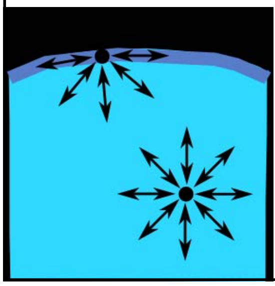
Adsorption at S/L interface

S+L

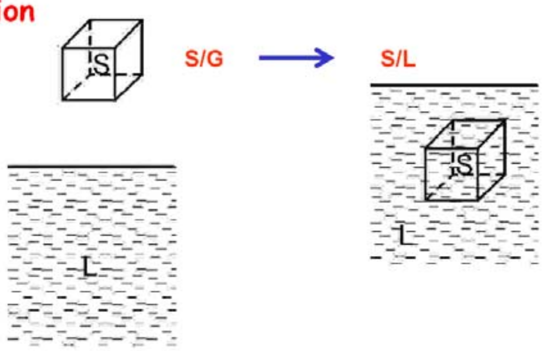
Applications/use:
- solvent purification, e.g. with molecular sieves
- water treatment
- decolorisation
- dyeing
- washing
- separation techniques (liquid chromatography)
- surface characterisation



TEXT: Physical chemisty of surfaces Part 2

PURE (SINGLE COMPONENT) LIQUID:

immersion



heat of immersion: $q_w = h_{S/L} - h_S$

orientation on the surface

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Multicomponent liquid phase

Players:

- dissolved material (B)
- solvent (A)
- surface site (S)

Interactions: A – A; B – B; A – S; B - S

Mechanism:

- wetting
- sorption
- mixing
- exchange

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1) non-electrolytes or weak electrolytes

dispersive/hydrophobic/H-bond/van der Waals interactions

competition

Mechanism of S/L adsorption

$$\beta A^{L} + B^{s} \Longleftrightarrow \beta A^{s} + B^{L}$$ exchange

$$\beta = \frac{a_{m,B}}{a_{m,A}}$$ Cross sectional area of B and A

2) electrolytes

electrostatic interactions
(attraction, repulsion)

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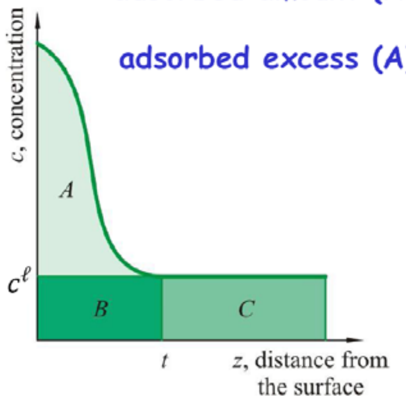
Quantitative description of the adsorption

$$S_A = \frac{\text{surface area}}{\text{mass of solid}}$$

adsorbed amount (A+B)

adsorbed excess (A)



$$n = A_s\int_0^t c\,dz + c^{\ell}V^{\ell} \quad (A+B+C)$$

$$n^{\sigma} = n - c^{\ell}V^{\ell} - c^{\ell}V^{s} \quad (A)$$

$$n^{s} = n^{\sigma} + c^{\ell}V^{s} \quad (A+B)$$

$$n^{s} \approx n^{\sigma}$$

only if c^{ℓ} is low
(ONLY for dilute solutions)

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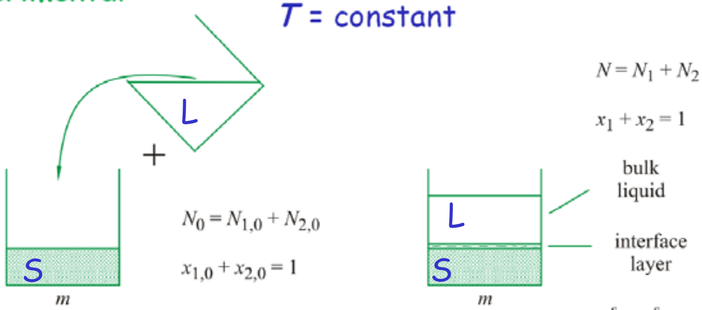
Experimental

