

4. S/L INTERFACES: ADSORPTION AT S/L INTERFACES

4.1. Practical relevance

Enrichment from the liquid phase at solid/liquid interfaces provides the basis of several industrial technologies. When adsorption occurs from the liquid phase, an interface of a new composition may develop, and consequently the energy conditions of the surface change as well. Adsorption at S/L interfaces can be used to influence the stability of dispersions, which is often a significant step in industrial or lab scale processes. The S/L adsorption phenomenon is also utilised, e.g., in water purification, in solvent recovery and regeneration, in decolouring (in food industries), in the textile industry (dyeing and printing), in ore enrichment (flotation), oil recovery, washing, etc. Further examples are liquid chromatography, heterogeneous catalysis; the size of nanoparticles can be controlled if synthesised within the interfacial layer. Occasionally, it may serve as an alternative method for determining the surface properties (e.g., surface area) of solid materials (adsorbents, catalysts, fillers in composite materials) that apply in the liquid medium, as S/L conditions are more relevant to their application than standard nitrogen adsorption measurements.

In electrochemical processes adsorption may lead to the alteration of the electrode potential, thus unwittingly disturbing the electrode processes.

S/L interactions have significant ecological relevance as well. The fundamentals of adsorption are also a requirement for understanding the processes that occur at the interfaces of soil particles exposed to rainfall, ground water or waste waters, or of particles floating in lakes, rivers or oceans, etc., and the consequences of all these interactions in the natural environment.

4.2. S/L interactions in pure liquids

It was shown earlier that solid surfaces possess excess energy compared to the bulk phase. When the surface of a solid material is in contact with a pure liquid phase, just as with S/G interactions, the molecules of the liquid phase also tend to reduce this excess energy. An interface develops where the orientation (and thus the density) of the liquid molecules differs from that in the bulk liquid owing to their different environment (see Fig. 1.1). In extreme cases the effect can be followed macroscopically, e.g., with a liquid pycnometer.

Wetting also involves a heat effect. The heat of wetting or heat of immersion can be measured with high sensitivity microcalorimeters. In the case of powders, where determination of the contact angle is not straightforward, the heat of wetting or the heat of

immersion can be alternatively used to characterize the wettability of the solid surface with the liquid in question.

4.2.1. Heat of immersion

In immersion wetting the S/G interface is completely replaced by an S/L interface. As explained earlier this is an exothermic process. The heat evolved per unit mass or surface area is called the heat of immersion (q_w):

$$q_w = h_{S/L} - h_S, \quad (87)$$

where $h_{S/L}$ and h_S are respectively the specific enthalpies of the completely wet surface and the originally dry solid surface. The experimentally determined heat of immersion is the gross heat change, which reflects the quality of the interacting phases and is influenced by both the chemical composition and the morphology of the surface.

In the case of solids of identical chemical composition and morphology the heat of wetting is proportional to the surface area of the probe. Thus, at constant temperature and immersion liquid the solid probe materials of various surface treatments exhibit heat effects that reveal the surface treatment, or even the nature and density of the surface groups that decorate the surface.

The relationship between the contact angle and the calorimetric results (heat of wetting) can be given as

$$q_w = T \cdot \gamma_{LG} \frac{d \cos \vartheta}{dT} - (\gamma_{LG} - T \frac{d\gamma_{LG}}{dT}) \cos \vartheta \quad (88)$$

where T is the temperature (K), γ are the corresponding surface tensions (L liquid, G gas or vapour), and ϑ is the contact angle. If the temperature interval is narrow enough the temperature dependence of the surface tension can be neglected. E.g., for water $\gamma_{LG} = 71.97$ mJ/m² and $d\gamma_{LG}/dT = -0.16$ mJ/m²K at 25 °C.

4.3. Multicomponent liquid phases

When a homogeneous solid phase is in contact with a multicomponent liquid the interactions with the different components may be different. As a result, components that have a stronger interaction with the surface sites of the solid will be enriched on the surface.

In contrast to vapour (gas) adsorption, coverage by liquids is always complete, i.e., when the solid is in contact with enough liquid (the minimum is the amount needed for the formation of a complete adsorbed layer) all the surface sites are occupied. However, this does not mean that the actual distribution of the liquid molecules corresponds to an energy minimum, i.e., **competition** takes place. The adsorption equilibrium is achieved through exchange of molecules A in the bulk liquid and molecules B already in the interface, which can be described by the following equation:



where β is the ratio of the cross sectional area $a_{s,i}$ of the corresponding molecules:

$$\beta = \frac{a_{s,2}}{a_{s,1}} \quad (90)$$

The composition of the surface layer is determined by the interactions of the A and B molecules within the liquid (A-A, B-B, A-B) and in the adsorbed phases, and their interactions with the surface sites. Therefore, the description of ionic and non-ionic systems has to be treated separately. In the following section the sorption behaviour of non-ionic liquids and weak electrolytes with solid surfaces will be discussed first. Our considerations will be limited to binary liquid mixtures.

