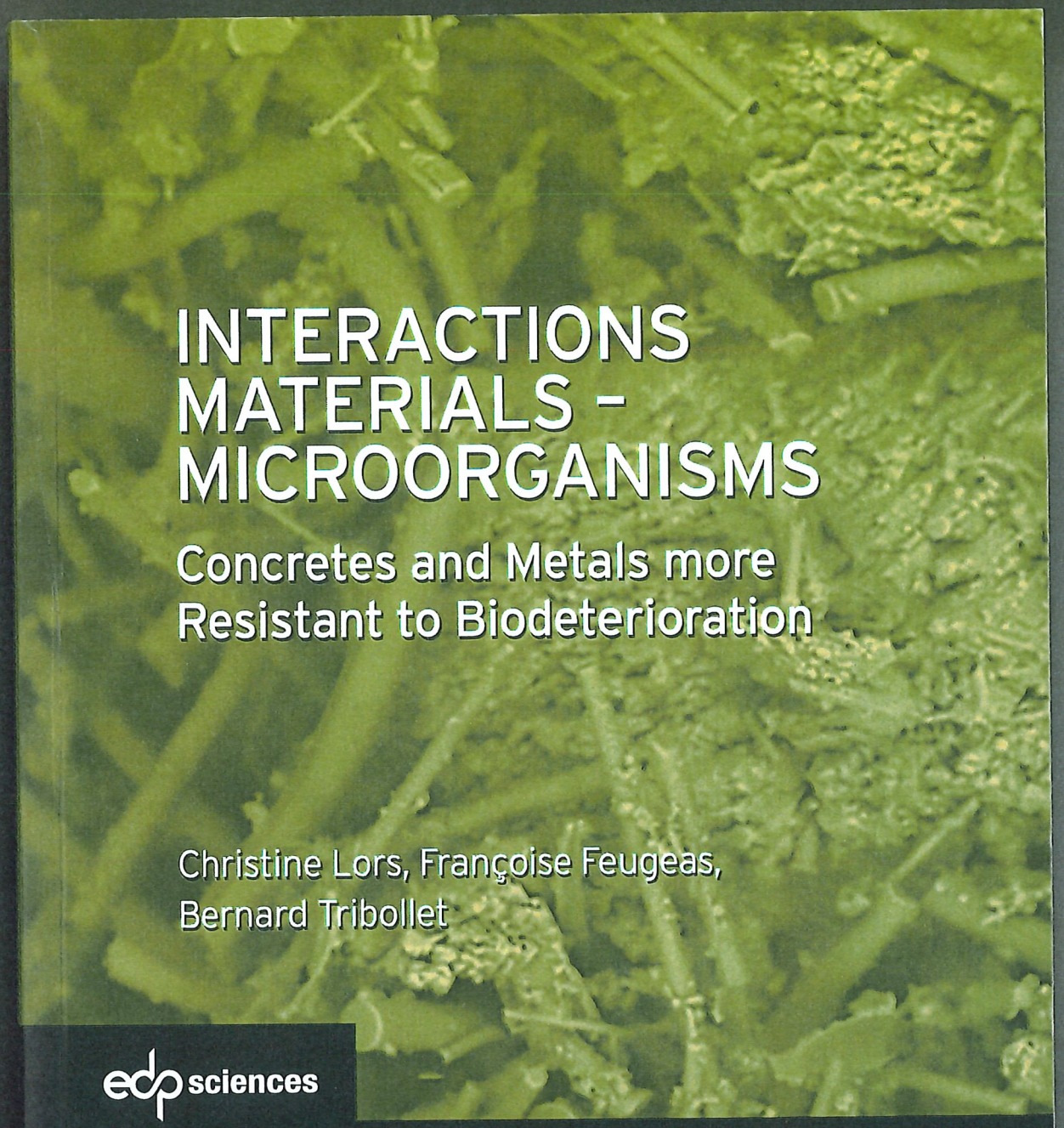

INTERACTIONS MATERIALS - MICROORGANISMS

Concretes and Metals more Resistant to Biodeterioration

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1 Introduction to the physical chemistry of surfaces

Christine Dupont-Gillain

1.1. Generalities

A surface (or interface) is the area of a biphasic system located at the frontier between the two phases. Surfaces are found between two distinct solid phases (as in alloys), between a solid and a liquid phase, between two immiscible liquids (as in emulsions), or between a solid phase and a gas phase. A transition between the properties of two phases occurs at the interface. Although the surface is often considered as a plane, for reasons related to geometrical description and application of mathematical models, this transition operates over a given thickness, and the surface is actually tridimensional [1].

