Apontamentos da aula nº9

Química-Física

BETTER MINDS
De estudantes para estudantes

AULA Nº9

Sumário

V - Fenómenos de superfície:

Isotérmicas de adsorção:
- Processo de adsorção
- Caracterização do sistema de adsorção
- Tipos de adsorção
- Equilíbrio de adsorção (isotérmicas linear, Langmuir, Freundlich, BET)

Ref. anexas, Cap. 23, pg. 843 – 851

Caracterização do sistema de adsorção

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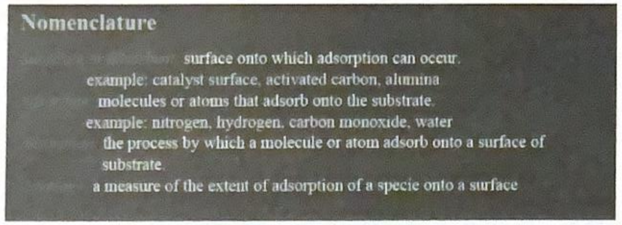


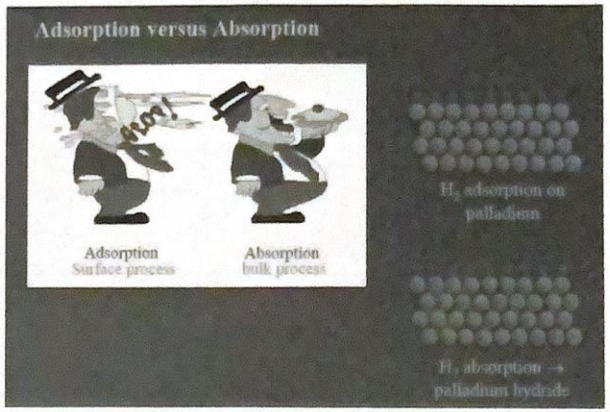
Nomenclature

surface onto which adsorption can occur.
example: catalyst surface, activated carbon, alumina
molecules or atoms that adsorb onto the substrate.
example: nitrogen, hydrogen, carbon monoxide, water
the process by which a molecule or atom adsorb onto a surface of substrate.
a measure of the extent of adsorption of a specie onto a surface

Isotérmicas de adsorção:

- Adsorção – processo em que as moléculas aderem a superfície de outra substância, sem penetrarem. Ex: carvão ativado adsorve impurezas, sendo usado como filtro.

Processo de adsorção



- Absorção → processo em que uma substância é incorporada / penetra no interior de outra, distribuindo em todo o volume do material.

Tipos de adsorção

Specific solid-solute interaction

o adsorbato pode-se mover

Substância que fica na superfície

Adsorção física é mais fraca

- Physical adsorption: The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer adsorption.

- Chemical adsorption: Some degree (→ grau) of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness. Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible.

raramente

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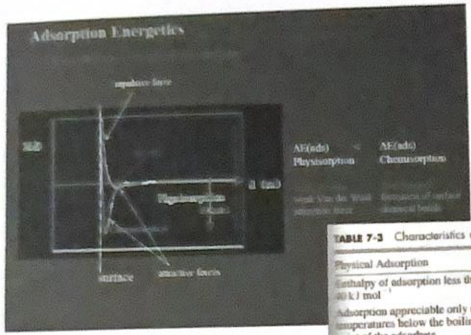


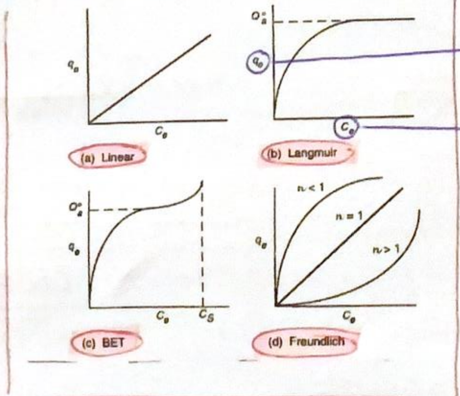
TABLE 7-3 Characteristics of Physical Adsorption and Chemisorption