Let's redraw Figure 2.4 for a binary liquid mixture (Figure 4.1.):

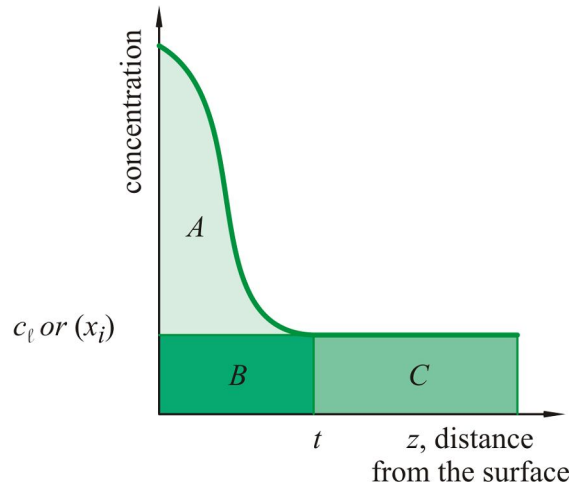


Figure 4.1. Shape of the concentration profile developing at S/L interface; t is the thickness of the adsorbed layer. Area $(A+B)$ is related to the amount of the more strongly adsorbed component in the interface; area A is its surface excess, C and c_t (or x_i) are respectively the amount and concentration of the preferentially adsorbed component i in the bulk liquid.

4.3.1. Quantitative description of the adsorption; the adsorption isotherm

The adsorption here again is characterized by the isotherms and their parameters deduced from various fitting models.

They can be measured either by static (batch) or dynamic (flow) methods. The measurement (or rather the estimation) of the increased mass is also an alternative. Direct determination of the composition of the adsorbed layer nevertheless is fairly challenging. Therefore, indirect methods are widely applied: the composition change in the free bulk liquid combined with a material balance is used to determine the amount and composition of the adsorbed layer. This can be done correctly only if we are assured that the change in the composition of the free bulk liquid is caused strictly by adsorption alone. That is, neither the liquid nor any of its components should dissolve the solid or any impurities of the solid, no chemical reaction occurs between any of these players, evaporation loss is eliminated, etc. Any suitable method for monitoring the composition of the liquid mixture (UV absorption, IR, etc.) can be used. In the case of multicomponent mixtures, particularly gas or liquid, chromatography assisted concentration determination is recommended.

Batch method

The solid sample of known mass is placed in contact with the liquid phase of known amount and concentration in a sealed container at constant temperature. The equilibration time is

determined from kinetic measurements prior to the equilibrium series. Shaking or rotating the sample may shorten the contact time. The adsorbed amount can be calculated from the initial and equilibrium concentrations and from the masses of the contacting phases. Two methods are widely used: i) *Constant solid/liquid ratio*. Solid probes of identical mass are placed in contact with solutions of identical volume, but with systematically varied initial concentration. The volume of the liquid used depends on the sensitivity of the concentration determination method. The theoretical minimum of the liquid volume is the amount needed for the adsorbed layer. ii) *Systematically varied solid/liquid ratio*. An increasing amount of the solid probe is placed in contact with the liquid phase of identical initial concentration and volume, respectively, or solid probes of identical mass are placed in contact with the liquid phase of the same initial concentration but systematically changed volume.

Dynamic method

Both elution and frontal chromatographic techniques can be used. The column is filled with the solid probe and the adsorbed amount is determined in experiments at constant temperature either from the area of the chromatographic peak or from the break-through curve respectively, after calibration.

4.3.2. Adsorption from completely miscible binary liquid mixture

Figure 4.2 may help to introduce the abbreviations.