Surface science is of uttermost importance in many scientific and technological fields. Challenges such as increasing the adhesion between materials, improving the biocompatibility of a material, designing a biosensor, developing a catalyst, or mitigating (bio)corrosion can only be taken up based on surface modification and characterization techniques.

Is there a good reason to consider surfaces apart from other systems and to devote a branch of science to them? Surfaces actually display very peculiar properties, as a result of the discontinuity which characterizes them. In contrast with a molecule (or atom) located in the bulk of a material, a molecule located at the interface may be submitted to very different interactions depending on the direction. Take, for example, the oil-water interface: the interfacial water molecule can only establish hydrogen bonds from the water side. This discontinuity of interactions generates particular phenomena. Surfaces are highly reactive, a feature that is largely exploited in heterogeneous catalysis, for example. They also tend to be modified in contact with the surrounding environment, either through the adsorption of compounds present in one of the two phases, or through the reorganization of one of these phases (surface enrichment or depletion of one constituent or chemical function of this phase).

Surface science is tightly related to colloid science, with colloids being small particles with a size in the range 1-1000 nm. Finely divided materials do indeed develop very large surface areas. Powders made of particles in the nanometer range, or materials with a porosity at this scale, exhibit specific surface areas

of hundreds of square meters per gram. In these materials, the ratio between the developed surface and the volume is very high, and their behaviour is then largely described through concepts of the physical chemistry of interfaces [1, 2]. For example, activated carbon is used in filtration given its large specific surface area which allows the elimination of undesired compounds through their adsorption. This is illustrated in figure 1.1, which shows the discoloration of a food dye solution through its contact with activated charcoal (typically used for purification of water in aquariums). Within a few hours, the dye molecules are adsorbed in the pores of the activated charcoal. The tendency of the surface of the activated carbon to bind dye molecules finds its origin in the high surface energy of the material, which will be reduced after adsorption. The concept of surface energy will be detailed in section 1.2, while adsorption processes will be discussed in section 1.3 of this chapter.

This introductory chapter aims at giving an overview of important concepts in surface science, and at stimulating curiosity regarding this topic. Since the chapter is written for a readership with a diversity of backgrounds, it does not enter into theoretical details, for which the reader is invited to consult more specialized articles or textbooks, as for example those cited in the text.

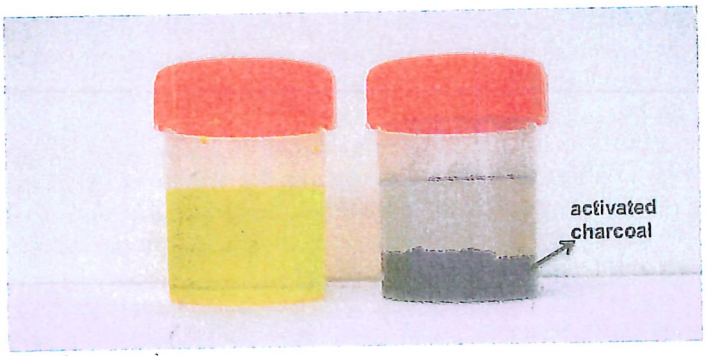

FIG. 1.1. – Solution of a yellow food dye, before (left) and after (right) treatment with activated charcoal particles, which were directly introduced in the solution.

1.2. Surface tension and wettability

1.2.1. Concepts

You have certainly observed the following: an insect walking on water, as if there was a kind of superficial skin on top of the latter; that it is possible to fill a water glass above its upper level, ending up with a water dome; you may have seen mercury droplets rolling on a surface, hardly touching it; you may have noted also that the thin water trickle that gets out of a tap breaks down into a series of droplets. These observations are all related to surface tension, or

surface energy, of these liquids. It costs energy to enlarge the surface of a liquid. Therefore, a liquid will spontaneously tend to decrease its surface area, with a view to reducing the total energy of the system [1].

