

Adsorption Processes

Adsorption is the process of transferring material from a fluid phase to a solid phase. We will analyze the transport process involved in adsorption by progression in complexity from batch adsorption, one-dimensional, equilibrium adsorption on a column, and one-dimensional, non-equilibrium adsorption.

Adsorption Isotherms

Adsorption is a separation process in which some materials, (*adsorbate*) is concentrated from a bulk vapor or liquid phase on to the surface of a porous solid (*adsorbent*). Usually the amount adsorbed is only a fraction of a monolayer. Thus to adsorb a substantial amount of material, the adsorbent must have a large specific surface area. The specific surface area of typical adsorbents range from 0.1 to 1.0 km²/kg, i.e. the area of a football field in a kg of adsorbent. Some common examples of adsorption are the carbon canister to adsorb gasoline vapor in automobile fuel tanks, silica gel packets to adsorb moisture from packaged electronic or optical equipment, and carbon "filter" to deodorize drinking water.

The Langmuir Model (Adamson, 1990)

Often the amount adsorbed is measured as a function of the partial pressure or concentration at a given temperature and the result expressed as an *adsorption isotherm*. There are many empirical adsorption models, but the most common is the *Langmuir adsorption isotherm model*. This model assumes that the adsorbent has S sites per unit mass, of which S_o are unoccupied and S_1 are occupied by adsorbate molecules. The assumption of having S number of sites implies that there is a limit to the amount that can be adsorbed, i.e. saturation value of adsorption.

$$S = S_o + S_1$$

It is assumed that the rate of adsorption or condensation of a gas on to the sites is proportional to the product of the number of unoccupied sites and the gas pressure.

$$r_{condensation} = k_2 P S_o$$

The rate of desorption or evaporation is assumed to be proportional to the number of occupied sites.

$$r_{evaporation} = k_1 S_1$$

At equilibrium, the rate of adsorption is equal to the rate of desorption.

$$r_{condensation} = r_{evaporation}$$

$$k_2 P S_o = k_1 S_1$$

$$k_2 P (S - S_1) = k_1 S_1$$

The amount adsorbed can be expressed as a fraction of the sites that are occupied.

$$\theta = S_1 / S$$

$$k_2 P (1 - \theta) = k_1 \theta$$

$$\theta = \frac{k_2 P}{k_1 + k_2 P} = \frac{K P}{1 + K P}$$

where

$$K = \frac{k_2}{k_1}$$

The equilibrium constant, K , is the ratio of the adsorption rate constant and the desorption rate constant. It has the units of the reciprocal of pressure.

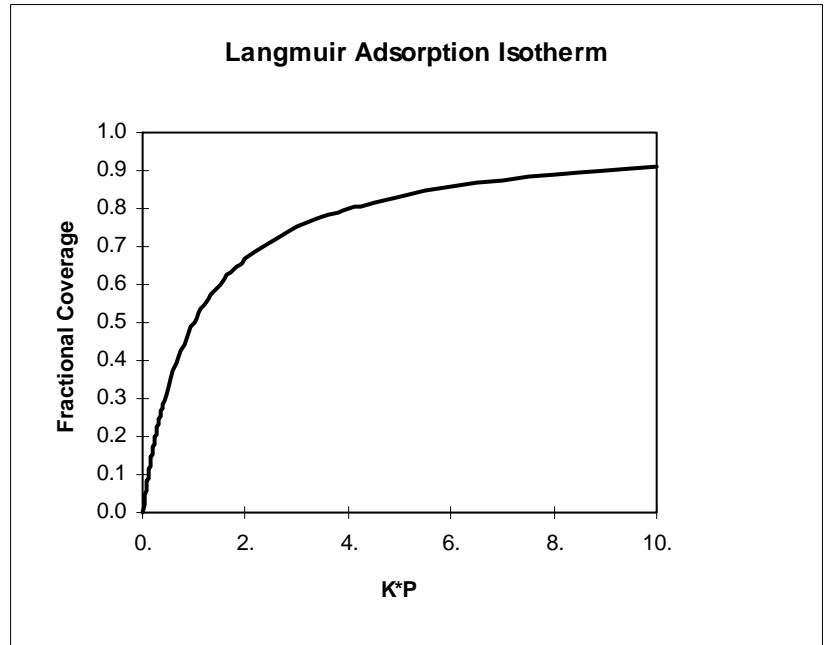


Fig. 2.11 Langmuir adsorption isotherm

In the limit of low pressures, the adsorption is linear in pressure and the isotherm has a slope equal to the equilibrium constant.

$$\theta \approx K P, \quad P \rightarrow 0$$

$$S_1 \approx S K P, \quad P \rightarrow 0$$

$$= H P, \quad P \rightarrow 0$$

where

$$H = S K$$

The linear adsorption in the limit of low pressure is the Henry's law isotherm and the coefficient H is the Henry's law constant.