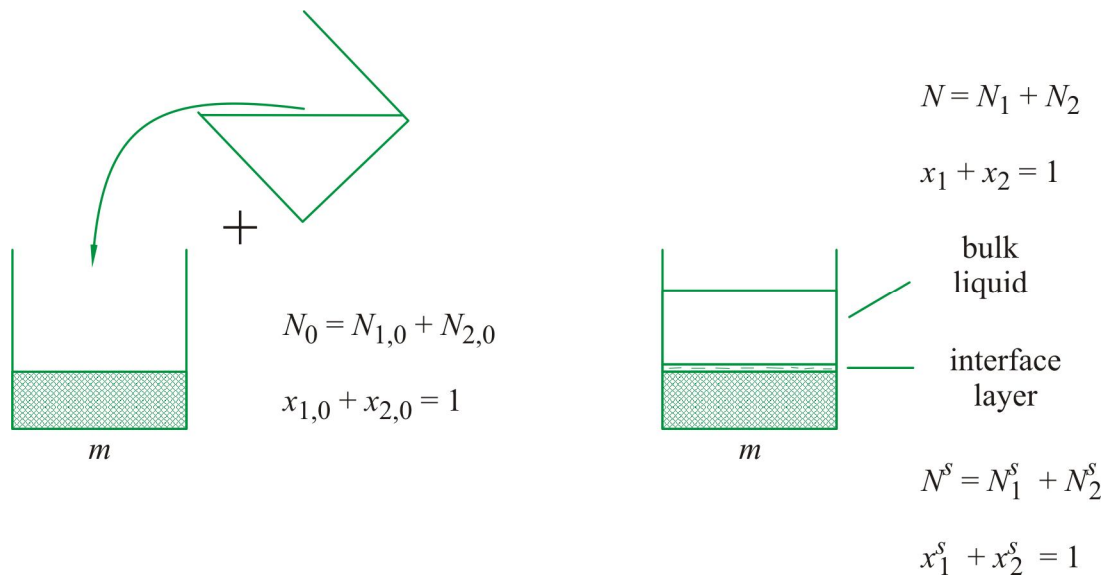


Figure 4.2. Adsorption from a completely miscible binary liquid mixture.

N_i and x_i , respectively, are the number of moles and the mole fraction of the component i in the liquid phase. The subscript 0 distinguishes the initial state (no index is used for the equilibrium state). The superscript s is used for the interface. m is the mass of the solid probe.

$n_i = \frac{N_i}{m}$ will be used for the specific amounts (relative to unit mass of the solid). The mass balance of the equilibrated system for component (1) can be written as

$$n_0 x_{1,0} = n_1^s + (n_0 - n^s) x_1 \quad (91)$$

After rearrangement

$$n_0 (x_{1,0} - x_1) = n_1^s - n^s x_1 \quad (92)$$

n_1^s corresponds to the area $A+B$, and $n^s \cdot x_1$ to the area B in Figure 4.1. Their difference is thus equal to the excess adsorbed amount of component (1) in the interface layer, given by the area A in this figure. The surface excess n_1^σ can be also calculated from the data referring to the bulk liquid phase as

$$n_1^\sigma = n_0(x_{1,0} - x_1) = n_1^s - n^s x_1 \quad (93)$$

The expression between the two equality signs in Eq. 93 contains the instructions for experimentally determining the adsorption excess isotherms, i.e., the functions $n_1^\sigma = f(x_1)$, ($T = \text{constant}$): the initial amounts must be known and the concentrations at the beginning and in the equilibrium condition should be measured.

Excess isotherms

The isotherms are U or S shaped (Figure 4.3.). The U shape means that the same component adsorbs preferentially throughout the whole concentration range. S-shaped isotherms possess an intercept. The preferentially adsorbing component depends on the bulk liquid composition. In this case also the adsorbed excess amount is zero not only at $x_i = 0$ and 1, but also at the intercept, i.e.,

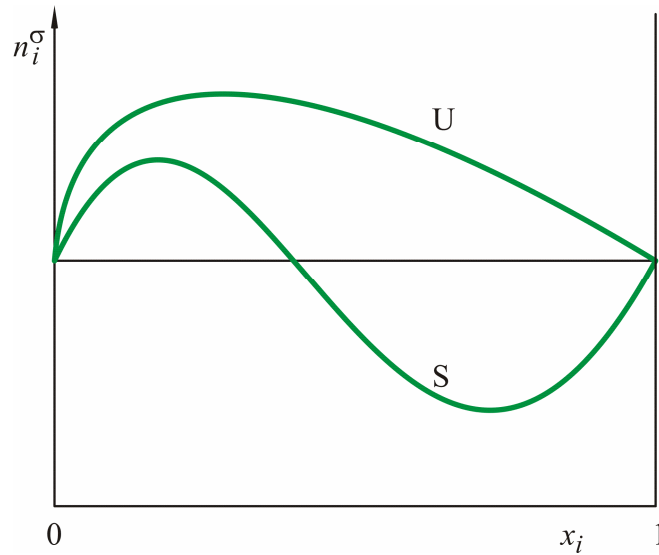


Figure 4.3. Adsorption excess isotherms.

$$n_1^\sigma = n_0(x_{1,0} - x_1) = n_1^s - n^s x_1 = 0 \quad (94)$$

Since

$$n_1^s - n^s x_1 = n^s x_1^s - n^s x_1 = n^s (x_1^s - x_1), \quad (95)$$

therefore

$$x_1^s = x_1, \quad (96)$$

i.e., the composition of the bulk phase and the interface layer is identical. This particular composition – which resembles liquid/vapour equilibrium – is called the adsorption azeotropic composition.

