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# Discontinuous formation and desorption of clusters during particles adsorption at surfaces

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**Abstract**

A theoretical model was derived to describe the discontinuous formation and desorption of clusters during particle adsorption at surfaces. Two steps were investigated: (1) time-dependent adsorption, where we found that the initial slope and the limiting magnitude of an adsorption isotherm depend on the clusters' distribution. A higher magnitude of both the adsorption and desorption rates appear to contract the time scale and hence increase the initial slope. Decreasing the geometrical parameter, $q$, which represents the shape of an adsorbed cluster, enhances the growth of large clusters on the surface. (2) A concentration dependence model shows that the number of adsorbed molecules increases with increases in the value of $n$ (nucleation capacity). Furthermore, higher rates of adsorption provide steeper initial slopes (higher affinity of, molecules to surface). Decreasing $q$ from 2 to 1, i.e. from a circular to a linear cluster formation, slightly decreases the magnitude of the isotherms.

*Keywords:* Protein adsorption; Aggregation; Ferritin; Clusters

## 1. Introduction

Macromolecular reactions at surfaces have many common characteristics. The initial reaction is often cooperative [1,2], leading to an autocatalytic binding reaction, and equilibrium is reached slowly through a logarithmic decrease of the reaction rate [3–5]. The dualistic kinetics of the reaction probably reflect fundamental properties of macromolecules dissolved in water. Ferritin adsorption, a model system of macromolecular reactions at interfaces, has been extensively described experimentally [1,6]. The main finding is that clusters of molecules are formed during the accelerated binding reaction [1], and that these clusters desorb during the retarded phase of binding [4,7]. The aim of the present study was to find a proper theoretical approach to describe the discontinuous formation and desorption of clusters during particle deposition at surfaces.

## 2. Theory

In this theory it is assumed that: there is a continuous, ideal surface immersed in a colloidal solution; particle adsorption to the clean surface occurs with a certain probability; cluster formation is controlled by adsorption of molecules from the solution; desorp-

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tion and transition rates (probabilities) depend on the geometry of the adsorbed cluster.

### 2.1. Basic model

A process is modelled whereby single molecules attach either to an empty nucleation site, $S_0$, or an existing cluster, $S_j$. There is also a competing mechanism in which clusters are desorbed from the surface, $S_j \rightarrow S_0$, leaving the site unoccupied. No attempt was made to model interactions between clusters on the surface or situations in which part of a cluster desorbs, $S_j \rightarrow S_{j-a}$.

### 2.2. Mathematical model

Consider a surface upon which a flow of particles hits the surface at right angles. We present a mathematical model which describes the number of attached particles on the surface under the following assumptions:

There are a finite number of sites where the particles may adhere.

A particle may also adhere to an occupied site, thus forming a cluster.

Clusters may desorb from the surface and thus leaving an empty site behind (fractions of the clusters are not allowed to desorb).

Sufficiently large clusters desorb with a probability arbitrarily close to one.

We define $S_0$ to be the number of empty sites and $S_j$ ($j = 1,2, \ldots$) the number of sites containing $j$ particles. The transition probability from $S_i$ to $S_j$ is denoted by $P_{ij}$. The desorption probability per unit time for clusters containing $j$ particles is denoted by $D_j$. Under the assumptions stated above we may formulate the following linear system of ordinary differential equations, modelling the evolution of $S_j$ (see Fig. 1):

