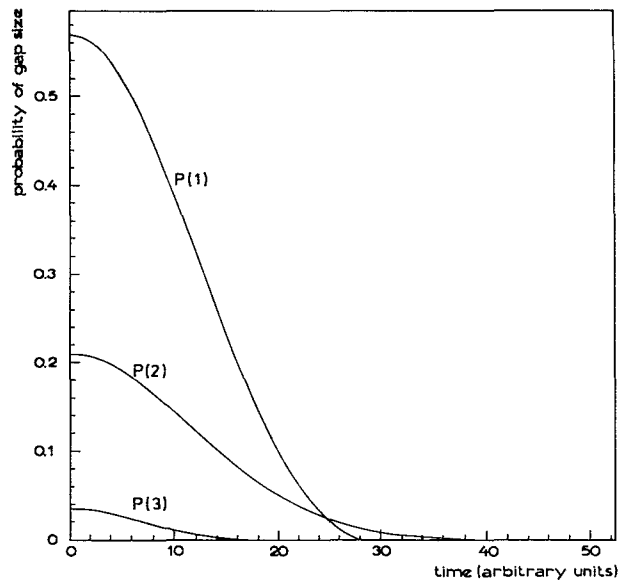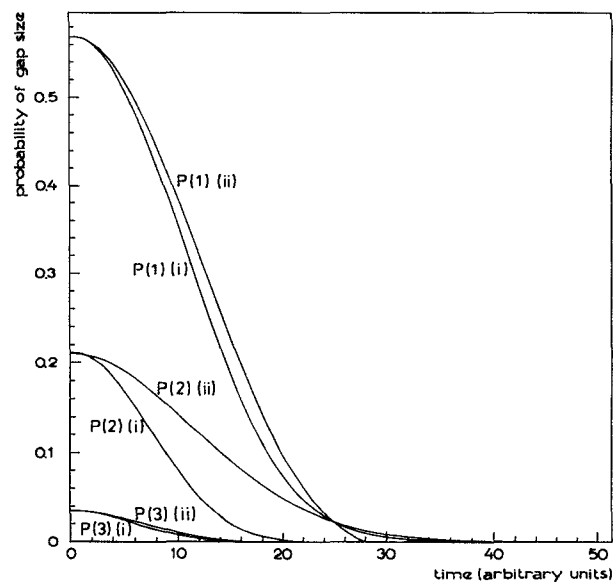FIG. 10. A comparison of the probability per site of gaps of length 1, 2, and 3 for adsorption sequences (i) and (ii).

By using the differential rate equations of the random sequential adsorption of k-mers to describe the first and third stages of adsorption and statistically demonstrating the effect of molecule orientation change within stage 2, all three stages can be described analytically. The analytical results were in complete agreement with the numerical work. The plots of number of molecules placed against time have the same shape as the concentration isotherms for the five stage model.

By taking a realistic but at the same time simple model we have been able to describe all the stages of the deposition process in terms of master equations and hence to study the process analytically. It may be possible for future work to use these analytical results to analyze adsorption isotherms that have been obtained experimentally. Isotherms could be fitted using Eq. (13) with α, k_1, k_2, and the length of stage 1 as free parameters.

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