Physical Adsorption	Chemisorption
Enthalpy of adsorption less than about 40 kJ mol^{-1}	Enthalpy of adsorption greater than about 80 kJ mol^{-1}
Adsorption appreciable only at temperatures below the boiling point of the adsorbate	Adsorption can occur at high temperatures
Incremental increase in amount adsorbed increases with each incremental increase in pressure of adsorbate	Incremental increase in amount adsorbed decreases with each incremental increase in pressure of adsorbate
Amount of adsorption on surface a function more of adsorbate than adsorbent	Amount of adsorption characteristic of both adsorbate and adsorbent
No appreciable activation energy involved in adsorption process	Activation energy may be involved in adsorption process
Multilayer adsorption occurs	Adsorption leads to a monolayer, at most

Saber identificar o tipo de isotérmicas a usar em determinadas adsorvâncias ⚠

Isotherm models:

The figures below show that there are four common models for isotherms.



q_e → (moles adsorvidas pelo adsorvente) / massa de adsorvente

C_e → concentração de equilíbrio ✱

Check list 9

Equilíbrio de adsorção

If the adsorbent and adsorbate are contacted long enough an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by isotherms.

adsorbato a diminuir

quantidade de adsorbato que há na solução

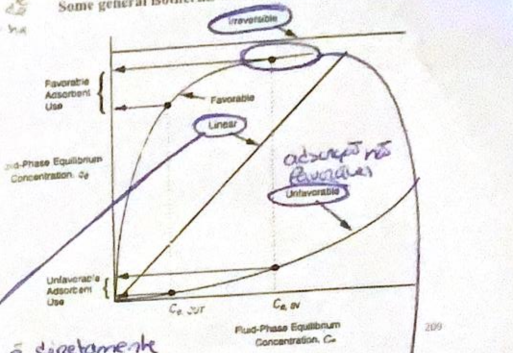
Define the following:

q_e = mass of material adsorbed (at equilibrium) per mass of adsorbent.

C_e = equilibrium concentration in solution when amount adsorbed equals q_e.

q_e/C_e relationships depend on the type of adsorption that occurs, multi-layer, chemical, physical adsorption, etc.

Some general isotherms are shown in the figure below.



- LINEAR → o volume adsorvido é diretamente proporcional à P; ainda não há saturação

- Por mais que ↑[adsorvato], a concentração de equilíbrio mantém-se, não adsorve mais.

Table 2.1 A selection of adsorption isotherms.[a]

Name	Isotherm equation	Applicability	Equation no.
Langmuir[b]	$\frac{V}{V_m} = \theta = \frac{bp}{1+bp}$	Chemisorption and physical adsorption	(41)
Henry[c]	$V = k'p$	Chemisorption and physical adsorption at low coverages	
Freundlich	$V = kp^{1/n}(n > 1)$	Chemisorption and physical adsorption at low coverages	(49)
Temkin	$\frac{V}{V_m} = \theta = A \ln Bp$	Chemisorption	(50)
Brunauer–Emmett–Teller (BET)	$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \frac{p}{p_0}$	Multilayer, physical adsorption	(51)
Polanyi[d]	$\varepsilon = RT \ln(p_0/p)$	Physical adsorption	(53)
Dubinin–Radushkevich[e]	$\ln x = \ln(W_0 \rho) - D[\ln(p_0/p)]^2$	Multilayer formation in microporous solids	(58)
Dubinin–Kaganer–Radushkevich (DKR)	$x = x_m \exp(-B\varepsilon^2)$	Physical adsorption up to a monolayer	(62)
Virial	$\frac{p}{RT} = x(1 + a_1 x + a_2 x^2 + \ldots)$	Multilayer formation in micropores	(63)

[a] Amounts adsorbed at pressure p are represented either by volume V or mass x. Unless otherwise specified, all other symbols in these equations are constants.