$$\frac{\partial S_0}{\partial t} \equiv -P_{01}S_0 + \sum_{j=1}^{n} D_j S_j$$

$$\frac{\partial S_1}{\partial t} \equiv +P_{01}S_0 - (D_1 + P_{12})S_1$$

$$\frac{\partial S_2}{\partial t} \equiv +P_{12}S_1 - (D_2 + P_{23})S_2$$

$$\frac{\partial S_3}{\partial t} \equiv +P_{23}S_2 - (D_3 + P_{34})S_3$$

$$\cdots$$

$$\frac{\partial S_n}{\partial t} \equiv +P_{(n-1)n}S_{n-1} - D_n S_n$$

$$S_0(0) \equiv S_{\text{total}}, \quad S_j(0) \equiv 0,$$

$$n \geq j, \quad j > 0 \tag{1}$$

where $S_{\text{total}}$ is the total number of nucleation sites; $S_j(0)$ is the number of occupied nucleation sites at time $t = 0$; $S_j$ is the number of occupied sites with $j$ molecules in each site; $P_{01}$ is the binding rate to an empty site; $P_{jj+1}$ ($j > 0$) is the adsorption probability (related to the cooperativity of the solvent), given that a cluster which contains $j$ molecules increases in size to $j + 1$ molecules; $D_j$ ($j > 0$) is the desorption rate (probability) of a cluster containing $j$ molecules; and the term $\Sigma\, D_j\, S_j$ is the probability rate or the rate at which the occupied nucleation sites become empty (see also Zhdanov [8]). The cause of inserting this term is to preserve the number of empty ($S_0$) and occupied ($S_1$, $S_2$, ..., $S_n$) nucleation sites that must be constant at all times. Hence the rate at which the nucleation sites become empty depends only on the desorption probabilities and the number of occupied nucleation sites.

We note that the total number of particles attached to the surface at time $t$ is given by

$$N(t) \equiv \sum_{j>0}^{n} jS_j(t) \tag{2}$$

The strength of the model presented is that the probability rates, $P_{j,j+1}$ and $D_j$, are now determined

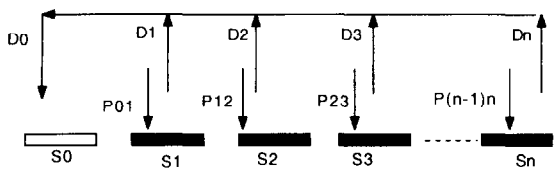


Fig. 1. Illustrated model used to evaluate molecule adsorption onto clusters of size 1, 2, ... or $n-1$ molecules. The first rectangle represents the naked surface, and the dark one is the occupied surface. $S_0$ is the number of empty nucleation sites, $S_{j,j+1}$ is the number of occupied nucleation sites with maximum $j$ molecules in each site, $P_{j,j+1}$ is the probability rate of adsorption onto a nucleation site which contains $j$ molecules, and $D_j$ ($j > 0$) is the probability rate of desorption of a cluster of size $j$ molecules.

by the details of the interaction between molecules in solution and a given cluster size and not by a general interaction parameter.

### 2.3. Adsorption and desorption rates

The boundary length of a circular cluster is proportional to the square root of its area, and hence to its molecule count. This is true (with a different proportionality constant) even if the clusters are not really circular but grow uniformly (in probability) along different directions of the surface. The binding rate to previously occupied nucleation sites is given by

$$P_{jj+1} \cong a * j^{1/q}, \quad 1 \le q < 3 \tag{3}$$

where $a$ depends on the flux of incoming molecules and binding forces between the molecule–molecule and the molecule–surface, and $q$ is related to the topographical formation of the adsorbed clusters and is expected to have the value between (1 and 3), for example $q = 2$ for circular cluster formation. Some comments regarding the parameter $q$ are of interest. As it is difficult to describe the cluster formation prior to adsorption, the parameter $q$, which indeed depends on the shape of the adsorbed clusters, will have to be determined experimentally. The binding to an empty nucleation site is defined by

$$P_{01} \cong b \tag{4}$$

where $b$ depends on the flux (molecule concentration close to the surface) of incoming molecules, binding forces between the molecules and the surface, and the sticking coefficient.

For cluster desorption, we start with a very simple model which increases linearly with the dimension of adsorbed clusters.

$$D_j = cj \tag{5}$$

where $c$ is related to the strength of molecular desorption at the surface.

A possible explanation behind the assumption in Eq. (5) is that: aggregates should be more stable toward desorption than single adsorbed molecules, since they are bound to each other by the 'condensation' energy. However, the stability of a small aggregate, or cluster, consisting of only a few molecules, is not determined only by the bulk 'condensation' energy. This is because the molecules in such a cluster usually have fewer nearest neighbours than in the bulk, and almost always fewer nearest or no next-nearest neighbours. Thus, their surface-to-volume ratio is very high. The resulting high surface energy makes the large clusters less stable.