A more complete classification and analysis of the liquid excess isotherms was proposed by Schay and Nagy¹ (Figure 4.4.). Like the gas adsorption isotherms, the shape of the isotherms reflects typical behaviour that is simultaneously characteristic of both the adsorbent and the liquid mixture of the system (see the isotherms in Figure 4.6 below). The upper and lower lines of Figure 4.4 are the excess isotherm and the individual isotherms of the liquid components, respectively. The individual isotherms show the absolute amount of the given component in the interface.

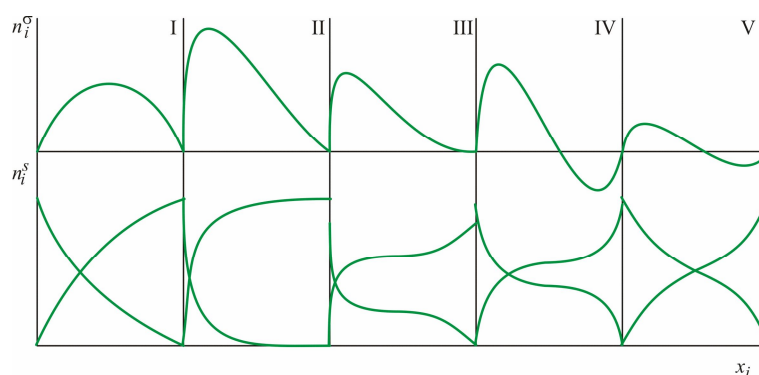


Figure 4.4. Schay – Nagy classification of the excess isotherms of completely miscible binary systems. Upper line: excess isotherms; lower line: individual isotherms.

The interpretation of the excess isotherms is more complex than that of gas adsorption isotherms and also requires knowledge of the thermodynamic behaviour of the liquid mixture. The models generally employ approximations involving the thickness, the composition and/or the structure of the adsorbed layer. For instance, the surface area of the solid can be derived from the excess isotherms if they contain a long enough linear region (Types II, III and IV). The analysis proposed by Schay and Nagy is demonstrated for isotherms of Type IV = Figure 4.5.

¹ Géza Schay (1900-1991) and Lajos György Nagy (1930-1999), Hungarian physico-chemists, published their classification in 1961. Schay worked with Polányi in Berlin between 1927 and 1930.

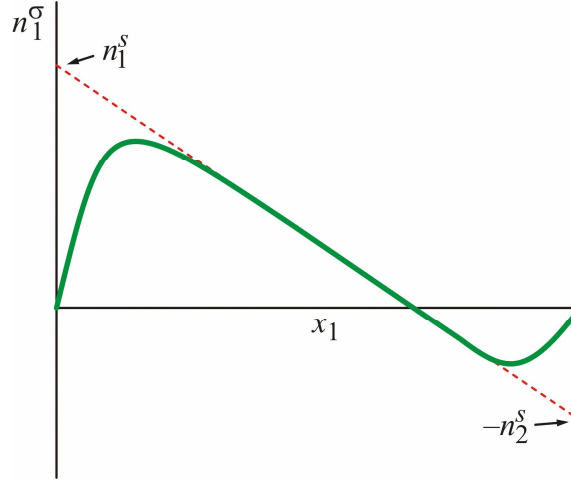


Figure 4.5. Schay – Nagy analysis of excess isotherms of Type IV.

For the linear section

$$y = n_1^s - n^s x_1 = ax + b \quad (97)$$

where a and b are the slope and intercept of a straight line. Based on Eq. 97 in the linear range, $b = n_1^s$ and $a = -n^s$. The extrapolated value of the linear plot at $x_1 = 0$ and $x_1 = 1$ yield n_1^s and n_2^s , respectively. As the a and b parameters of the straight line are constant, it follows that in the linear range the composition of the adsorbed layer is constant and is not influenced by the equilibrium composition of the free bulk liquid. Since

$$x_1^s = \frac{n_1^s}{n^s} = \frac{n_1^\sigma}{n^s} + x_1 \quad (98)$$

the corresponding individual isotherms can be derived as

$$n_i^s = n_i^\sigma + n^s x_i \quad (99)$$

In the case of physisorption, owing to the strong distance dependence of the adsorption potential (Figure 2.8), monolayer adsorption can be assumed. If the cross-sectional area ($a_{s,i}$) is a fixed property of the adsorbed molecules and is not influenced by the adsorption site, the surface area of the solid can be calculated as:

$$A_s = n_1^s a_{s,1} + n_2^s a_{s,2} \quad (100)$$

The molar cross sectional area of several liquids is listed in Table 4.1.

