CHEE 310 – Solved examples - Adsorption

Problem 1:
The data given below are for the adsorption of CO on charcoal at 273 K. Describe the adsorption using an appropriate adsorption isotherm and calculate the corresponding Gibbs energy of adsorption.

<table>
<thead>
<tr>
<th>$p$ / kPa</th>
<th>13.3</th>
<th>26.7</th>
<th>40.0</th>
<th>53.3</th>
<th>66.7</th>
<th>80.0</th>
<th>93.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$ / cm$^3$</td>
<td>10.2</td>
<td>18.6</td>
<td>25.5</td>
<td>31.5</td>
<td>36.9</td>
<td>41.6</td>
<td>46.1</td>
</tr>
</tbody>
</table>

Problem 2: Batch tests were performed in the laboratory using solutions of phenol in water and particles of granular activated carbon. The equilibrium data at room temperature are shown in the table below as the dependence of phenol surface concentration on the equilibrium concentration in the solution. Determine the isotherm that fits the data.

| $c$ / kg m$^{-3}$ | 0.322 | 0.117 | 0.039 | 0.0061 | 0.0011 |
| $\Gamma$ / kg kg$^{-1}$ | 0.15 | 0.122 | 0.094 | 0.059 | 0.045 |

Problem 3: Equilibrium isotherm data for adsorption of glucose from an aqueous solution to activated alumina are as follows:

| $c$ / g cm$^{-3}$ | 0.0040 | 0.0087 | 0.019 | 0.027 | 0.094 | 0.195 |
| $\Gamma$ / g$_{\text{solute}}$ g$_{\text{alumina}}$ -$^{-1}$ | 0.026 | 0.053 | 0.075 | 0.082 | 0.123 | 0.129 |

Determine the isotherm that fits the data and give the constants of the equation using the given units.

Problem 4:
Interaction of serum and plasma proteins with implanted biomaterials plays one of the major roles in the biocompatibility of the biomaterial. This is especially significant in the first few hours after the implantation, during which biomaterial-protein interactions occur. Adsorption of a protein layer onto medical implants in the body can lead to adverse effects such as inflammation, clot formation, and increase corrosion of metallic implants. Hence, it is of the major importance to characterize adsorption of major blood/serum proteins onto biomaterials’ surfaces.

(a) Table 1 below lists equilibrium adsorption data for the adsorption of serum protein fibrinogen onto a medical-grade stainless steel surface (316LVM) at 303 K. Your task is to use the Langmuir isotherm to describe this interaction, and subsequently to calculate the Gibbs energy of adsorption. Evaluate a suitability of the Langmuir isotherm by examining both the $\Gamma = f(c)$ and $\theta = f(c)$ relationships.

(b) You are also required to determine the orientation of the protein on the surface (side-on, end-on, or tilted and at what angle) at 100% coverage. The dimensions of the protein molecule are 6.5 nm $\times$ 47.5 nm, while the molecular weight is 340000 g/mol.

(c) As mentioned above, the first few hours after the implantation are crucial due to the adsorption of serum proteins on the biomaterial’s surface. An experiment was performed at 303 K with 316LVM coupons (1$\times$1 cm$^2$) in which the dependence of the surface amount (concentration) of fibrinogen was measured with time, and the corresponding data is presented in Table 2. The experiment was done using an advanced version of a FTIR technique, and the table shows the dependence of the integrated intensity of Amide I peak on time. Amide I peak is an IR ‘fingerprint’ of proteins, and the listed integrated intensity values ($A_{\text{amide I}}$ / cm$^{-1}$) are directly proportional to the corresponding surface concentration ($\Gamma$ / mg m$^{-2}$) of the protein as:
\[A_{amide I} = 0.4379 \times \Gamma.\]

Your task is to apply a first-order kinetic adsorption model to fit the data in Table 2, and to calculate the corresponding adsorption and desorption constants, the equilibrium constant, and the Gibss energy of adsorption. Compare the latter value to the Gibss energy of adsorption you calculated in (a), and comment the difference (if any). How long it would take to completely cover the implant’s surface under the conditions applied? To solve the problem, you can use either a Solver function in Excel, Mathlab or any other similar software package.