### 2.4. Steady state

After a long adsorption time, $t$, the model approaches a state where single free molecules adsorb to the surface and clusters of different shape, $q$, and size, $j$, desorb. As a consequence, a steady state is set up where the cluster distribution on the surface is constant. Hence for an arbitrary cluster size $j$, we have

$$P_{j,j+1}S_j \equiv (D_{j+1} + P_{j+1,j+2})S_{j+1}, \quad j > 0 \tag{6}$$

and for the whole system of $n$ different cluster size we can write the following system of linear equations:

$$\begin{aligned} P_{01}S_0 &\equiv (D_1 + P_{12})S_1 \\ &\vdots \\ P_{n-1n}S_{n-1} &\equiv D_nS_n \end{aligned} \tag{7}$$

We shall keep in mind that $S_j$ is the probability theoretical expectation value for the number of occupied nucleation sites. Using Eq. (7), the number of occupied nucleation sites, $S_j$ can be written as a function of the nucleation sites, $S_1$, and the rates of adsorption and desorption, $P_{j,j+1}$, $D_j$,

$$S_j \equiv S_1 \prod_{i=2}^{j} \left( \frac{P_{i-1\,i}}{D_i + P_{i\,i+1}} \right),$$

$$j \le n, \quad P_{n\,n+1} = 0 \tag{8}$$

where $S_1$ is the number of occupied nucleation sites that contain one single molecule. Furthermore, there is the following relation between $S_1$ and $S_0$:

$$S_1 \equiv \frac{P_{01}}{D_1 + P_{12}} S_0 \tag{9}$$

This equation, together with Eqs. (8) and (2), give the total number of adsorbed molecules versus the

number of empty nucleation sites, the adsorption and the desorption rates.

$$N(t) \equiv \frac{P_{01}}{D_1 + P_{12}} S_0 \left[ 1 + \sum_{j=2}^{n} j \prod_{i=2}^{j} \left( \frac{P_{i-1\,i}}{D_i + P_{i\,i+1}} \right) \right]$$

$$j \leq n, \quad P_{n\,n+1} = 0 \qquad (10)$$

This is the binding isotherm of the total number of adsorbed molecules.

For the case in which a nucleation site contains a maximum of one single molecule, $S_j = S_1$, i.e. there is no interaction between neighbour molecules, Eq. (10) reduces to the general equation derived by Langmuir [9]

$$N_1 = S_{\text{total}} \frac{P_{01}}{D_1 + P_{01}} \qquad (11)$$

where $S_{\text{total}} = S_1 + S_0$, $D_1$ is the desorption rate of clusters containing one molecule.

## 3. Results and discussion

To solve the system of differential equations (Eq. (1)), we must designate some values for the following parameters: $n - 1$, the maximum number of molecules that can be contained in a nucleation site; $q$, the geometrical shape factor; and $S_0(0)$, the total number of empty nucleation sites. To solve the system of differential equations, we choose the following programme 'ode 45 4th/5th order Runge–Kutta–Fehlberg method' with the values $n = 33$, $q = 2$, and with the initial conditions $= [S_{\text{total}}, 0, 0, \ldots, 0_n]$. The remaining parameters, $P$ and $D$, will be chosen to give the best overview of the adsorption isotherms.

The conclusion of this model is: (a) different isotherms (time or concentration dependent) with aggregate of size 1, 2, ..., $n$ molecules can be obtained; (b) electron micro graphs of adsorbed molecules [5] can be modelled if we count the percentage of adsorbed cluster with different size $j$. For example let us say we got the following values: 10% $S_1$, 40% $S_2$, 30% $S_{16}$, and 20% $S_n$. Then the total adsorption isotherm (depending on whether the variable is the adsorption time or the concentration of free molecules) can be described by Eq. (2) or Eq. (10) where only the values $j = 1$, 2, 16, and $n$ are to be considered.

### 3.1. Time dependence

Fig. 2 shows three adsorption isotherms. The solid line (adsorption onto empty nucleation sites) shows no cooperativity of binding as expected, where the others (adsorption onto nucleation sites that contain 3, 5, and 8 molecules) show cooperative binding followed by a decreasing number of clusters.