T = constant



$N_0 = N_{1,0} + N_{2,0}$

$x_{1,0} + x_{2,0} = 1$

$N = N_1 + N_2$

$x_1 + x_2 = 1$

$N^s = N_1^s + N_2^s$

$x_1^s + x_2^s = 1$

$$n_i = \frac{N_i}{m}$$

Material balance for component 1:

$$n_0 x_{1,0} = n_1^s + (n_0 - n^s)x_1$$

$$n_0(x_{1,0} - x_1) = n_1^s - n^s x_1$$

$$n_1^{\sigma} \equiv n_1^s - n^s x_1 = n_0(x_{1,0} - x_1) \quad \text{Adsorbed excess}$$

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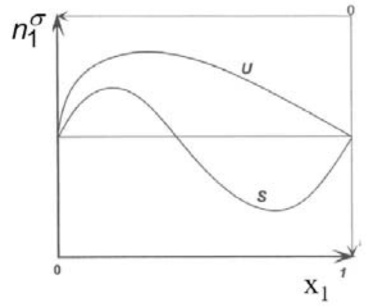
*COMPLETELY MISCIBLE LIQUIDS
(non-electrolytes or weak electrolytes)

$$n_0\left(x_{1,0}-x_1\right)=n_1^s-n^s x_1 \equiv n_1^\sigma\left(x_1\right) \qquad \text{T = constant}$$

excess isotherm



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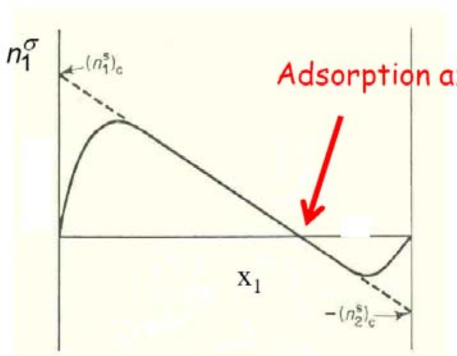
Analysis of the isotherms having a linear section



$$n_0\left(x_{1,0}-x_1\right)=n_1^s-n^s x_1 \equiv n_1^\sigma\left(x_1\right) \qquad y=a+bx$$

Condition: monomolecular coverage $\quad A_s = n_1^s a_{s,1} + n_2^s a_{s,2}$

Alternative way of surface area determination

Molar cross sectional area of pure liquids

liquid	cross sectional area, $m^2/mmol$
methanol	94
ethanol	120
butanol	172
benzene	180
cyclohexane	208
heptane	256
toluene	206

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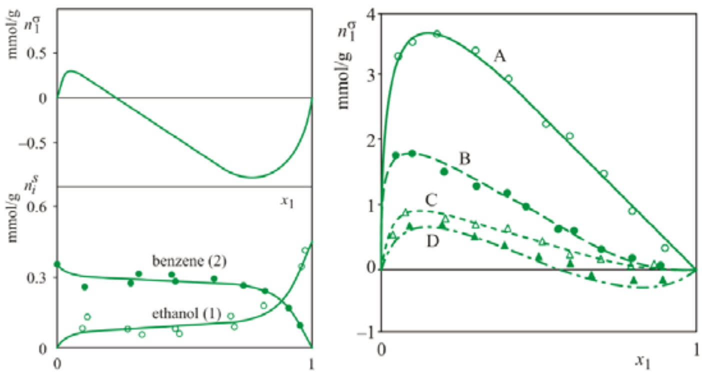
The isotherm simultaneously characterizes the solid surface and the binary liquid



ethyl alcohol (1) – benzene (2) on activated carbon

A: methanol – benzene
B: ethanol – benzene
C: n-propanol – benzene
D: i-propanol – benzene
on palygorskite

$$x_1^s = \frac{n_1^s}{n^s} = \frac{n_1^\sigma}{n^s} + x_1$$

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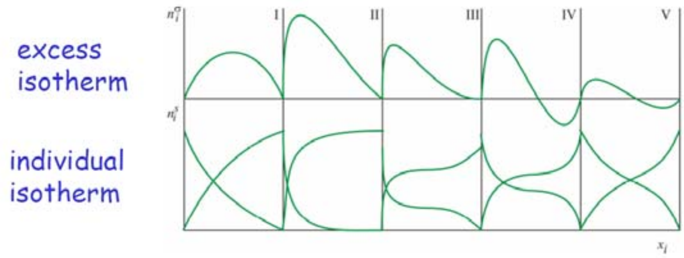
The individual isotherm (the total adsorbed amount of each component) can be calculated?