![Fibrinogen molecule – dimensions: 6.5 nm × 47.5 nm](image)

**Figure 1:**

<table>
<thead>
<tr>
<th>Table 1. Dependence of the fibrinogen surface concentration on the corresponding equilibrium concentration in the bulk solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_{fib} / \text{g L}^{-1})</td>
</tr>
<tr>
<td>(\Gamma / \text{mg m}^{-2})</td>
</tr>
<tr>
<td>(c_{fib} / \text{g L}^{-1})</td>
</tr>
<tr>
<td>(\Gamma / \text{mg m}^{-2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Dependence of the integrated intensity on time for the adsorption of fibrinogen on 316LVM from a solution containing 0.1 g/L of fibrinogen.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{amide I} / \text{cm}^{-1})</td>
</tr>
<tr>
<td>Time / min</td>
</tr>
</tbody>
</table>
**Problem 1:**

Using the Langmuir isotherm, \( \frac{p}{V} = \frac{1}{BV_{\text{mono}}} + \frac{p}{V} \)

Plot \( \frac{p}{V} \) vs. \( p \)

![Graph](image)

\[ y = 0.009x + 1.1972 \]
\[ R^2 = 0.998 \]

In order to determine \( \Delta G_{\text{ads}} \), we first evaluate \( V_{\text{mono}} \) from the slope of the curve: \( V_{\text{mono}} = 111.1 \text{ cm}^3 \).

Then from the intercept of the curve we calculate \( B = 0.0075 \text{ kPa}^{-1} = 0.76 \text{ atm}^{-1} \).

Now \( \Delta G_{\text{ads}} \) is:

\[ B = \frac{1}{P_o} \exp \left[ \frac{-\Delta G_{\text{ads}}}{RT} \right] \]

\[ 0.76 = \frac{1}{1} \exp \left[ \frac{-\Delta G_{\text{ads}}}{8.314 \times 273} \right] \]

\[ \Delta G_{\text{ads}} = 623.1 \text{ J/mol} \]
Problem 2:

Using the Langmuir isotherm, plot $c/\Gamma$ vs. $c$. Also using the Freundlich isotherm plot $\log(\Gamma)$ vs. $\log(c)$.

The Freundlich isotherm shows a better fit ($R^2=0.9941$) than the Langmuir isotherm ($R^2=0.9922$).
Problem 3:

Using the Langmuir isotherm, plot \( \frac{c}{\Gamma} \) vs. \( c \). Also using the Freundlich isotherm plot \( \log(\Gamma) \) vs. \( \log(c) \).

It is obvious from the plots that the data fits the Langmuir isotherm \( (R^2=0.9991) \) better than the Freundlich isotherm \( (R^2=0.899) \).

From the slope of the curve: \( \Gamma_{\text{mono}} = 0.14 \text{ g solute g alumina}^{-1} \).

From the intercept \( B = 60.5 \text{ cm}^3 \text{ g solute}^{-1} \).
Problem 4:

(a) Using the Langmuir isotherm, plot $c/\Gamma$ vs. $c$.

In order to determine $\Delta G_{ads}$, we first evaluate $\Gamma_{mono}$ from the slope of the curve: $\Gamma_{mono}= 2.29 \times 10^{-3}$ g m$^{-2}$. Then from the intercept of the curve we calculate $B= 0.041$ m$^3$ g$^{-1}$

In order to calculate $\Delta G_{ads}$ we need to convert B’s units to L/mol. We do that by multiplying by the molar weight of fibrinogen.

$B = 0.041$ m$^3$ g$^{-1} \times 340000$ g mol$^{-1} \times 1000$ L m$^{-3} = 1.394 \times 10^7$ L mol$^{-1}$.