In Fig. 3, the slope of the isotherm becomes steeper when increasing the constant $b$ from 1 to 10. This is in accordance with the fact that increasing the sticking probability increasing the slope of the adsorption isotherm, i.e. higher energy interaction between single molecules(monomers) and a surface. Another effect of increasing $b$ is that most of the adsorbed clusters are monomers. This is due to the fact that increasing the interaction energy between monomers and a surface decreasing the rate of surface diffusion, thereby making the formation of large aggregates less probable.

Changing the shape parameter, $q$, from 2 to 1 (circular to linear cluster formation) increases the

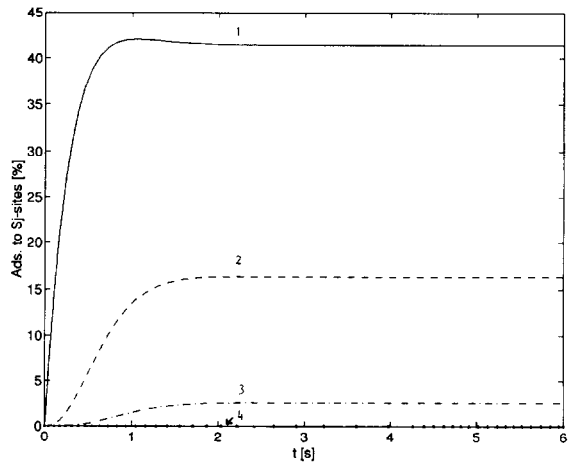


Fig. 2. Results of calculations on the model in Fig. 1 with $q = 2$, $a = b = c = 1$, $S_{\text{total}} = 10$. (1) Adsorption to empty nucleation sites, (2) adsorption to occupied nucleation sites each containing 3 molecules (cooperative adsorption), (3) adsorption to occupied nucleation sites that contain 5 molecules each, and (4) adsorption to nucleation sites with 8 molecules per nucleation site, nearly visible.

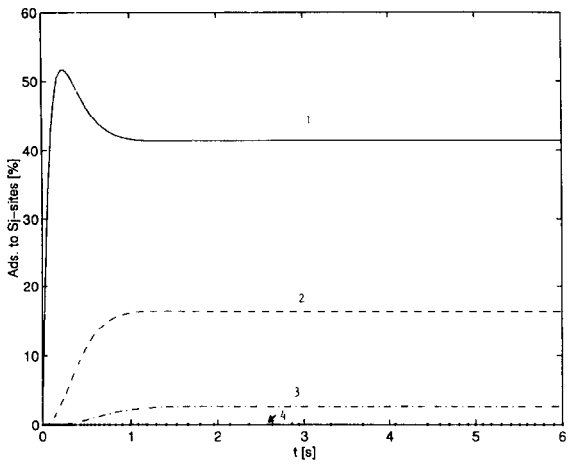


Fig. 3. The effect of increasing $b$ from 1 to 10 leading to a steeper slope of the isotherm (compare Fig. 2). Note the over-shot on the solid line ($j = 1$) before reaching steady state. Observe the time scale.

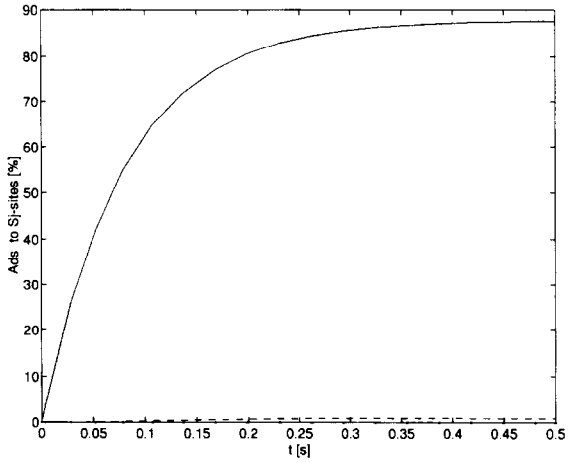


Fig. 5. Calculation on the model in Fig. 1 with $q = 2$, $a = b = 1$, $c = 10$, $S_{total} = 100$. By increasing the rate of desorption, the percentage of larger clusters ($j = 5$, 8) on the surface has disappeared. The notation of the lines are the same as explained in the previous figures.