Table 4.1. 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

The shape of the isotherm is determined jointly by the adsorbent and the two completely miscible liquids. Figure 4.6a shows the excess and individual isotherms measured on an activated carbon with ethanol (1) – benzene (2) mixtures. The isotherms in Figure 4.6 b were obtained with various alcohol (1) – benzene (2) mixtures on a clay mineral (palygorskite). Both data sets were collected at ambient temperature.

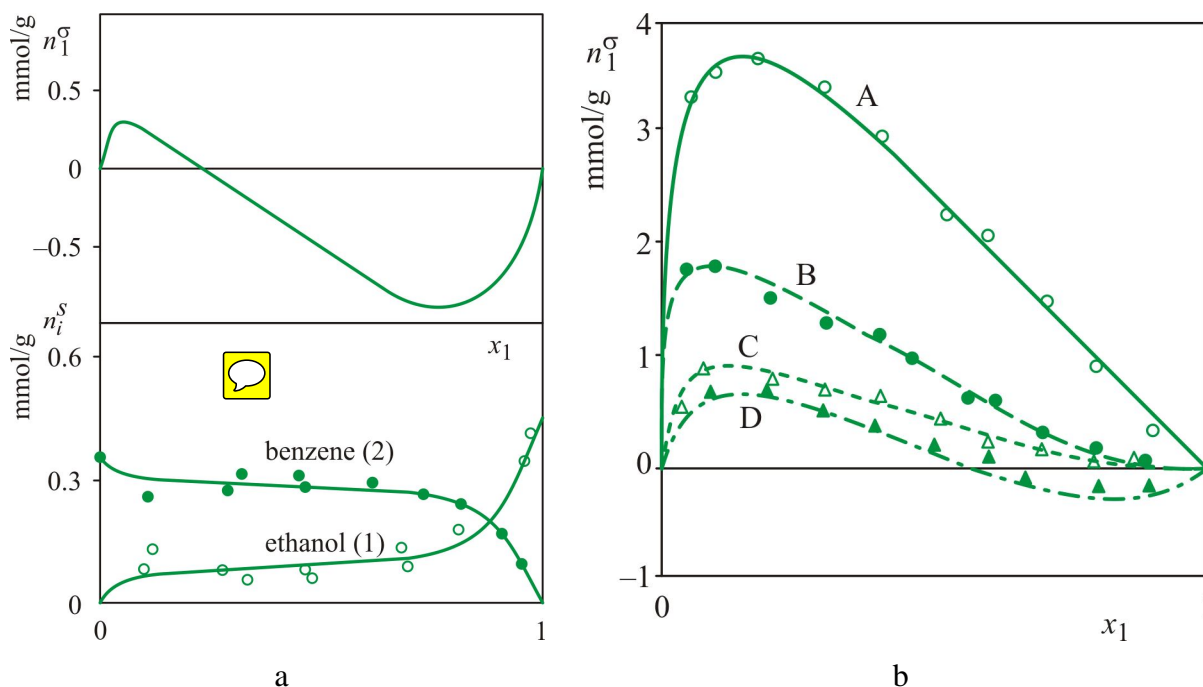


Figure 4.6. Adsorption isotherms from alcohol (1) – benzene (2) binary mixtures
a) ethanol – benzene on activated carbon; b) A: methanol - benzene, B: ethanol - benzene,
C: n-propanol - benzene, D: i-propanol – benzene on palygorskite.

The shape of the ethanol – benzene isotherms perfectly reflects the fact that the less polar carbon preferentially adsorbs the nonpolar benzene, while the polar clay mineral adsorbs exclusively the ethanol. As the hydrophobic chain of the alcohol becomes longer its adsorption is less preferred.

4.3.3. Adsorption from dilute non-electrolytes and weak electrolytes

In this case the dissolved material(s) and the solvent(s) can be clearly distinguished. Having only a single dissolved material and a single solvent, the concentration of the first one is very low, therefore the significance of the dissolved molecule –dissolved molecule interactions in the solution are negligible. The role of dissolved molecule – solvent molecule interactions – as we will see later – is much more significant. Of course, if we have a more complex system all the potential interaction should be considered.

