

ADSORPTION

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from *absorption*, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while *desorption* is the reverse process.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc. We will deal with Langmuir isotherm in more details:

Langmuir isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

For liquids (*adsorbate*) adsorbed on solids (*adsorbent*), the Langmuir isotherm (Fig. 1) can be expressed by

$$m = \frac{A_{\max} k \cdot c}{1 + kc} \quad (1)$$

where m is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent, the unit of m is mol.g^{-1} , resp. mol.kg^{-1} . A_{\max} is the maximal substance amount of adsorbate per gram (or kg) of the adsorbent. The unit of A_{\max} is mol.g^{-1} , resp. mol.kg^{-1} . k is the adsorption constant ($\text{mol}^{-1}.\text{dm}^3$); c (mol.dm^{-3}) is the concentration of adsorbate in liquid.

In practice, activated carbon is used as an adsorbent for the adsorption of mainly organic compounds along with some larger molecular weight inorganic compounds such as iodine and mercury.

Activated carbon, also called **activated charcoal** or **activated coal**, is a general term that includes carbon material mostly derived from charcoal. For all three variations of the name, "activated" is sometimes substituted by "active." By any name, it is a material with an exceptionally high surface area. Just one gram of activated carbon has a surface area of approximately 500 m² (for comparison, a tennis court is about 260 m²). The three main physical carbon types are granular, powder and extruded (pellet). All three types of activated carbon can have properties tailored to the application. Activated carbon is frequently used in everyday life, in: industry, food production, medicine, pharmacy, military, etc. In pharmacy, activated charcoal is considered to be the most effective single agent available as an emergency decontaminant in the gastrointestinal tract. It is used after a person swallows or absorbs almost any toxic drug or chemical.

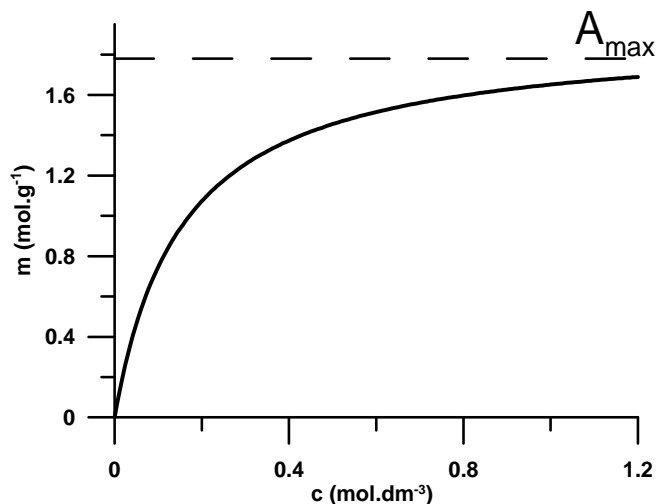


Fig. 1. Langmuir isotherm

Objective:

Determination of adsorption isotherm of acetic acid on activated charcoal. Determine the adsorption constant (k) and the maximal adsorbed substance amount of acetic acid per gram of charcoal (A_{max}) of Langmuir isotherm.

Equipment and chemicals:

6 boiling flasks (250 ml), 6 Erlenmeyer's flasks (250 ml), 6 funnels, 3 burettes (50ml), 10 titrimetric flasks, 3 pipettes, holders for funnels, holders for burettes, filtering paper, glazed paper for weighing, spoon, rubber stoppers, solution of acetic acid ($c=1 \text{ mol dm}^{-3}$), solution of NaOH ($c=0.2 \text{ mol dm}^{-3}$), activated charcoal, phenolphthalein.

Method:

1. Prepare aqueous solutions of acetic acid into numbered flasks following the scheme given in the table Tab. 1. The total volume of each solution is 60 ml. Use flasks fitted with stoppers.
2. Transfer 10 ml of the solution from each flask into numbered titrimetric flask, so final volume of acetic acid solution is $V_A=50 \text{ ml}$ per flask.
3. Determine the actual concentration of acetic acid in flasks by titration in this way:
4. For titration, modify the volume in each titrimetric flask. Take away defined volume of the solution, to obtain in each flask the volume as given in the table Tab.2
5. Add 2-3 drops of phenolphthalein and titrate by NaOH.
6. Once the endpoint has been reached, read the burette. The volume of the base X_i^0 (ml) that was required to reach the endpoint write down to the Tab.3.
7. Calculate the actual concentration of acetic acid c_i^0 in the flask No. 1 – 6, respectively, and write it down to the table Tab. 3.
8. Using practical balance and glazed paper, weigh 6 portions of activated charcoal, each portion 5 g. The accuracy of weighing must be 0.01 g.
9. Put activated charcoal into numbered flasks with stoppers (1 portion per flask). Plug up the flasks, and shake them. Wait for 20 minutes, the process of adsorption is in progress. Mix the mixtures for several times by flasks shaking within this period. (*Remark: The process of adsorption is a function of time too. It is important to put charcoal into flasks at the same time, to provide adsorption for the same period in each flask*).
10. Filter the mixtures into clean and dry flasks. To avoid disturbing effect of adsorption of acetic acid into filtering paper, remove away the first portion of filtration, app. 5 ml.
11. Determine the final concentration of acetic acid c_i in each of the flasks after adsorption: From each solution, transfer the asked volume into clean and dry titrimetric flask, again following Tab. 2.
12. Repeat points 5-7, and from the consumed base X_i (ml) determine the concentration of acetic acid c_i after adsorption. Write them down to the Tab. 3.
13. Finishing experiment, wash carefully used flasks, pipettes, etc.

Data treatment:

1. Determination of the concentration of acetic acid before (c_i^0) and after (c_i) adsorption:

$$c_i^0 = \frac{X_i^0 c_T}{V}, \quad (2)$$

where X_i^0 is the volume of the titrant (NaOH), c_T is the concentration of the titrant, V is the volume of the analyte (acetic acid according to Tab. 2), $i=1-6$ is the number of flask. Calculate the concentration of acetic acid after adsorption (c_i), using the Eq. 2 and data from Tab. 3 after adsorption.

2. Determination of the substance amount of acetic acid adsorbed per gram of the charcoal m (mol.g^{-1}) in individual flask:

$$m_i = \frac{(c_i^0 - c_i)V_A}{g}, \quad (3)$$

where c_i^0 , c_i are the concentrations of acetic acid before and after adsorption, respectively. V_A is the volume of the liquid phase in the mixture charcoal – acetic acid, g is the mass of the adsorbent – charcoal (in grams), $i=1-6$ is the number of flask. Eq. 3 supposes that V_A is the same for $i=1-6$, and also the mass of the charcoal (g). Write down the obtained values of m_i to the Tab. 3.

3. Determination of k and A_{max} : The Eq. 1 one can rearrange into a form:

$$\frac{1}{m} = \frac{1}{A_{max}k} \frac{1}{c} + \frac{1}{A_{max}}, \quad (4)$$

thus $\frac{1}{m} = f\left(\frac{1}{c}\right)$ should be a straight line.

Use MS Excell to create the dependence $\frac{1}{m} = f\left(\frac{1}{c}\right)$, where c is the concentration of acetic acid after adsorption. Fit the experimental points with a linear function. The slope represents the value of $\frac{1}{A_{max}k}$, and the intercept corresponds to $\frac{1}{A_{max}}$.

Calculate A_{max} and k from the slope and the intercept.

Tab. 1. Scheme for acetic acid dilution.

Flask No.	1	2	3	4	5	6
Acetic acid (ml)	6	12	18	30	42	60
Distilled water (ml)	54	48	42	30	18	0
Total volume (ml)	60	60	60	60	60	60

Tab. 2. Volumes of the acetic acid solutions used for titration before and after the adsorption.

Titrimetric flask No.	1	2	3	4	5	6
Volume V (ml)	10	10	5	5	5	2

Tab. 3. Experimental data

Flask No.	X_i^0 (ml)	c_i^0 (mol/dm ³)	X_i (ml)	c_i (mol/dm ³)	m_i (mmol/g)	$1/c_i$ (dm ³ /mol)	$1/m_i$ (g/mmol)
1							
2							
3							
4							
5							
6							

The report must include:

- Theory (adsorption, Langmuir isotherm, etc.)
- Equipment and chemicals
- Experimental procedure
- Tables of results, calculations and graphs: $m=f(c)$, $1/m=f(1/c)$.
- Conclusion with parameters characterizing Langmuir isotherm (k and A_{max}).

Used literature:

Kopecký F., Kacník P., Fazekaš T.: Laboratory manual for physical chemistry, Pharmaceutical faculty of Comenius University, Bratislava, 1996

<http://en.wikipedia.org/wiki/Adsorption>

<http://www.chemvironcarbon.com>

J. Oremusová, Manual for laboratory practice in physical chemistry for students of pharmacy, Department of Physical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, 2007, in Slovak

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