affinity (slope) of adsorption, making larger cluster appear more probable (compare Fig. 3 and Fig. 4). These phenomena (i.e., pseudo linear cluster formations are more probable than the circular ones) have been experimentally confirmed by Stenberg and Nygren [6]. Fig. 5, where the probability of desorption, $D$, increased by a factor 10, shows that small cluster formation (1, 3 molecules per nucleation site) is more probable than a larger one. One of many situation in which such a event occurs is possibly when larger clusters gain higher surface tension,

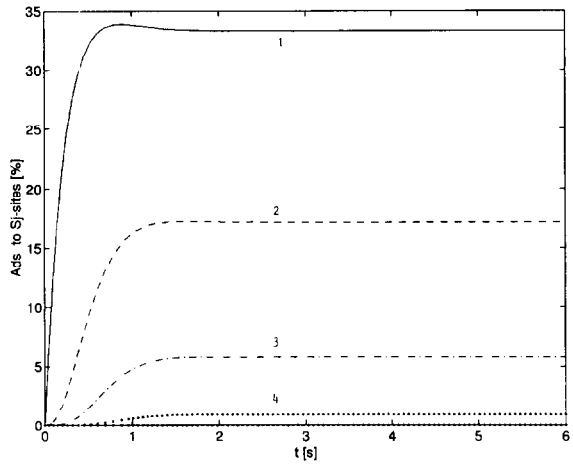


Fig. 4. Calculation on the model in Fig. 1 with $q = 1$, $a = b = c = 1$, $S_{total} = 10$. Pseudo linear cluster formation $1 < q < 2$ enhancing the appearance of larger cluster. The dotted curve (4) is now clearly visible. (2) adsorption to occupied nucleation sites each containing 3 molecules (cooperative adsorption) and (3) adsorption to occupied nucleation sites that contain 5 molecules each.

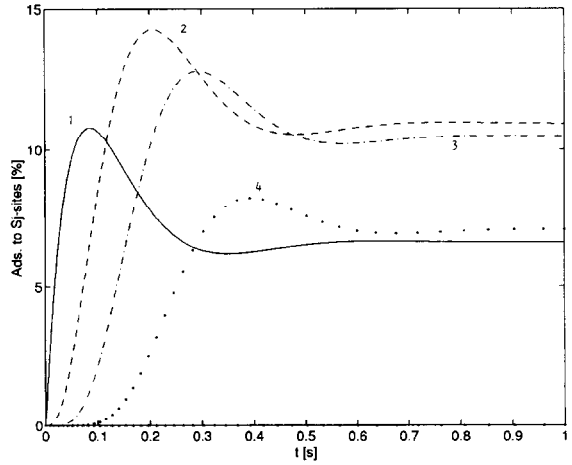


Fig. 6. Evaluation of the model with $q = 2$, $a = 10$, $b = c = 1$, $S_{total} = 100$. A dramatic change in cluster formations appear owing to an increase in the rate of adsorption. Almost the inverted situation of that shown in Fig. 2, the larger clusters seem to increase their representation on the surface. All the isotherms show over-shot characteristics. For higher rates of adsorption ($a > 20$), a total inversion appears, i.e. the probability of large cluster formation on the surface is higher than the probability of small cluster formation.

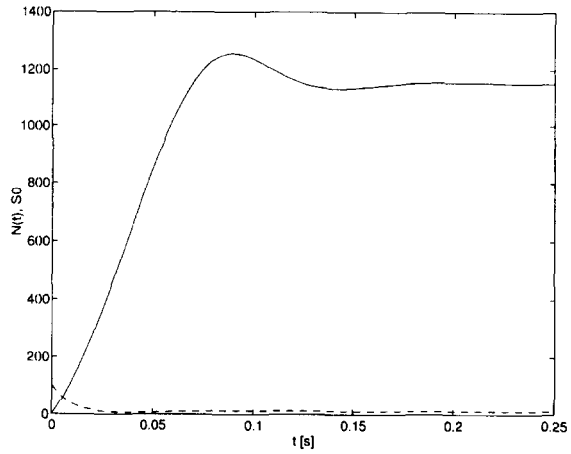


Fig. 7. The total number of adsorbed molecules versus the time $t$ without considering cluster size (solid line). The dashed line is the number of empty nucleation sites. $q = 2$, $a = 100$, $b = c = 1$, $S_{total} = 100$.