The concept of surface energy, illustrated here above for the case of liquid-air interfaces, may be extended to all kinds of interfaces. The surface tension γ is the change in free energy dG related to the increase by one unit of the interfacial area dA:

$$dG = \gamma \, dA \tag{1.1}$$

Since the natural tendency of systems is to reduce their free energy ($dG < 0$), interfacial areas are spontaneously reduced. This explains the spontaneous coalescence of the dispersed phase of an emulsion, or Ostwald ripening, as it is called, observed when solid precipitates are aged.

The surface tensions γ_{LV} of a few liquids are given in table 1.1. The notation LV in index underlines the fact that these values are linked to the interface between a liquid (L) phase and a vapour (V) phase. Note that the vapour phase is commonly assimilated to a vacuum. In the case of a liquid - solid (S) interface, surface tension will be noted γ_{LS}, and so on for other kinds of interfaces. The units of surface tension are given in units of energy per unit of surface area ($J\ m^{-2}$), or in units of force per unit of length ($N\ m^{-1}$). Liquids found in table 1.1 are ranked by order of increasing surface tension. In this way, the link between the value of the surface tension and the nature of intermolecular (or interatomic) interactions does appear. The stronger the interactions within the liquid, the higher the amount of energy needed to create a new unit of surface area, the higher the surface tension. Hence, the low γ_{LV} value for hexane is associated to the weak London-van der Waals interactions acting between apolar hexane molecules. The increasing values found for ethanol, 2-aminoethanol and water are reflecting the increasing influence of hydrogen bonds established between these molecules. Finally, mercury atoms are interacting through metallic bonding, which is even stronger. A correlation can actually be established between the boiling temperature of liquids and their surface tension.

TABLE 1.1. – Surface tension γ_{LV} of selected liquids [3].

liquid	γ_{LV} ($mJ\ m^{-2}$)
hexane	18.4
ethanol	22.4
2-aminoethanol	48.3
water	72.9
mercury	486.5

Starting from surface tension, it is quite straightforward to assess the work of cohesion and adhesion [1, 4]. Cohesion refers to the attraction between two entities from the same substance, while adhesion is the attraction existing between

different substances, as illustrated in figure 1.2. The work of cohesion W_{11} can be extracted from the balance of lost and created interfaces when trying to separate a material by one unit of surface area:

$$W_{11} = 2\,\gamma_1 = 2\,\gamma_{SV} \tag{1.2}$$

Two units of solid-vacuum surface area are indeed created upon separation. As far as adhesion between solids 1 and 2 is concerned, the same approach allows calculating the work of adhesion W_{12} as follows:

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{1.3}$$

The separation process indeed leads to the creation of one unit of solid 1 - vacuum surface area and one unit of solid 2 – vacuum surface area, as well as to the loss of one unit of solid 1 - solid 2 interfacial area.

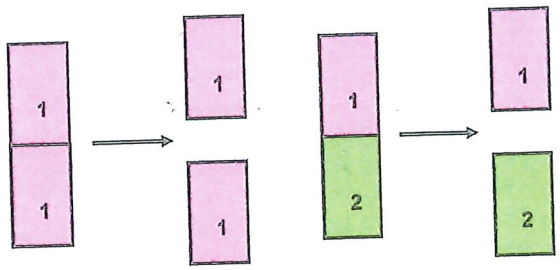

FIG. 1.2. – Illustration of the work of cohesion (left) and of adhesion (right). Solids 1 and 2 are placed in an environment that can be assimilated to a vacuum.

When a droplet of liquid is deposited on the surface of a solid material, this droplet takes a shape that depends on the equilibrium between the tendency of the liquid to be cohesive, and its tendency to adhere to the solid. The wettability of a solid can be quantified through the measurement of the contact angle of the liquid on this solid. The contact angle θ is the angle formed between the surface plane and the tangent to the droplet, taken at the contact point between the three phases: solid, liquid and vacuum (or gas), as illustrated in figure 1.3. Hence, mercury has a very high contact angle on most solid substrates, while the contact angle of water is low on polar substrates, which are said to be hydrophilic and higher on more apolar substrates, which are said to be hydrophobic. If water molecules can establish hydrogen bonds with the solid surface, the tendency to adhere on this solid will indeed compensate the high cohesion of water.

