ME 599 L18 — Langmuir isotherm (SAM adsorption)

John Hart
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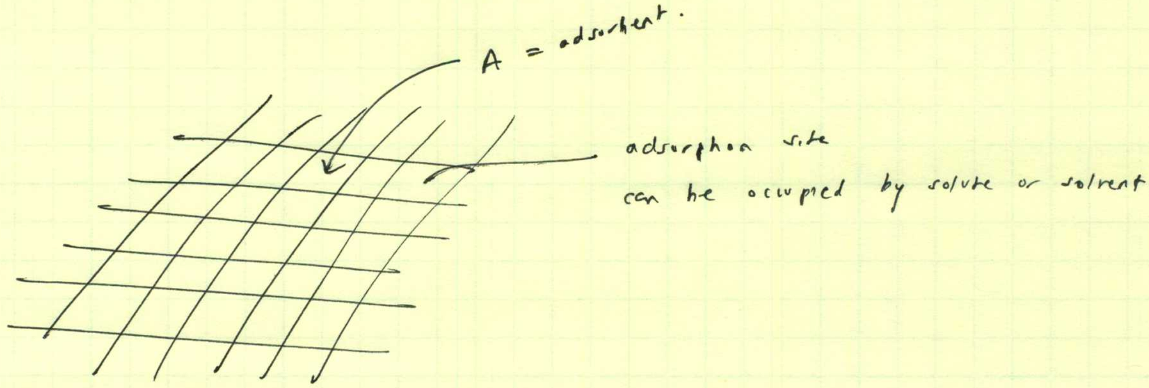
adsorption on a solid surface – same model for gas adsorption at low pressure (there we have pressure instead of concentration)



e.g. alkanethiols on Au (solid surface)

$$2R-SH + Au_s \rightarrow 2RS-Au + H_2$$

R: alkyl group; SH: sulfur end

$$A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A\text{-surface}$$

k_a: adsorbing; k_d: desorbing — in equilibrium w/ solution

θ = % of sites occupied

C = concentration of A in solution, really $c(\theta)$ but assume infinite supply

N_0 = maximum number of sites that will be occupied

rates of:

$$\frac{d\theta}{dt} = (\text{sites occupied}) - (\text{sites free}) = \frac{k_a(c)}{N_0}(1-\theta) - \frac{k_d\theta}{N_0}$$

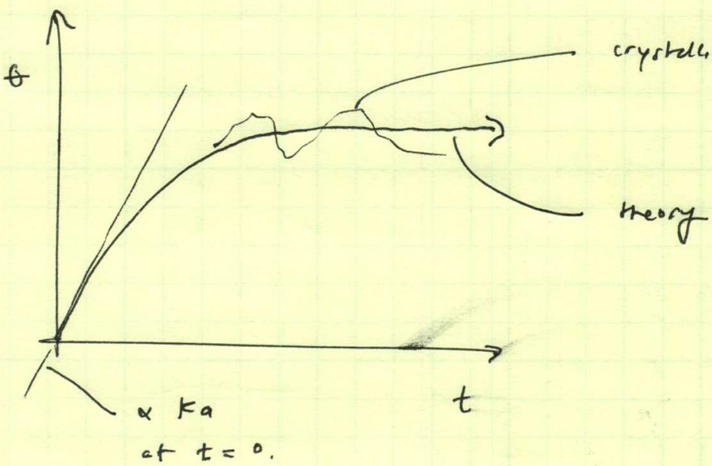
(sites occupied) ↓, (sites free) ↑

solve for θ $\left(\frac{d\theta}{dt} \cdot \frac{1}{\theta} \{\sim\} = \{\sim\} \right)$

$$\theta(t) = \frac{k_a \cdot c}{k_a \cdot c + k_d} \left\{ 1 - e^{-\frac{k_a}{\mu_0}\left(c + \frac{k_d}{k_a}\right) t} \right\}$$

$$\theta(t \to \infty) = \frac{k_a c}{k_a c + k_d} = \frac{c}{c + K}$$

$K = k_a / k_d$, $K \propto e^{-\Delta G_a / kT}$



limitations of this simple model:

- adsorption involves several different steps / intermediate mechanisms
- can't assume a homogeneous surface or ideal monolayer
- can't always assume dilute concentrations

TOPS 35500