In case of dilute solutions, the difference between the absolute and excess adsorbed amount can be neglected, as the bulk concentration is low and therefore area B in Figure 4.1. is negligible compared to area A. That is, in Eq. (93) term $n^s x_1$ can be neglected as x_1 is small:

$$n_1^\sigma = n_1^s - n^s x_1 \approx n_1^s \quad (101)$$

In case of dilute solutions instead of mole fractions the concentration is more often given in mol/L or g/L units. Therefore, it might be more convenient to use them also to express the specific adsorbed uptake as

$$n^s = \frac{c_0 V_0 - c_e V_e}{m} = \frac{(c_0 - c_e)V}{m} \quad (102a)$$

if molar concentration is used or as

$$m^s = \frac{c_0 V_0 - c_e V_e}{m} = \frac{(c_0 - c_e)V}{m} \quad (102b)$$

when the concentrations are given e.g., in g/L units. c is the concentration of the dissolved non-electrolyte, V is the volume of the solution contacted with the adsorbent of mass m . Subscripts 0 and e refer to initial and equilibrium states, respectively (the latter one will be not

marked in the text follows). If the volume does not change during the experiment, the expression is simpler, as shown in the last terms of Eqs. 102. As we already excluded evaporation loss, what would result in volume change? Several solids (cellulose, clay, several polymer gels, even porous carbon) may swell when contacted with certain solvents. Part of the solvent then will be *absorbed* (!) by the solid thus reducing the volume of the free solution.

The shape of the typical isotherms (Figure 4.7.) reminds to gas adsorption isotherms but we also may recall some of the individual isotherms in the previous chapter. They might be of L or S shaped or stepwise (SW).

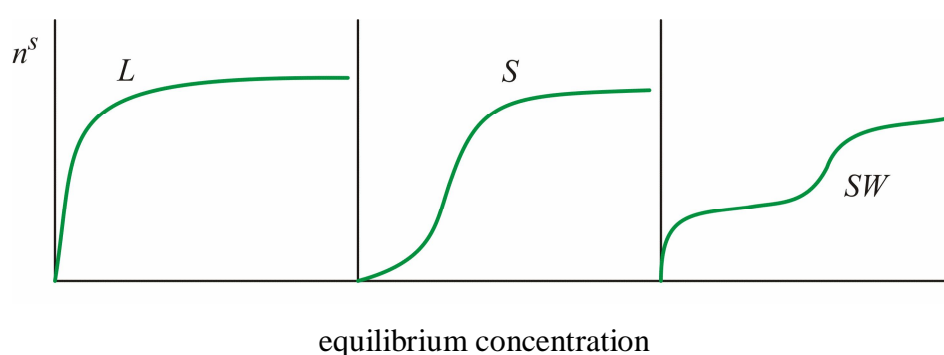


Figure 4.7. *Types of adsorption isotherms for dilute non-electrolytes or weak electrolytes.*

As it was shown earlier, the initial section of the isotherm is related to the strength of the interaction between the solid and the adsorbate. L shaped isotherms are obtained when this interaction is strong. S shaped isotherms can be measured when the interaction between the solute and the solvent are stronger than between the solute (adsorbative) and the surface. Here, similarly to Type III for gases, that adsorption of the solute starts at a few specific sites which work as nucleation centres for further adsorption. In both cases the uptake n^s (or m^s) reaches a saturation plateau. SW type isotherms generally indicate bilayer adsorption of assembled adsorbates. It is typical in case of surfactant molecules: the first layer adsorbs in an oriented way on the solid surface: if the surface is typically polar the adsorbates are anchored with their polar end. Thus, the completion of the monolayer converts the surface nonpolar. The second layer develops by the self-assembly of the amphiphilic molecules: the nonpolar end interacts with the nonpolar adsorbate.

The energy of the interaction is influenced concurrently by the energy (-distribution) of the surface sites, the properties of the dissolved solute and the solvent molecules. It is well

demonstrated in Figure 4.8. The adsorption of aliphatic acids with increasing nonpolar chain was investigated from a polar solvent (water) on an adsorbent with nonpolar surface (activated carbon) and from nonpolar toluene on a polar surface (silica).