making the energy of interaction between the cluster–solution stronger than that for the cluster–surface (see page 213, this issue for more details). The effect of increasing the rate of adsorption is shown in Fig. 6. All isotherms curves with cluster size (1, 3, 5, and 8) appear to have over-shot in the range of.01 to 6 seconds (time values can alter depending on whether the magnitude of $P$ and $D$ is high, short time, or low, long time). These over-shots have been experimentally obtained by [10,11]. Fig. 6 also shows that larger cluster formation are more probable than

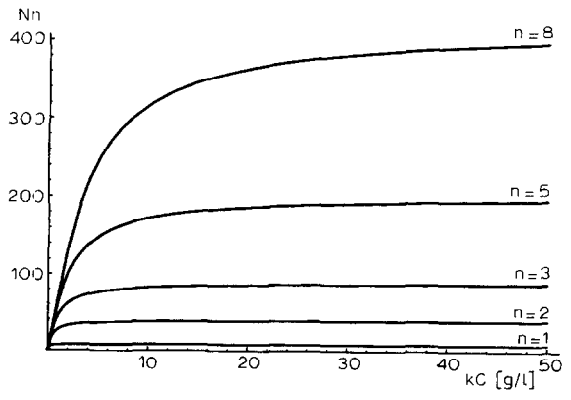


Fig. 8. The number of adsorbed molecules, $Nn$, versus the scaled bulk concentration, $kC$. Calculation from Eq. (16) with $q = 2$, $a/c = 8$, $b = 1$. Isotherms from top to bottom: $n = 8$, 5, 3, 2, and 1 molecule per nucleation site.

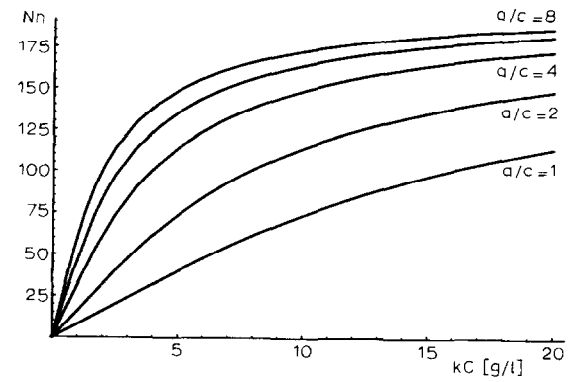


Fig. 9. The isotherms' variation with different values of the ratio a/c. Top to bottom: $a/c = 8$, 6, 4, 2 and 1, $b = 1$. The initial slope becomes steeper when increasing the value of $a/c$. $n = 8$ and $S_{total} = 10$.

smaller ones. The total number of molecules, regardless whether they adsorb to a cluster with 1, 2, ... or 31 molecules, is shown in Fig. 7.

### 3.2. Concentration dependence

Assuming that the probability rate of adsorption, $P_{jj+1}$, is proportional to the bulk concentration, $C_0$, and that the rate of desorption defined by the same definition given in Eq. (11), different shapes of isotherms will be obtained. Fig. 8 represent the number of adsorbed molecules versus the scaled bulk concentration, $kc$. As shown, the number of adsorbed molecules increases owing to an increase in the

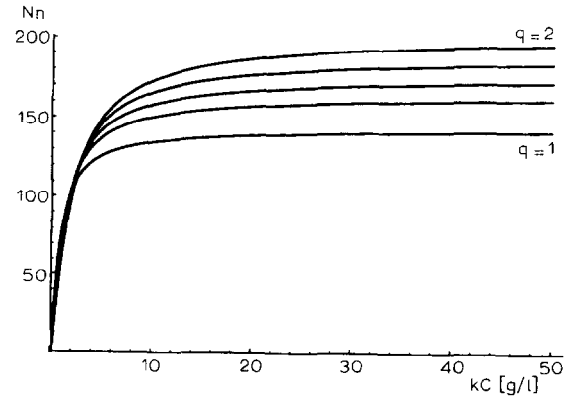


Fig. 10. Model calculation from Eq. (17) with $n = 8$, $a/c = 8$, $b = 1$, $S_{total} = 10$ and for different values of the geometrical parameter, $q$. Top isotherm $q = 2$, bottom isotherm $q = 1$.