[b] V_m (and x_m) correspond to monolayer coverage.

[c] This equation is the limiting form of the Langmuir equation.

[d] The adsorption potential ε is defined by this equation.

[e] W_0 stands for the total volume of all the micropores in a solid.

→ superfície

Assumptions of Langmuir adsorption isotherm :

1. **The adsorbed species are held onto definite points of attachment on the surface.**
(This implies that the maximum adsorption possible corresponds to a monolayer.)
Each site can accommodate only one adsorbed species.

2. **The differential energy of adsorption is independent of surface coverage.**
(This implies that the surface is completely uniform so that there is the same probability of adsorption on all sites.
A further implication is that adsorbed molecules are localized.)
Attraction or repulsion forces between adjacent adsorbed molecules are taken to be negligible, so the energy of an adsorbed species or the probability of adsorption onto an empty site are independent of whether or not an adjacent site is occupied.

Single component systems:

A model used commonly to describe protein adsorption equilibrium is the Langmuir isotherm, which was originally developed for the adsorption of gases onto metal surfaces [3]. A simple derivation of this model assumes a stoichiometric association of an adsorbate molecule, P, with a surface-bound ligand, L, according to the following equation:

$$P + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} PL \tag{5.1}$$

where k_1 and k_2 are forward and reverse rate constants for adsorption and desorption, respectively. Accordingly, the adsorption rate is described by the following equation:

$$\boxed{\frac{d[PL]}{dt} = k_1[P][L] - k_2[PL]} \tag{5.2}$$

which is subject to the following constraint:

$$\boxed{[L] = [L_0] - [PL]} \tag{5.3}$$

CALHA !

LANGMUIR
→ monocamada
→ nº de ligandos = Liniciais – Los que se ligaram

where $[L_0]$ is the total concentration of surface-bound ligands. At equilibrium $d[PL]/dt = 0$. In this case, combining Equations 5.2 and 5.3 yields:

$$\boxed{q = \frac{q_m KC}{1 + KC}} \tag{5.4}$$

where $q = [PL]$ is the adsorbed concentration, $q_m = [L_0]$ the maximum adsorption capacity, $C = [P]$ the concentration in solution, and $K = k_1/k_2$ is the equilibrium constant for reaction 5.1. Note that q is normally expressed per unit volume or mass of stationary phase and can be defined in molar or mass units. Figure 5.2

Single component systems:

isotherm. As $C \to 0$, the Langmuir isotherm approaches the linear limit:

$$q = q_m KC = mC \tag{5.5}$$

where $m = q_m K$ is the initial slope of the isotherm, which is sometimes referred to as the *Henry constant*. On the other hand, as $C \to \infty$, the isotherm approaches the maximum capacity $q = q_m$. The term $1/K$ represents the liquid phase concentration at which q is equal to one-half of the maximum capacity, q_m.

The model parameters, however, have to be determined by data fitting at each mobile phase composition, this can be done either by non-linear regression or using linearized forms. For example, rearranging Equation 5.4 as follows:

$$\frac{q}{C} = Kq_m - Kq \tag{5.6}$$

provides a linear relationship between q/C and q. The data can be graphed accordingly (often referred to as a Scatchard plot) to test conformity with the Langmuir model and the parameters determined by linear regression.

Quanto ↑ declive, ↑ a afinidade entre o adsorbato e o adsorvente

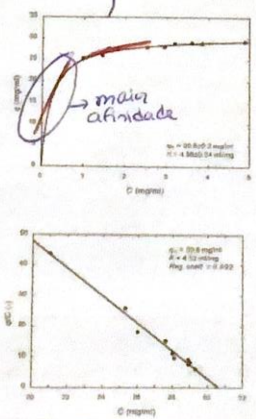


Figure 5.3 Example of a protein adsorption isotherm with Langmuir parameters determined by non-linear least square fit (left) and corresponding Scatchard plot with parameters determined from linear regression (right).