Two Dimensional van der Waals Equation of State Model (2D vdW EOS)

The Langmuir model is often used when experimental measurements are available. However, in the absence of experimental data it tells nothing about the effect of temperature and the properties of the adsorbate and adsorbent. The 2D vdW EOS can be used to derive an adsorption model for adsorbate that does not deviate too far from a spherical molecule and when the adsorbate-adsorbate and adsorbate-adsorbent molecular interactions are van der Waals interactions. The vdW interactions are due to the electronic vibrations and polarizability of materials. The most significant component is the *London dispersion forces*. It is present in all molecular materials, including the rare gases. The vdW interactions do not include Coulombic interactions between ions nor hydrogen bonding interactions (Lewis acid-base interactions). Thus vdW interactions are sometimes referred to as the nonpolar molecular interactions.

The intermolecular interaction potential of the 3D vdW model is as follows.

$$w(r) = \begin{cases} -\frac{C}{r^6}, & r > \sigma \\ +\infty, & r < \sigma \end{cases}$$

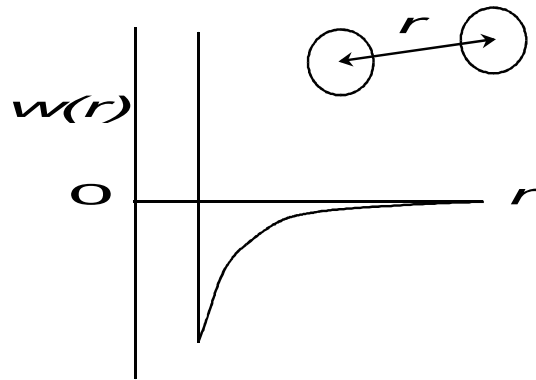


Fig. 2.12 van der Waals intermolecular interaction potential

where w is the potential energy of intermolecular interactions and r is the distance between the centers of molecules. It is sometimes called the attractive hard sphere model. It is a two parameter model. One parameter C gives the coefficient of the inverse sixth power attraction and the other parameter σ gives the distance where a hard repulsion occurs.

The vdW potential model results in the vdW EOS of a fluid that can have a liquid and vapor states below the critical temperature. The vdW EOS has two parameters, a cohesive parameter, a_3 , and an "excluded volume" parameter, b_3 . The subscript 3 is used for parameters of the 3D EOS.

$$\left(p + \frac{a_3}{v^2}\right)(v - b_3) = kT$$

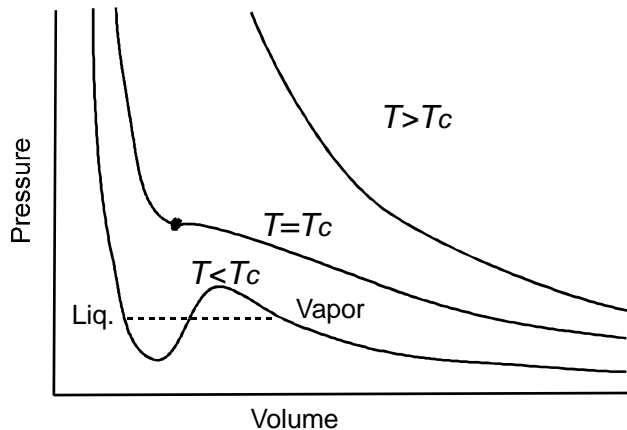


Fig. 2.13 PVT isotherms with vdW EOS

The volume is expressed here as the volume per molecule (rather than mole). This results in the equation having the Boltzmann's constant rather than the gas constant since the Boltzmann's constant is the gas constant divided by the Avogadro's number. This model predicts a critical temperature and pressure of one component fluid. Thus the two parameters can be calculated from the experimentally measured critical temperature and pressure of a one component fluid. Also, the two parameters of the interaction potential can be determined from the two parameters of the vdW EOS which can be determined from the critical temperature and pressure (Israelachvili, 1991).

