Pure Component Adsorption in Microporous Solids

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Adsorption in microporous solids

- An important adsorption mechanism applicable for microporous solids is called micropore filling.

- In this class of solids, micropore walls are in proximity to each other, providing an enhanced adsorption potential within the micropores.

- The strong potential is due to the dispersive forces. Theories based on this force include that of Polanyi and particularly that of Dubinin, who coined the term micropore filling.

- The Dubinin theory forms the basis for many equations which are currently used for the description of equilibria in microporous solids.

Activated carbon has a very complex structure with pores ranging from macropores (> 1000 Å) to micropores (10 Å).

In the micropore network most of the adsorption capacity resides.

Because of the pore dimension comparable to the dimension of adsorbate molecule, the adsorption mechanism is completely different from that of a large pore, where adsorption occurs by a layering process.

In micropores, the mechanism is due to micropore filling because of the adsorption force field encompassing the entire volume of micropores.

Such an enhancement in the adsorption potential would lead to higher heat of adsorption compared to that on a surface.
Experimental evidence of volume filling

The concept of micropore filling was demonstrated with zeolite CaA (5A) and NaX.

- Their specific surface areas obtained from X-ray are 1640 for CaA and 1400 m²/g for NaX.
- The amount calculated assuming monolayer adsorption is 2 to 3 times larger than the experimental values, indicating a micropore filling rather than surface layering mechanism.
- For a given adsorbate the ratio of the experimental amount adsorbed for the two zeolites is in perfect agreement with the ratio of the void volumes rather than with the ratio of surface areas.

\[
\frac{C_\mu (\text{CaA})}{C_\mu (\text{NaX})} \approx 0.861 \quad \frac{V(\text{CaA})}{V(\text{NaX})} = \frac{0.278 \text{ cc/g}}{0.322 \text{ cc/g}} \approx 0.863
\]

\[
\frac{S(\text{CaA})}{S(\text{NaX})} = \frac{1640 \text{ m}^2/\text{g}}{1400 \text{ m}^2/\text{g}} \approx 1.17
\]
Possible adsorption mechanisms in CaA and NaX
Dispersive forces

- Forces of adsorption are electrostatic forces, the valance energy force and the cohesive energy force.
- The van der Waals force, which exists between all atoms and molecules, can be classified into three groups:
  - dipole-dipole forces
  - dipole-induced dipole forces
  - dispersion forces
- The dispersion force is the most important force in physical adsorption.
Micropore filling theory

- The fundamental quantity in the micropore filling is the differential molar work of adsorption, given by:

\[ A = R_g T \ln \left( \frac{P_0}{P} \right) \]

- This is the work required by the surface to bring one mole from the gas phase to the liquid phase.

- The value of adsorption potential \( A \) is equal to the difference between the chemical potentials of the adsorbate in the state of normal liquid and the adsorbed state at the same temperature. For ideal fluids:

\[ A = \mu_L - \mu_a = \left[ \mu^{(0)} + R_g T \ln P_0 \right] - \left[ \mu^{(0)} + R_g T \ln P \right] = R_g T \ln \left( \frac{P_0}{P} \right) \]
Dubinin-Radushkevich (DR) equation

\[ \theta = \frac{W}{W_0} = \exp\left[-\left(\frac{A}{E}\right)^2\right] \]

\[ \frac{E}{E_0} = \frac{A}{A_0} = \beta \]

\( \theta \) : degree of filling
\( W \) : volume of adsorbate in the micropore
\( W_0 \) : maximum volume the adsorbate can occupy
\( A \) : adsorption potential
\( E \) : characteristic energy
\( \beta \) : similarity coefficient (\( \beta = 1 \) for benzene)
\( A_o \) and \( E_o \) : for reference adsorbate
The molar amount adsorbed

Knowing the volume $W$ taking up by the adsorbate and assuming the adsorbed phase behaves like a liquid phase, the number of moles adsorbed ($\text{moles/g}$) is:

$$C_{\mu} = \frac{W}{v_M}$$

$C_{\mu}$ : molar amount adsorbed ($\text{mole/g solid}$),
$W$ : liquid volume adsorbed per unit mass of the solid,
$v_M$ : liquid molar volume ($\text{cc of liquid/mole}$).

$$C_{\mu s} = \frac{W_0}{v_M}$$
Famous form of DR equation

\[ C_{\mu} = \frac{W_0}{\nu_M} \exp \left[ -\left( \frac{A}{\beta E_0} \right)^2 \right] \]
Dubinin-Astakhov (DA) equation

- For carbonaceous solids with high degree of burn-off during activation, the degree of heterogeneity increases because of a wider pore size distribution.

- The DR equation does not describe well the equilibrium data of such systems.

- Dubinin and Astakhov proposed the following form to allow for the surface heterogeneity:

\[
C_{\mu} = \frac{W^0}{v_M} \exp \left[ - \left( \frac{A}{\beta E_0} \right)^n \right]
\]
The characteristic energy (E) is a measure of the strength of interaction between adsorbate and adsorbent, and is different from the interaction energy in the Langmuir equation.

