Topic0140

Adsorption

Langmuir Adsorption Isotherm: One Adsorbate

The theoretical basis of Adsorption Isotherms is customarily described in terms of a balance of rates of adsorption and desorption. [1] Three important assumptions are made.

[1] The adsorbate covers the surface up to complete coverage as a monolayer on the substrate (adsorbent).

[2] There are no adsorbate—adsorbate interactions on the surface of the host substrate.

[3] On the substrate all binding sites are equivalent.

IUPAC recommends the use of variables expressed in terms of unit mass of adsorbent; \( \frac{n_{ad}}{w} \) is the specific reduced adsorption of chemical substance \( j \) where \( n_{ad} \) is the amount of adsorbate bound to mass \( w \) of adsorbent. In other words equations describing the process are transformed into intensive variables \([2,3]\).

In many interesting cases, small molecules (guest, adsorbate) bind to larger polymeric molecules (host, adsorbent) which provide a surface on which the smaller (guest) molecules are adsorbed. Adsorption data for such systems often follow a Langmuir pattern. Here we use a thermodynamic approach in descriptions of a thermodynamic equilibrium. Most texts describing Langmuir adsorption use a 'kinetic model', as indeed did Langmuir in his description of adsorption [1].

We consider the case where water is the solvent and substance \( j \) is the adsorbate. In the absence of adsorbate \( j \), the surface of the adsorbent is covered with water. When adsorbate \( j \) is added to the system, the adsorption is described by the following equation.

\[
j(aq; x_j) + H_2O(ad; x_{ad}^i) \rightarrow j(ad; x_{ad}^j) + H_2O(aq; x_i) \quad (a)
\]

The latter equation describes a physical process rather than a 'chemical' reaction but the symbolism is common. Thus \( x_j \) is the mole fraction of solute \( j \) in the aqueous phase; \( x_{ad}^i \) is the mole fraction of water in a thin solution adjacent to the surface of the adsorbate; \( x_i \) is
the mole fraction of water in the aqueous solution.; $x_j^{\text{ad}}$ is the mole fraction of the substance $j$ in the adsorbed layer. The process represented by equation (a) involves displacement of water from the ‘thin’ solution next to the adsorbent into the bulk solution. The reverse process describes the displacement of substance $j$ from this layer by water($\lambda$). At equilibrium, the two driving forces are balanced.

We use a simple on/off model for the adsorption in a closed aqueous system at fixed temperature $T$ and fixed pressure $p$ ($\cong p^0$).

Then, $\text{j(aq)} \leftrightarrow \text{j(ad)}$

At $t=0$, $n_j^0$ mol

At $t=\infty$, $n_j^0 - \xi$ mol

The latter condition refers to the equilibrium state; $\xi$ is the extent of binding of guest solute $j$ to the host adsorbate. To describe this equilibrium we need equations for the chemical potentials of $j$(aq) and $j$(ad). The fraction of adsorbent surface covered by chemical substance $j$ is defined as $\theta$. If there are $N$ sites on the adsorbate for adsorption, the amount of sites occupied equals $N \cdot \theta$ and the amount of vacant sites equals $\lfloor N \cdot (1 - \theta) \rfloor$.

The aim of the analysis is a plot showing the degree of occupancy of the surface of the adsorbent $\theta$ as a function of the equilibrium composition of the system. If the experiment involves calorimetry, we require equations which describe the heat $q$ associated with injection of a small aliquot of a solution containing the adsorbate into a solution containing the adsorbent.

The chemical potential of adsorbed chemical substance $j$, $\mu_j(\text{ad})$ is related to $\theta$ using a general equation.

$$\mu_j(\text{ad}) = \mu_j^0(\text{ad}) + R \cdot T \cdot \ln[f(\theta)]$$

(c)

In order to make progress we need an explicit equation for $f(\theta)$; $\mu_j^0(\text{ad})$ is the chemical potential of an ideal adsorbate on an ideal adsorbent where $\theta = 1/2$ at the same $T$ and $p$ [4]. At equilibrium the chemical potential of solute $j$ in solution equals the chemical potential
of the adsorbate. We express the composition of the solution in terms of the concentration of chemical substance $j$, $c_j$.