$$a_3 = \frac{27 k^2 T_c}{64 p_c}$$

$$b_3 = \frac{k T_c}{8 p_c}$$

$$\sigma = \left(\frac{3b_3}{2\pi} \right)^{1/3}$$

$$C = \frac{3\sigma^3 a_3}{2\pi}$$

The 2D vdW EOS describes the *film pressure* (two dimensional pressure) or surface energy as a function of the specific area a of the adsorbate on the adsorbent, see Fig. 2.14.

$$\left(\pi + \frac{a_2}{a^2} \right) (a - b_2) = k T$$

where the film pressure π is the change in surface tension of a liquid substrate due to adsorption or the reduction of the surface energy of a liquid or solid substrate.

$$\pi = \gamma_o - \gamma$$

The two parameters of the 2D vdW EOS can be determined from the two parameters of the interaction potential discussed above.

$$a_2 = \frac{\pi C}{4 \sigma^4}$$

$$b_2 = \frac{\pi \sigma^2}{2}$$

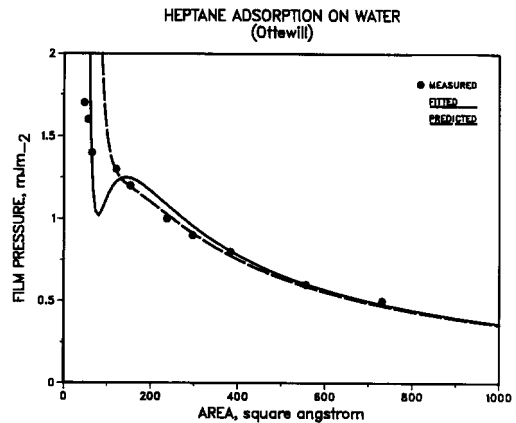


Fig. 2.14 Adsorption of *n*-heptane on water (Hirasaki, 1993)

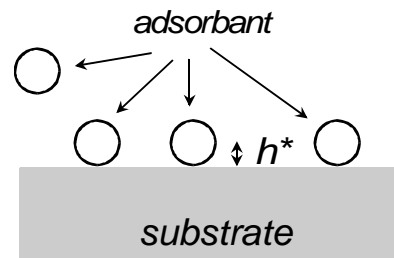


Fig. 2.15 Monolayer adsorption from vapor

An assumption implicit in the 2D and 3D vdW EOS is that the molecule is spherical and in two dimensions it has a projection on the substrate that is a disk. Thus the parameter b_2 is an "excluded area." Adsorption of a vapor on to a substrate as a monolayer can be derived from the 2D vdW EOS and the Hamaker-Lifshitz theory (Hill, 1946; de Boer, 1953; Adamson, 1990; Hirasaki, 1993).

$$\frac{p}{P^o(T)} = \frac{\theta}{1-\theta} \exp \left[\frac{1}{6\pi} \frac{A_{s\ell v}}{kT} \frac{v_\ell}{(h^*)^3} - \frac{2a_2\theta}{kTb_2} + \frac{\theta}{1-\theta} \right]$$

where

$A_{s\ell v}$	substrate-liquid-vapor Hamaker constant
p	partial pressure of the adsorbate
P^o	saturated or vapor pressure of the adsorbate
h^*	interaction distance from the substrate to the center of the adsorbate in the configuration that exists on the substrate, e.g., flat
v_ℓ	is the specific molecular volume of the saturated liquid phase
$\theta = \frac{b_2}{a}$	is the fractional surface coverage

The Hamaker constant is a material parameter for the interaction of a liquid film of the adsorbate on the substrate (Israelachvili, 1991). It can be calculated from the dielectric properties of the materials using the Lifshitz theory. In the limit of low pressure and coverage, the Henry's law model can be derived from the above adsorption model (Hirasaki, 1993).

$$\lim_{p \rightarrow 0} \frac{p}{P^o} = \theta \exp \left[\frac{1}{6\pi} \frac{A_{s\ell v}}{kT} \frac{v_\ell}{(h^*)^3} \right]$$

The 2D vdW EOS adsorption isotherm describes only monolayer adsorption. Multilayer adsorption is possible in systems that have a negative Hamaker constant. Multilayer adsorption is better described as a film thickness h rather than as a fractional coverage.

$$h = \frac{v_\ell}{a}$$

The partial pressure is included in the expression for the disjoining pressure Π (surface excess free energy of two interfaces separated by a distance h).