Interaction energy in the Langmuir mechanism (monolayer type adsorption) is a measure of the interaction between an adsorbate molecule and surface atoms.

In micropore filling, the interaction is between the adsorbent and the volume of adsorbate residing within the micropore.
The incorrect Henry law behavior

- “n” characterize the heterogeneity of the system. Since it is an empirical parameter, it does not point to the source of the heterogeneity. However, it can be used as a macroscopic measure of the sharpness of the micropore size distribution.

- Unfortunately, the DA as well as the DR equations do not have the correct Henry law when the pressure is approaching zero.
Modified Dubinin equations for Heterogeneous microporous solids

- Adsorption isotherms of many microporous solids do not usually conform to the simple DR equation.
- Even with the adjustable parameter n in the DA equation, it also can not describe well many experimental data. This is attributed to the heterogeneity of the system, that is the characteristic energy varies with the different regions in the solid.
There are a number of approaches to deal with such heterogeneous solids:

- The simple approach is to assume that the solid is composed of two distinct regions and there is no interaction between these two. Then, the DR or DA equation can be applied to each region, and the overall isotherm is simply the summation of the two equations.

- Assume an arbitrary continuous distribution of the characteristic energy in such a way that an analytical solution can be obtained from the averaging of a local isotherm over that distribution.
Ideal Inhomogeneous microporous solids

The simplest way of describing the adsorption isotherm of an inhomogeneous microporous solid is to use the equation:

\[ C_\mu = \frac{W_{0,1}}{v_M} \exp\left[ -\left( \frac{A}{\beta E_{0,1}} \right)^{n_1} \right] + \frac{W_{0,2}}{v_M} \exp\left[ -\left( \frac{A}{\beta E_{0,2}} \right)^{n_2} \right] \]

Practical solids do not easily break down into two distinct regions having two distinct characteristic energies, but rather they possess a distribution of energy.
Solids with distribution in characteristic energy $E_0$

With the concept of distribution of the characteristic energy, the adsorption isotherm equation can be written in general as follows:

$$W = W_0 \int_{\Omega(E_0)} f(E_0) \frac{\theta(A / \beta E_0, n)}{E_0} dE_0$$

where $W_0$ is the maximum specific volume of the micropore, $f(E_0)$ is the distribution of the characteristic energy based on the reference vapor (benzene), and $\theta$ is the local fractional loading corresponding to the characteristic energy $\beta E_0$. The parameter $n$ may vary with the variation of the characteristic energy, but for simplicity it is always taken as a constant. The range of integration, $\Omega(E_0)$, should reflect that of a micropore system, that is the proper range should be between $E_{\text{min}}$ and $E_{\text{max}}$. 
Solids with micropore size distribution (MPSD)

If we let the MPSD as \( f(x) \) such that \( W_0 f(x) \) is the micropore volume having micropore size between \( x \) and \( x + dx \), then the volume of micropore occupied by adsorbate at a given adsorption potential \( A \) is:

\[
W = W_0^0 \int_{x_{\text{min}}}^{x_{\text{max}}} \theta(A / \beta E_0, n) f(x) \, dx
\]

where \( x \) is the micropore half width, with \( x_{\text{min}} \) and \( x_{\text{max}} \) are its minimum and maximum, respectively.

\[
E_0 = \frac{k}{x}
\]

For benzene as the reference vapor: \( k = 12 \text{ kJoule - nm / mole} \)
DR Local isotherm and Gaussian distribution

\[ W = W_0 \exp(-mx^2A^2) \]

\[ m = \frac{1}{(\beta k)^2} \]

\[ W = \frac{W_0^0}{2\sqrt{1 + 2m\delta^2A^2}} \exp\left(-\frac{mx_0^2A^2}{1 + 2m\delta^2A^2}\right) \left[ 1 + \text{erf}\left(\frac{x_0}{\delta\sqrt{2}\sqrt{1 + 2m\delta^2A^2}}\right) \right] \]

Dubinin and Stoeckli (DS) equation
Using this equation to fit experimental data, three parameters can be extracted from this fitting process, namely $W_0^\circ$, $x_0$ and $\delta$ (variance). Knowing these parameters, the micropore size distribution in terms of volume can be calculated by:

$$\frac{dW_0}{dx} = \frac{W_0^0}{\delta \sqrt{2\pi}} \exp\left[-\frac{(x - x_0)^2}{2\delta^2}\right] = W_0^0 \ f(x)$$
Geometrical surface area of micropore

If the micropore volume is described by a Gaussian distribution given as previous equation, the geometrical surface of the micropore walls under the assumption of slit shaped pore is:

\[ S_g = \frac{W_0^0}{\delta\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{1}{x} \exp \left[ -\frac{(x-x_0)^2}{2\delta^2} \right] dx \]

C=0.25 nm for benzene (minimum accessible pore)