Outras isotérmicas foram propostas par explicar o equilibrio de adsorção

Freundlich Isotherm:

For the special case of heterogeneous surface energies in which the energy term, "K_F", varies as a function of surface coverage we use the Freundlich model.

$$\boxed{q_e = K_F C_e^{1/n}}$$

n and K_F are system specific constants.

BET (Brunauer, Emmett and Teller) isotherm:

This is a more general, multi-layer model. It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer.

$$\boxed{q_e = \frac{K_B \cdot C_e \cdot Q_a^0}{(C_S - C_e)\{1 + (K_B - 1)(C_e / C_S)\}}}$$

C_S = saturation (solubility limit) concentration of the solute (mg/liter)
K_B = parameter related to the binding intensity for all layers.
Note: when $C_e << C_S$ and $K_B >> 1$ and $K = K_B/C_s$ BET isotherm approaches Langmuir isotherm.

Determination of appropriate model:

To determine which model to use to describe the adsorption for a particular adsorbent/adsorbate isotherms experiments are usually run. Data from these isotherm experiments are then analyzed using the following methods that are based on linearization of the models.

For the **Langmuir model** linearization gives: $\boxed{\overset{y}{\frac{C_e}{q_e}} = \overset{m}{\frac{1}{K \cdot Q_a^0}} + \overset{x\quad b}{\frac{C_e}{Q_a^0}}}$ → Que confusão! Vê o meu resumo que está tudo bem explicado. Não usem estas formulas.

A plot of C_e/q_e versus C_e should give a straight line with intercept : $\frac{1}{K \cdot Q_a^0}$

and slope: $\frac{1}{Q_a^0}$

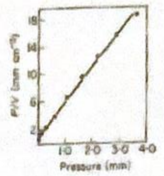
or: $\overset{y}{\frac{1}{q_e}} = \frac{1}{Q_a^0} + \frac{1}{K \cdot Q_a^0} \overset{x}{\frac{1}{C_e}}$

Here a plot of $1/q_e$ versus $1/C_e$ should give a straight line with intercept $1/Q_a^0$ and slope K

$$\overset{y}{\frac{p}{v}} = \frac{1}{bv_m} + \overset{x}{\frac{p}{v_m}}$$

V/P vs V $\quad \frac{v}{v_m p} + \frac{bv}{v_m} = b$

1/V vs 1/p $\quad \frac{v_m}{v} = \frac{1}{bp} + 1$



Slop = 1/Vm

FIG. 10. The Langmuir plot obtained from the data of Fig. 9.

$$\boxed{\frac{V}{Vm} = \theta = \frac{bp}{1+bp}}$$

Vm: the monolayer capacity

$$b = \frac{\theta}{P(1-\theta)}$$

For the **Freundlich isotherm** use the log-log version :

$$\boxed{\log q_e = \log K_F + \frac{1}{n} \log C}$$

The isotherm does not become linear at low pressures, but remains convex to the pressure axis.
A plot of ln *V* versus ln *C* gives a line with slope 1/*n* of the intensity of the adsorption, and the intercept (*VmKF*) gives a measure of adsorbent capacity.

A log-log plot should yield an intercept of $\log K_F$ and a slope of 1/n.

For the **BET isotherm** we can arrange the isotherm equation to get:

$$\boxed{\frac{C_e}{(C_S - C_e) \cdot q_e} = \frac{K_B - 1}{K_B \cdot Q_a^0} \cdot \frac{C_e}{C_S} + \frac{1}{K_B \cdot Q_a^0}}$$

Intercept = $\frac{1}{K_B \cdot Q_a^0}$

Slope = $\frac{K_B - 1}{K_B \cdot Q_a^0 \cdot C_s}$

Factors which affect adsorption extent (and therefore affect isotherm) are:

Adsorbate:

Solubility

In general, as solubility of solute increases the extent of adsorption decreases. This is known as the "Lundelius' Rule". Solute-solid surface binding competes with solute-solvent attraction as discussed earlier. Factors which affect solubility include molecular size, ionization, polarity.

pH

pH often affects the surface charge on the adsorbent as well as the charge on the solute.