$$\begin{aligned}\Pi &= -\frac{kT}{v_\ell} \ln\left(\frac{p}{P^o}\right) \\ &= -\frac{A_{s\ell v}}{6\pi h^3}\end{aligned}$$

$$\frac{p}{P^o} = \exp\left(\frac{A_{s\ell v} v_\ell}{6\pi k T h^3}\right), \quad \text{multilayer adsorption}$$

Monolayer and multilayer adsorption of heptane and octane on graphite is illustrated in Fig. 2.16 as disjoining pressure versus film thickness. The 2D vdW monolayer model merges with the Hamaker-Lifshitz multilayer model at a film thickness of about 5 Å. Also notice that the heptane data appears to have a 2D phase transition. The 2D vdW EOS has a critical temperature that is one half of the 3D vdW EOS. This puts the 2D critical temperature for *n*-heptane just below room temperature.

$$\begin{aligned}T_{c2} &= \frac{8}{27} \frac{a_2}{k b_2} \\ &= \frac{4}{27} \frac{C}{\sigma^6} \\ &= \frac{1}{2} T_c\end{aligned}$$

REFERENCES

- Adamson, A. W.: *Physical Chemistry of Surfaces*, 5th Ed., John Wiley & Sons, New York (1990).
- Israelachvili, J.: *Intermolecular & Surface Forces*, 2nd Ed., Academic Press, New York (1991).
- Hirasaki, G. J.: "Structural interactions in the wetting and spreading of van der Waals fluids," *J. Adhesion Sci. & Tech.*, Vol 7, No. 3, 285-322 (1993).

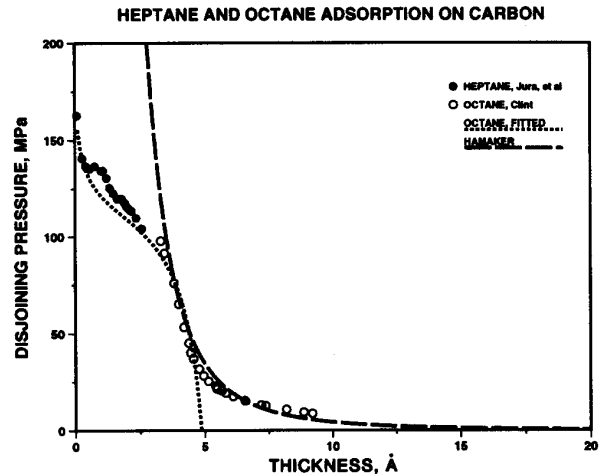


Fig. 2.16 Adsorption of *n*-heptane and *n*-octane on graphite (Hirasaki, 1993)

Assignment 1 Separation of *n*-Heptane from Air Stream, Part 1

A process air stream at 1.0 atmosphere contains 1.316×10^{-3} mole fraction of *n*-heptane. Environmental regulations require that it be reduced to a mole fraction of 7×10^{-7} . A carbon adsorption column is available to remove the heptane. Superheated steam at 247.5 °C and one atmosphere is available to regenerate the column. The column will be regenerated with steam until the heptane partial pressure is reduced to 33.6 mm Hg. Assume: (1) air and steam do not interfere with the adsorption of heptane on carbon, (2) heptane parameters other than the vapor pressure can be assumed constant over the temperature range of the process, (3) the column has a uniform concentration during regeneration, i.e. treat as a well-stirred tank or fluidized column, (concentration profile is next chapter) and (4) the outflow end of the column during adsorption does not change until the entire column is saturated.

- 1) Plot adsorption isotherms.
- 2) What is the fractional coverage after regeneration?
- 3) At what temperature must the adsorption be conducted if the air quality is to meet the regulations?
- 4) What is the fractional coverage of the column after adsorption from the air stream at this temperature?
- 5) Plot only the relevant adsorption isotherms and show the relevant pressures and fractional coverage.

Use the MATLAB code, *vdwdata.m* and *vdw.m*, available on the CENG 402 web site. The heptane-carbon parameters are in *vdwdata.m*. The vapor pressure is given in the following table.

Vapor Pressure of *n*-Heptane

Temperature, °C	Vapor Pressure, mm Hg
-34.0	1
-2.1	10
22.3	40
41.8	100
78.0	400
98.4	760
124.8	1520
165.7	3800
202.8	7600
247.5	15200
319.0	30400