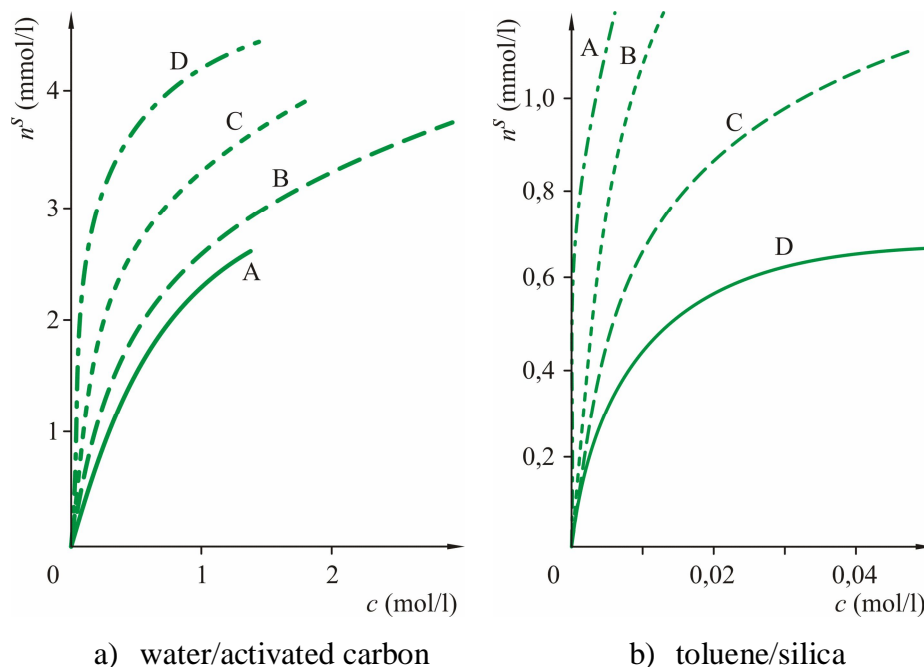


Figure 4.8. Adsorption of formic acid (A), acetic acid (B), propionic acid (C) and butyric acid (D) from water on activated carbon (a) and from toluene on silica (b).

Interpretation of the experimental data

If wish to go beyond the general description given in the previous paragraph models are needed. Several of them are identical with those already introduced in the gas adsorption chapter. In spite of all its deficiencies the most frequently applied is still the Langmuir model:

$$n^s = \frac{n_m \cdot K \cdot c}{1 + K \cdot c} \quad (103a)$$

or

$$m^s = \frac{m_m \cdot K \cdot c}{1 + K \cdot c} \quad (103b)$$

where n^s or m^s is the amount of dissolved material (in mol and g, respectively) uptaken by generally 1 g of adsorbent, K is the equilibrium constant of the adsorption and c is the

equilibrium concentration. The two parameters are generally derived by the linear fit (Figure 4.9)

$$\frac{c}{n^s} = \frac{1}{Kn_m} + \frac{c}{n_m} \quad (104)$$

The Langmuir model may work for L shaped or partly for SW isotherms but not for S shaped ones.

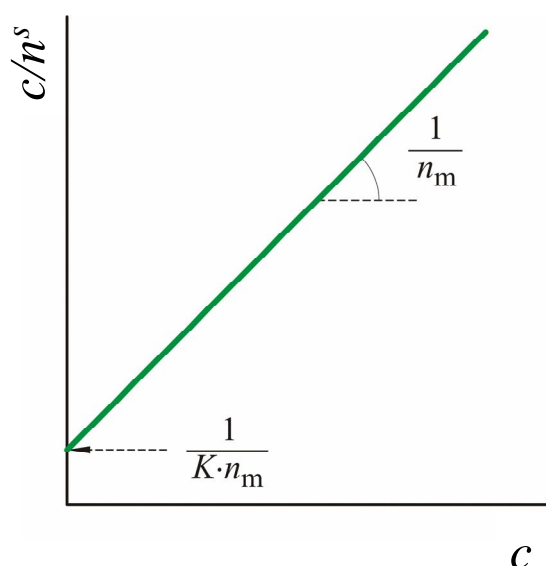


Figure 4.9. Derivation of the Langmuir parameters from the linear Langmuir fit.

Even if the strict conditions of the model are not met both the linear and the nonlinear fit might be of good quality. The attractiveness stems from the clear physical meaning of the two fitted parameters. In spite of this advantage special attention is needed for the interpretation of the observations. The system is much more sophisticated than in gas adsorption: the dissolved molecules are much more complex than the small and often spherical gas molecules and their position/conformation/orientation on the surface may be influenced by the energy (-distribution) of the surface sites and the nature of the solvent (and of course by other dissolved molecules and co-solvents). The solvent can significantly influence the structure of the adsorbed layer. We must not forget that the solute and the solvent molecules compete for the surface. The estimation of the surface area from monolayer capacity is not straightforward. The “monolayer” (saturation) capacity does not necessarily

mean complete coverage and the cross sectional area of the adsorbed molecules strongly depends on the conditions.