The balance between the vectors representing the projections in the horizontal plane of interfacial tensions acting at equilibrium along the contact line between the droplet and the solid (Fig. 1.3) allows Young's equation to be deduced [1, 2]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{1.4}$$

This equation links the three interfacial tensions involved. The contact angle θ can be measured directly, based on the analysis of images of the liquid droplet profile. These constitutes fast and low-cost measurements. The information obtained allows solid surfaces to be ranked according to their affinity for a given liquid of interfacial tension γ_{LV}. This thus constitutes a first-choice experimental approach to evaluate the success of surface modification strategies. It should however be noted that the obtained result depends on both γ_{SL} and γ_{SV}. Methods based on the use of several liquids (*i.e.*, different γ_{LV} values) allow γ_{SV} to be estimated. Such methods must be used with caution as the hypotheses underlying their use are seldom met (ideal smooth surface not penetrated by the liquid; state of thermodynamic equilibrium; approximations related to the quantification of interactions).

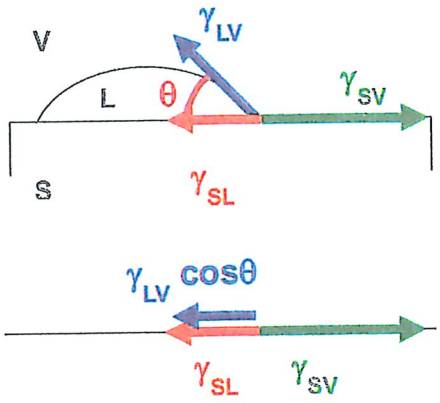

FIG. 1.3. – Top: Scheme of a liquid (L) droplet deposited on a solid substrate (S) in an environment assimilated to vacuum (V), illustrating the way the contact angle θ is defined, as well as the action of interfacial tensions. Bottom: Projection of the interfacial tensions on the horizontal plane, allowing Young's equation to be deduced (Eq. (1.4)).

1.2.2. *Applications*

The tendency for systems to reduce their interfacial energy explains the instability of colloidal systems, *i.e.*, small particles tend to aggregate to decrease interfacial areas. It also drives adsorption (Section 1.3), including the surface contamination of solid materials. Materials with a high surface energy have a particularly strong tendency to be contaminated. For a material in contact with air, indeed, the adsorption of rather apolar organic molecules from the atmosphere results in a decrease of the surface energy. Therefore, carbon, for example, is the most abundant element found at the extreme surface of stainless steel, while the metallic elements typical of that material are under-represented at the outermost surface compared to the bulk of the material.

Surface tension and wettability are also key concepts to understand capillary adhesion [4]. This latter is observed when two solid surfaces are contacting each other through a thin film of a liquid that wets these surfaces well (*i.e.*, low value of θ). This is what we experience when we touch sand with wet hands, or less often, when we stick a spoon to our nose (Fig. 1.4a).

Capillary adhesion results from the low pressure created within the liquid film that separates two solid surfaces, as long as the liquid meniscus is concave, which is the case if the surfaces are well wetted by the liquid (Fig. 1.4c). Hence, two glass slides can adhere to each other owing to a thin water film (water contact angle of clean glass is close to zero). Conversely, two polytetrafluoroethylene (PTFE, more commonly named Teflon) plates, with a high water contact angle value of about 110°, do not adhere through a water film. In this case indeed, the liquid meniscus is convex, and the pressure within the liquid film is higher than the atmospheric pressure. This is illustrated in fig. 1.4b and fig. 1.4c. The relationship between the surface tension of the liquid and the pressure across the liquid meniscus is described by Laplace's equation [1], the development of which is however beyond the scope of this introductory chapter.