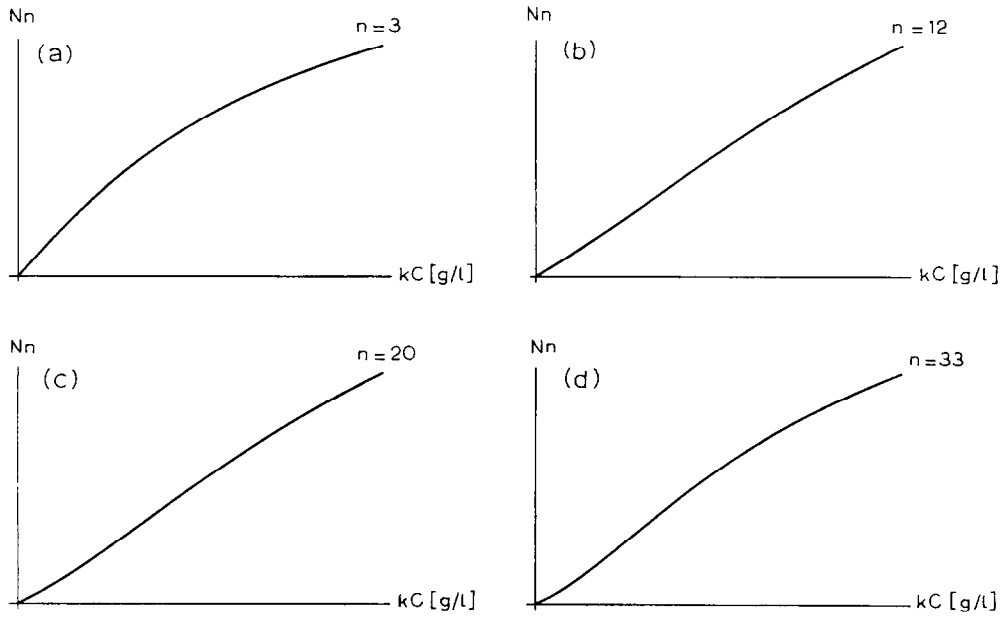


Fig. 11. The effect of the density of the occupied nucleation site on the isotherms. Higher values of $n$ promote positive cooperativity of adsorption. This cooperativity can be changed by changing the value of $a/c$. The number of adsorbed molecules and the bulk concentration are not to scale. Simulation of Eq. (17) with (a) $n = 3$, (b) $n = 12$, (c) $n = 20$, (d) $n = 33$. $a/c = 3$, $b = 1$.

capacity of a nucleation site, $n$. This increase seems to be reasonable, as the rate of adsorption is proportional to the number of available empty sites. It is useful to point out that, for higher $n$ values ($> 20$), the initial slope of the isotherms show a positive cooperativity pattern (see Fig. 11). In Fig. 9, a constant value of $n$ has been used. The illustrated isotherms represent different values of the ratio between the adsorption and desorption rate constants. The higher the ratios, the higher the initial slop of the isotherms. This seems to be in accordance with Dulm and Norde [11] as the rate of adsorption is proportional to the affinity between the molecules and the sorbent. Fig. 10 shows the variation of the parameter $q$. As $q$ decreases from 2 to 1 (from circular to linear cluster formation), the surface concentration slightly decreases.

The cluster distribution of particles (Figs. 2–6) may be used in order to describe adsorption of water on sodium ions [12]; the adsorption isotherm of ferritin on solid surfaces [13]; adsorption of virus particles [14] and adsorption of bacteria on surfaces [15] where the cluster distribution can be obtained experimentally. The statistical description of aggregation may be generalised to describe equilibrium of aggregation in solution where information on cluster distribution can be obtained experimentally [16,17]. It should be noted that the model presented here approaches a steady state after long times where single molecules are adsorbed and whole clusters desorb. These desorbed clusters (free clusters) make the most stable state in the observed system [18]. Thus the surface will act as a catalyst for aggregate formation in solution.

## Acknowledgements

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