Now the $\Delta G_{ads}$ value is:

$$B = \frac{1}{c_{sohent}} \exp \left[ \frac{-\Delta G_{ads}}{RT} \right]$$

$$1.394 \times 10^7 = \frac{1}{55.5} \exp \left[ \frac{-\Delta G_{ads}}{8.314 \times 303} \right]$$

$$\Delta G_{ads} = -51.6 \text{ kJ/mol}$$
In order to calculate the orientation (angle $\Phi$) of fibrinogen molecules adsorbed on the surface, we need to calculate length $l$ at 100% coverage. From the fit obtained in part (a) $\Gamma_{\text{mono}} = 2.29 \times 10^{-3}$ g m$^{-2}$.

Using the relationship:

$$\frac{\Gamma_{\text{mono}}}{M_{\text{wt}}} = \frac{\# \text{molecules}}{N_A}$$

$$\frac{2.29 \times 10^{-3}}{340000} = \frac{\# \text{molecules}}{6.022 \times 10^{23}}$$

# molecules = $4.056 \times 10^{15}$ molecules/m$^2$

The number of molecules per square meter ($n_{\text{total}}$) is defined as the no. of molecules in the y direction ($n_y$) multiplied by the no. of molecules in the x direction ($n_x$), where:

$$n_y = \frac{1 \text{moleucle} \cdot m}{6.5 \times 10^{-9} m} = 1.538 \times 10^8 \text{molecules/m}$$

$$n_x = \frac{n_{\text{total}}}{n_y} = \frac{4.056 \times 10^{15}}{1.538 \times 10^8} = 2.637 \times 10^7 \text{molecules/m}$$

$$\ell = \frac{1m}{2.637 \times 10^7} = 3.79 \times 10^{-8} m = 37.9 \text{nm}$$

$$\cos \Phi = \frac{37.9 \text{nm}}{47.5 \text{nm}} = 0.8$$

$\Phi = 37^\circ$
(c) Using a first order kinetic adsorption model to describe the adsorption of fibrinogen on the solid surface at constant temperature, we get:

\[
\frac{d\theta}{dt} = k_{ads} \times c_{fib} \times (1 - \theta) - k_{des} \times \theta
\]

Integrating the above expression and solving for \(\theta\), we get the following:

\[
\theta(t) = \frac{k_{ads} c_{fib}}{k_{ads} c_{fib} + k_{des}} \left[1 - \exp\left(-\left(k_{ads} c_{fib} + k_{des}\right)t\right)\right]
\]

We also know that \(\theta(t) = A/A_{max}\), where,

\[
A_{max} = 0.4379 \times \Gamma_{max}
\]

\(\Gamma_{max} = 1.69 \text{ mg} \text{ m}^{-2}\), which can be read from table 1 at \(c_{fib} = 0.1 \text{ g} \text{ L}^{-1}\).

Therefore \(A_{max} = 0.74 \text{ cm}^{-1}\).

Using Excel or any solver program, we can minimize the sum of error between the experimental data in table 2 and the data obtained from the model. Therefore we find:

\[
k_{ads} = 0.98 \text{ L g}^{-1} \text{ min}^{-1} = 3.3 \times 10^5 \text{ M}^{-1} \text{ min}^{-1}
\]

\[
k_{des} = 3.63 \times 10^{-2} \text{ min}^{-1}
\]

\[
B = \frac{k_{ads}}{k_{des}} = 26.96L/ g \times 340000g / mol = 9.17 \times 10^6 L / mol
\]

\[\Delta G_{ads} = -50.5 \text{ kJ/mol}\]

The values of \(\Delta G_{ads}\) obtained in parts (a) and (c) are very close to each other. The discrepancy between the two values is due to experimental error.

Under the conditions applied, the equilibrium coverage reached is ca. 74%. This maximum coverage is achieved at the time when the coverage becomes independent of time. This can be observed from the following curve where the surface coverage becomes flat at ca. 60 min.
The graph shows the comparison between experimental data (Exp data) and a model (model). The x-axis represents time in minutes, while the y-axis represents absorbance $A_{\text{exp}}$ and $A_{\text{model}}$ in $\text{cm}^{-1}$. The graph indicates a trend where the absorbance increases with time, reaching a plateau after a certain period.