At equilibrium, $\mu_j (aq) = \mu_j (ad)$  \hspace{1cm} (d)

For solute, $j(aq)$, $\mu_j (aq) = \mu_j^0 (aq) + R \cdot T \cdot \ln[c_j (aq) \cdot y_j (aq) / c_r]$ \hspace{1cm} (e)

By definition, $c_r = 1 \text{ mol dm}^{-3}$; $y_j$ is the solute activity coefficient where,  

$$\lim (c_j \to 0) y_j (aq) = 1 \text{ at all } T \text{ and } p$$ \hspace{1cm} (f)

$\mu_j^0 (aq)$ is the chemical potential of solute $j$ in solution having unit concentration $c_j$, the thermodynamic properties of solute $j$ being ideal.

From equations (c) and (e) the equilibrium condition (d) requires, by definition, that

$$\Delta_{ad}G^0 = \mu_j^0 (ad) - \mu_j^0 (aq)$$

$$= -R \cdot T \cdot \ln[f(\theta)] + R \cdot T \cdot \ln[c_j (aq) \cdot y_j (aq) / c_r]$$

$$= -R \cdot T \cdot \ln(K_{ad})$$

The dimensionless property $K_{ad}$ is the equilibrium adsorption constant which depends on both $T$ and $p$ [5].

Then, $K_{ad} = f(\theta) \cdot c_r / c_j (aq) \cdot y_j (aq)$ \hspace{1cm} (h)

We envisage a solution volume $V$ prepared using $n_j^0$ moles of chemical substance $j$. [The assumption is usually made that the volume of the system is the volume of the solution.] The equilibrium concentration of substance $j$, $c_j^{eq}(aq)$ is given by equation (i) where $\xi^{eq}$ is the equilibrium extent of adsorption

$$c_j^{eq}(aq) = (n_j^0 - \xi^{eq}) / V$$ \hspace{1cm} (i)

$$K_{ad} = [f(\theta) / (n_j^0 - \xi)] \cdot [V \cdot c_r / y_j (aq)]$$ \hspace{1cm} (j)

Equation (j) describes the composition of the system. Granted therefore the applicability of equation (i) we anticipate specific applications of this equation will, at minimum, yield two pieces of information.

(i) Dependence of $\theta$ on total concentration of $j$ in the system, $n_j^0 / V$. 
(ii) Dependence of percentage of chemical substance $j$ bound on total concentration of $j$ in the system, $n_j^0 / V$.

If the system is prepared using $n_1$ moles of water, the enthalpy of the system is given by equation (k).

$$H(\text{system}) = n_1 \cdot H_j(\text{aq}) + (n_j^0 - \xi_{eq}) \cdot H_j(\text{aq}) + \xi_{eq} \cdot H_j(\text{ad}) \quad (k)$$

The dependence of enthalpy on the extent of adsorption is given by equation $(\lambda)$.

$$\frac{\partial H(\text{system})}{\partial \xi} =$$

$$n_1 \cdot \frac{\partial H_j(\text{aq})}{\partial \xi} + (n_j^0 - \xi_{eq}) \cdot [\partial H_j(\text{aq})/\partial \xi] - H_j(\text{aq}) \quad (\lambda)$$

$$+ H_j(\text{ad}) + \xi_{eq} \cdot [\partial H_j(\text{ad})/\partial \xi]$$

As a working hypothesis we assume that the properties of substance $j$ are ideal both in solution and as adsorbate. In other words there are no solute $j \leftrightarrow$ solute $j$ interactions in the aqueous solution, no bound $j \leftrightarrow$ bound $j$ interactions between adsorbed molecules and no solute $j \leftrightarrow$ bound $j$ interactions.