In case of very dilute solutions ($c \rightarrow 0$) – which is often the case for example in environmental samples - the isotherm simplifies to a straight line: $Kc \approx 0$ and therefore the nominator $1+Kc \approx 1$. Thus, the adsorbed amount is directly proportional to the equilibrium concentration (Henry type isotherm), where n_m and K cannot be separately determined:

$$n^s = K_H \cdot c \quad (105)$$

Instead of the Langmuir model (surface sites with identical binding energy) the empirical model established by H.M.L. Freundlich² may give a better fit. It is presumed in this model that the energy of the surface sites show a Gaussian energy distribution. No physical interpretation corresponds to its two parameters, k and m' .

$$n^s = k \cdot c^{1/m'} \quad (106)$$

k and $m' > 1$ are derived from a linear fit (Figure 4.10.):

$$\ln n^s = \ln k + \frac{1}{m'} c \quad (107)$$

² Freundlich, H.M.F., (1906). Über die adsorption in Lösungen. Z. Phys. Chem., 57 A, 385-470

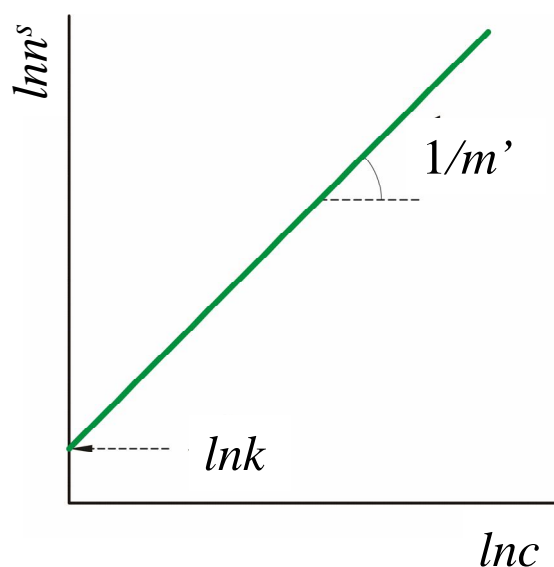


Figure 4.10. Derivation of the Freundlich parameters from the linear Freundlich fit.

In Table 4.2. we collected the most frequently applied isotherm models for dilute nonelectrolyte solutions.

Table 4.2. Model equations for dilute nonelectrolyte solutions.

Model	Equation	Comment
Henry	$n^s = k_H \cdot c$	
Langmuir	$n^s = \frac{n_m \cdot K \cdot c}{1 + K \cdot c}$	surface sites have equal binding energy
Freundlich	$n^s = k \cdot c^{1/m'}$	fails at high concentrations
equations derived from the Langmuir model	$n^s = \frac{a_1 c}{1 + b_1 c} + \frac{a_2 c}{1 + b_2 c}$	Generalized formula for i) single solute on a surface of bimodal energy distribution or ii) surface is monoenergetic but the single solute has two different binding sites
	$n^s = n_m \frac{K_1 c}{1 + K_1 c} + n_m \frac{K_2 c}{1 + K_2 c}$	Surface is monoenergetic but the single solute (having a saturation capacity of n_m), e.g., chiral/achiral separation, adsorption of protein, etc.

	$n_i^s = n_{m,i} \frac{K_i c_i}{1 + \sum K_i c_i}$	competitive adsorption of solute species i . n_m and K is determined independently from the corresponding single solute Langmuir isotherms
	$n^s = n_m \frac{(K_{LF} c)^\eta}{1 + (K_{LF} c)^\eta}$	Langmuir-Freundlich
Radke-Prausnitz	$n^s = n_m \frac{K' c}{1 + (1/\eta)(K' c)^\eta}$	A. Deryło-Marczewska, M. Jaroniec, in: E. Matijević (Ed.), Surface and Colloid Science, Plenum Press, New York, 14 (1987) 301

Large planar dye molecules are often applied to estimate surface area from liquid phase adsorption assumed that their adsorption on the surface is exclusive and they form a closely packed monolayer on the surface. Due to their extension, we have to consider size exclusion effect, i.e., only the internal area of narrow pores are not measured. It might be useful to estimate the area in large pores (external surface) which cannot be detected with gas adsorption. Methylene blue is among the most frequently applied molecules (Figure 4.11.).

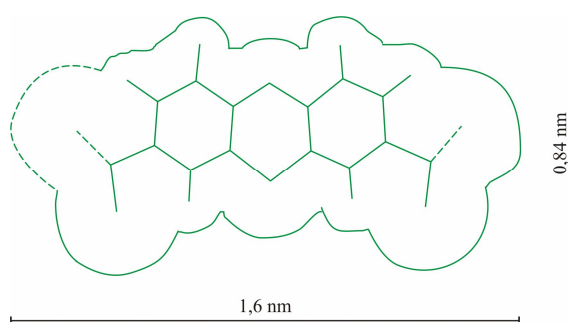


Figure 4.11. The typical sizes of the methylene blue dye molecule.

4.4. References

1. F. Rouquerol, J. Rouquerol, P. Llewellyn, G. Maurin, K. Sing: Adsorption by Powders and Porous Solids, 2nd Edition. Principles, Methodology and Applications, 2013, Elsevier
2. J. J. Kipling: Adsorption from Solutions of Non-Electrolytes. Academic Press, 1965.