Temperature Check Ext 9

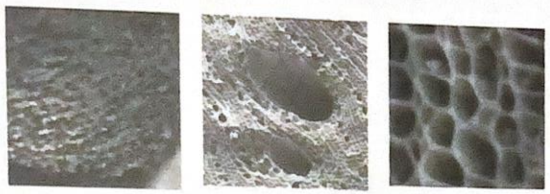
Adsorption reactions are typically exothermic i.e., ΔH_{rxn} is generally negative. Here heat is given off by the reaction therefore as **T increases extent of adsorption decreases. (Basic role is not always like this!)**

→ o calor é libertado, portanto, à medida que a T aumenta, a extensão da adsorção diminui

Adsorbent:

Virtually every solid surface has the capacity to adsorb solutes. From the wastewater/water treatment point of view activated carbon (AC) is the adsorbent of choice. AC prepared from many sources: Wood, Lignite, Coal, Nutshells, Bone

Increasing magnification



Surface area of the AC is huge (enorme). Most of the surface area is interior in micro- and macropores. Typical surface area is in the range of 300-1500 m^2/gram.

Quality and hardness of the AC are a function of the starting material and the activation process.

Pore size distribution:
micropores: <2nm diameter
mesopores: 2nm to 20 nm macropores: > 20 nm

Most of the surface area is in pores of molecular sized dimensions. This results in slower (+ devagar) mass transfer during the adsorption process but also results in greater (maior) binding capacity of the adsorbate.

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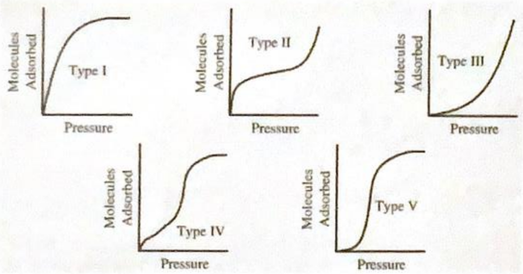
Why 5 Types Of Adsorption Isotherms?



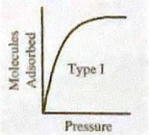
Classification of isotherms according to the BET theory.

- Pressões baixas → a quantidade adsorvida cresce proporcionalmente ao ↑ da P, pois quase todas as superfícies estão disponíveis para adsorção.

- Pressões elevadas – a quantidade adsorvida atinge a saturação, pois todas as superfícies já estão ocupadas (formação completa da monocamada), pelo que não há um aumento significativo mesmo com o ↑ da P.

Type I

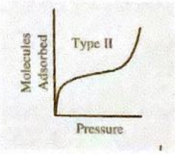
(Langmuir)



- Type I arises (surge) when only one type of site:
  - Initially surface fills (preenche) randomly
  - Eventually saturates when surface filled (or pores filled with a porous material)

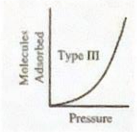
Check Est 9

Type II



- Type II arises when the is more than one adsorption site
  - Initial rapid adsorption
  - Saturates when first site filled
  - Second rise when second site fills
- Second site could be a second monolayer, a second site on the surface. In porous materials, it can also be a second type of pore.

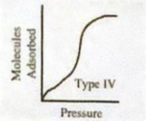
Type III



- Type III arises when there are strong attractive interactions Initially, no adsorption
  - Pressure increases lead to nucleation and growth of islands

aumenta ↗ ligações

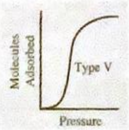
Type IV



- Type V occurs when there are multiple phase transitions due to a mixture of attractive and repulsive interactions
- Can also [illegible] arise in multilayer adsorption where adsorption on second layer starts before first layer saturates

Type V

- Type V is another case for attractive interactions
  - Initially no adsorption
  - Next nucleation and growth of islands
  - Coverage saturates when no more space to hold adsorbates



A equação de Henry é para concentrações baixas