In summary the adsorbed $j$ molecules form monolayers and the adsorbed molecules are non-interacting with other adsorbed $j$ molecules and with $j$ molecules in solution [6].

(a) $y_j(\text{aq}) = 1.0$  
(b) $\frac{\partial H_j(\text{aq})}{\partial \xi} = 0.0$  
(c) $\frac{\partial H_j(\text{aq})}{\partial \xi} = 0.0$  
(d) $\frac{\partial H_j(\text{ad})}{\partial \xi} = 0.0$  

Therefore, $[\partial H(\text{system})/\partial \xi] = H_j(\text{ad})^0 - H_j(\text{aq})^\infty = \Delta_{ad}H^0 \quad (n)$

Here $H_j(\text{aq})^\infty$ is the limiting partial molar enthalpy of solute $j$ meaning that in effect the solute molecules in solution are infinitely apart. $H_j(\text{ad})^0$ is the standard partial molar enthalpy of the adsorbate, implying that on the surface of the host adsorbent the adsorbate molecules are infinitely far apart; i.e. there are no adsorbate-adsorbate interactions. $\Delta_{ad}H^0$ is the standard molar enthalpy for the adsorption of substance $j$ from aqueous solution on to the adsorbate.

In the next stage we require an equation for $f(\theta)$ in order to obtain an explicit equation for the chemical potential of adsorbed substance $j$. We use the Langmuir model [4];
\[ f(\theta) = \theta / (1 - \theta) \quad \text{(o)} \]

\( \theta \) is the fraction of the surface covered by the adsorbate at equilibrium, the fraction \((1 - \theta)\) being left bare; note that \( \theta \) is an intensive variable.

Then \( \mu_j(\text{ad}) = \mu_j^0(\text{ad}) + R \cdot T \cdot \ln[\theta / (1 - \theta)] \quad \text{(p)} \)

The standard state for adsorbed \( j \) molecules corresponds to the situation where \( \theta = \frac{1}{2} \); i.e \([\theta / (1 - \theta)]\) is unity. It is interesting to put some numbers to these variables. We set \( \chi = \ln[\theta / (1 - \theta)] \). Then for \( \theta = 0.1 \), \( R \cdot T \cdot \chi = -2.197 \cdot R \cdot T \). Hence when the surface is less than 50% covered the chemical potential of the adsorbate is less than in the adsorbed standard state. For \( \theta = \frac{1}{2} \), \( R \cdot T \cdot \chi = 0 \); at this stage the chemical potential of substance \( j \) in the adsorbed state equals that in the reference (standard) state. For \( \theta = 0.9 \), \( R \cdot T \cdot \chi = 2.197 \cdot R \cdot T \). As the surface occupancy passes 0.5, the chemical potential of the adsorbate increases above that in the reference state. According to equation (i) for a system where solute \(-j\) and adsorbate \(-j\) have ideal thermodynamic properties,

\[ K_{\text{ad}} = [\theta / (1 - \theta)] \cdot [V \cdot c_r / (n^0_j - \xi)] \quad \text{(q)} \]

With increase in \( \xi \) so \( \theta \) increases. Unfortunately we do not know how \( \theta \) and \( \xi \) are related. One procedure assumes that \( \theta \) is proportional to \( \xi_{\text{eq}} \), the constant of proportionality being \( \pi [4] \).

\[ K_{\text{ad}} = [\pi \cdot \xi_{\text{eq}} / (1 - \pi \cdot \xi_{\text{eq}})] \cdot [V \cdot c_r / (n^0_j - \xi_{\text{eq}})] \quad \text{(r)} \]

Hence, \((K_{\text{ad}} / V) \cdot (1 / c_r) \cdot (n^0_j - \xi_{\text{eq}}) = \pi \cdot \xi_{\text{eq}} / (1 - \pi \cdot \xi_{\text{eq}}) \quad \text{(s)} \)

By definition, \( \beta = [K_{\text{ad}} / V \cdot c_r]^{-1} \)