$$x_1^s = \frac{n_1^s}{n^s} = \frac{n_1^\sigma}{n^s} + x_1 \qquad n_i^s = n_i^\sigma + n^s x_i$$

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*Dilute non-electrolytes or weak electrolytes

$$n_i^s = n_i^\sigma + n^s x_i$$

$$x_i \to 0 \qquad n^\sigma \approx n^s$$

Experimental:

$$n^s = \frac{c_0 V_0 - c_e V_e}{m} = \frac{(c_0 - c_e) V}{m}$$

Swelling?

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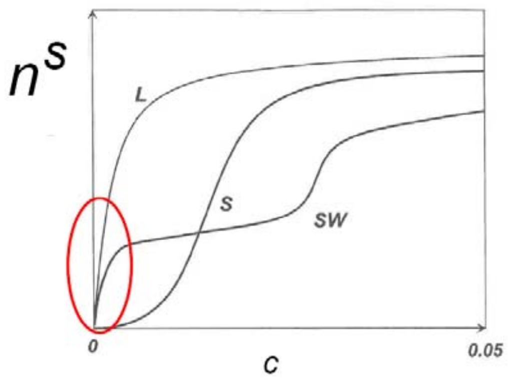
CLASSIFICATION



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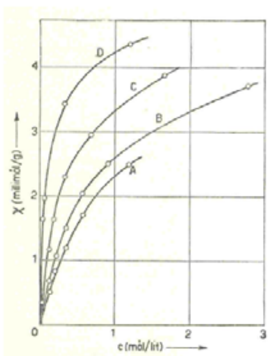
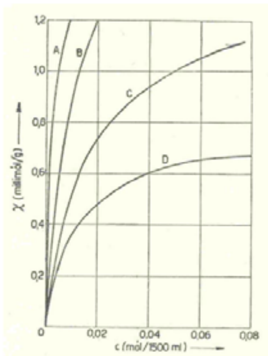
A: formic acid
B: acetic acid
C: propionic acid
D: butyric acid



From water on activated carbon



From toluene on silica

Oriented adsorption

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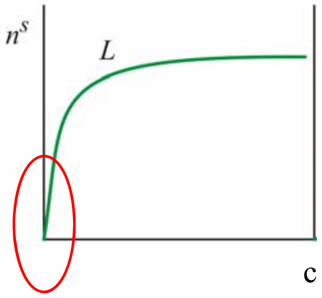
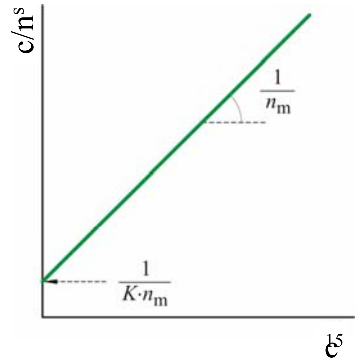
Models

1. **Langmuir** $n^s = n^s_m \frac{Kc}{1+Kc}$ **Henry** $c \to 0$

$$\frac{c}{n} = \frac{1}{Kn_m} + \frac{c}{n_m}$$





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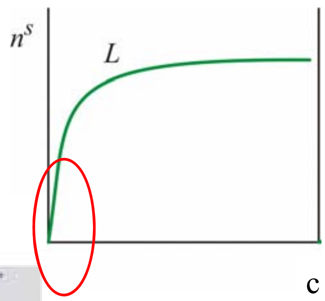
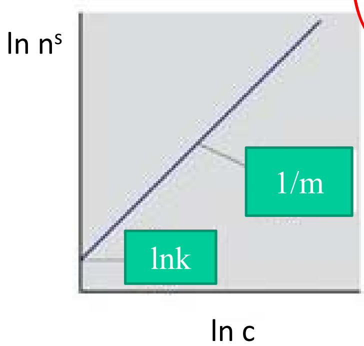
2. **Freundlich**