Then, \( \pi \cdot (\xi_{\text{eq}})^2 - \xi_{\text{eq}} \cdot [1 + \pi \cdot n^0_j + \beta \cdot \pi] + n^0_j = 0 \quad \text{(t)} \)

Equation (t) is a quadratic in the required variable \( \xi_{\text{eq}} \). With increase in amount of solute \( j \) in the system so the extent of adsorption increases. Recognising that \( \beta \) is taken as a constant,

\[ [d\xi_{\text{eq}} / dn^0_j] = [1 - \pi \cdot \xi_{\text{eq}}] / [(\beta \cdot \pi + \pi \cdot (n^0_j - \xi_{\text{eq}}) + (1 - \pi \cdot \xi_{\text{eq}})] \quad \text{(u)} \]

Equation (u) leads to an estimate of the dependence of \( \theta \) on the concentration of chemical substance \( j \) in the system. This analysis
assumes no interactions between adsorbed molecules on the adsorbent. This assumption is probably too drastic. One approach which takes account of such interactions is the Freundlich Adsorption Isotherm [7].

The chemical potentials of the adsorbed chemical substance j is related to θ using equation (v).

$$\mu_j(\text{ad}) = \mu_j^0(\text{ad}) + R \cdot T \cdot \ln[\theta / (1 - \theta)] - R \cdot T \cdot a \cdot \theta$$  \hspace{1cm} (v)

The parameter ‘a’ is an adsorbate-adsorbate interaction parameter. For systems where a < 0 (where θ is always positive) repulsion between adsorbed molecules raises the chemical potential above that described by the Langmuir model and disfavours adsorption. For system where a > 0, attraction between adsorbed j molecules lowers their chemical potentials below the chemical potentials described by the Langmuir model; i.e. adsorption is enhanced above that required by the ideal model. But as for the Langmuir model, θ is dependent on the extent of adsorption and thus almost certainly on the geometric properties of guest and host.

If the thermodynamic properties of the solute j in solution are assumed to be ideal, equation (r) is rewritten as follows.

$$K_{ad} = [\pi \cdot \xi_{\text{eq}} / (1 - \pi \cdot \xi_{\text{eq}})] \cdot \exp(-a \cdot \pi \cdot \xi_{\text{eq}}) \cdot [V \cdot c_j / (n_j^0 - \xi_{\text{eq}})]$$  \hspace{1cm} (w)

Another approach writes f(θ) using a general equation having the following form.

$$f(\theta) = \left[ \frac{\theta}{1 - \theta} \right] \cdot \left[ \frac{1}{n^\pi} \right] \cdot \left[ \frac{\theta + n \cdot (1 - \theta)}{1 - \theta} \right]^{n-1}$$  \hspace{1cm} (x)

For the Langmuir adsorption isotherm, n is unity. Otherwise n is a positive integer; n = 1, 2, 3,….Thus when n is set at 2 [5],

$$f(\theta) = \left[ \frac{\theta}{1 - \theta} \right] \cdot \left[ \frac{1}{4} \right] \cdot \left[ \frac{2 - \theta}{1 - \theta} \right]$$  \hspace{1cm} (y)

We comment on terminology. In enzyme chemistry, the term **substrate** refers to (in relative terms) small molecules which bind to an enzyme, a macromolecule. However in the subject describing **adsorption** of molecules on a surface, the molecules which are adsorbed are called the adsorbate. The macromolecular host is the **adsorbent** or **substrate**. In
other words the meaning of the term ‘substrate’ differs in the two subjects.

In general terms each enzyme has a unique site at which the adsorbate (substrate) is bound. However the term adsorbent implies that the ‘surface’ has a number of sites at which the adsorbate is adsorbed. The extent to which the sites are specific to a particular adsorbent is often less marked than in the case of enzymes. Nevertheless there is a common theme in which a substance j ‘free’ in solution loses translational freedom by coming in contact with a larger molecular system, being then held by that system.

Footnotes