$n^s = kc^{1/m}$ m>1





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3. Complex models: surface heterogeneity

- bi-Langmuir

$$n^s = \frac{a_1 c_e}{1 + b_1 c_e} + \frac{a_2 c_e}{1 + b_2 c_e}$$

-adsorption sites on the solid with two different energies

or

- the adsorptive has two kinds of binding sites
  e.g. - chiral molecules
  - proteins

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- competitive Langmuir

$$n_i^s = n_{m,i}^s \frac{K_i c_{i,e}}{1 + \sum K_i c_{i,e}}$$

Competitive adsorption for the same sites

n_m and K from single component Langmuir parameters

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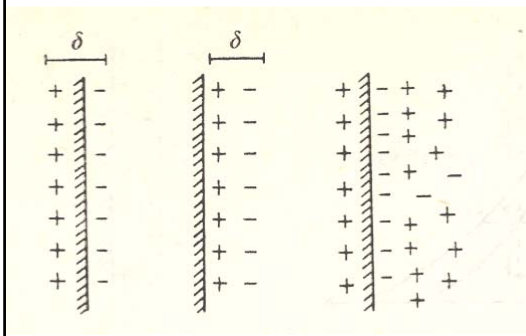
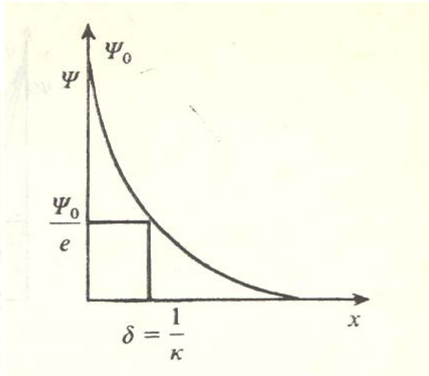
* Ionic systems

Electrostatic interactions: attraction
repulsion





The role of the counterion

Thickness of the electric double-layer δ

Brownian motion
Diffuse double-layer
Stern-layer

$$\Psi = \Psi_0 e^{-\kappa x}$$

$$\kappa = \text{konst} \cdot z\sqrt{c}$$

z the charge of the counterion (symmetric electrolites)
$1/\kappa$: fictive thickness

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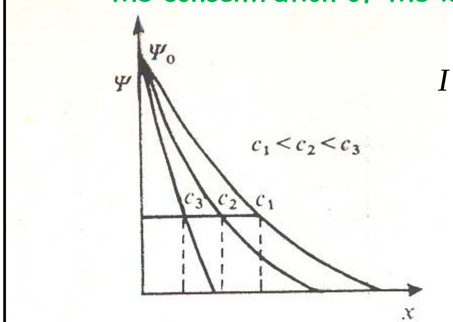
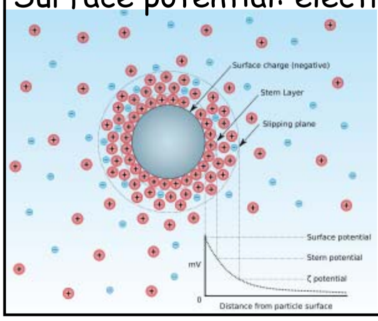
The thickness of the double-layer is influenced by the concentration of the ions



$$I = 0.5\sum_i z_i^2 c_i$$ ionic strength

Surface potential: electrokinetic potential or *ζ - potential*



$$\zeta = \frac{q}{4\pi\varepsilon r}$$

q: surface charge density
ε: permittivity of the medium
r: radius of the spherical particle

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Zeta potential [mV]	Stability behavior of the colloid
from 0 to ±5,	Rapid coagulation or flocculation
from ±10 to ±30	Incipient instability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

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