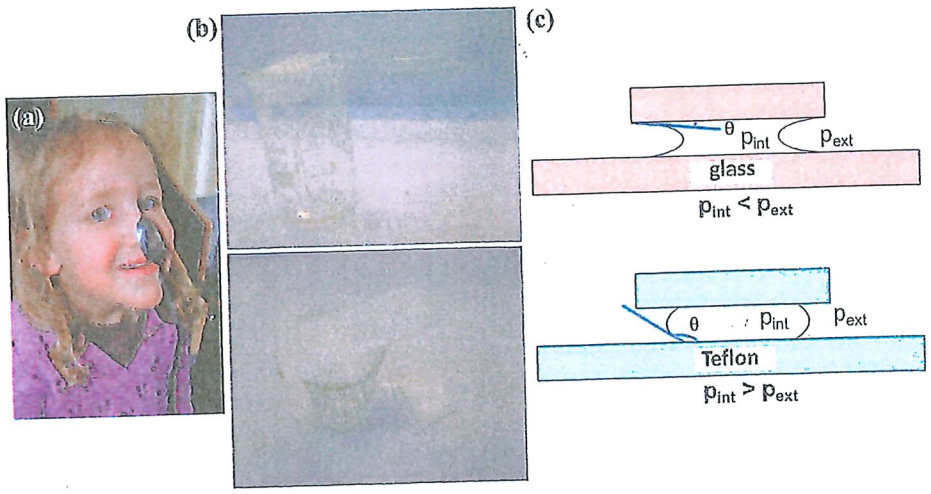

FIG. 1.4. – Illustrations (a and b-top) and principle (c-top) of capillary adhesion. (b, c) Top: capillary adhesion between two microscope slides, between which a drop of water was deposited. One slide is immobilized above a beaker; the second one is placed perpendicular below this first slide. (b, c) Bottom: absence of capillary adhesion in the same conditions but using this time two Teflon plates.

Understanding and controlling capillary adhesion opens many perspectives, whether it is to use it or to avoid it. There are building approaches that are based on the use of wet mineral particles, which form robust materials once linked together through the action of capillary forces acting upon drying, as clay plasters,

for example. On the contrary, in industrial processes aiming at producing powders (pigments, drugs, food, *etc.*), capillary forces are generally unwanted, with a view to obtain aggregate-free powders that can easily be dispersed in water. To reach this goal, approaches such as freeze-drying (technically known as lyophilisation) or drying with supercritical CO_2 are used. The common aim of these approaches is to prevent capillary adhesion between particles, because this would force the intimate contact between particles and would later hinder their dispersion.

Superhydrophobic surfaces have a water contact angle value higher than 150°. Such surfaces are found in Nature (Lotus, Nasturtium or cabbage leaves) and their properties are actually referred to as "the Lotus effect" [5]. Observing and analysing the surface of these vegetal species has allowed to understand that the very high water contact angle value is resulting from a combination of a particular surface chemical composition (the epicuticular wax is very hydrophobic) and of a similarly particular topography (with the juxtaposition of roughness on the microscale, owing to the presence of vegetal cells, and on the nanoscale, due to wax crystals). Biomimetic approaches, *i.e.*, approaches inspired by Nature, are now used to design superhydrophobic materials [6, 7]. Their main advantage resides in the fact that water droplets have a small contact area with the surface, and are rolling on the material, collecting dust or other fouling particles on their way. Superhydrophobic surfaces are thus self-cleaning, as illustrated in figure 1.5.

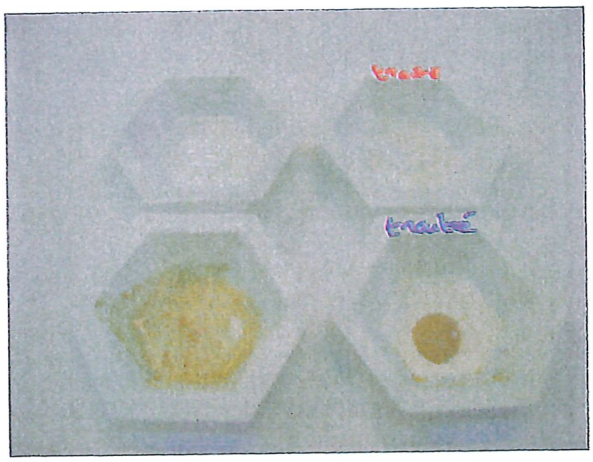

FIG. 1.5. – Four polyethylene weighing scoops. Left: weighing scoops as such. Right: weighing scoops treated with a coating that makes them superhydrophobic (Tegotop 105 in spray; commercial product). Top: a water droplet was deposited on the weighing scoop. Bottom: the weighing scoop was fouled with pepper, then a water droplet was deposited and was moved along the surface plane to tentatively collect pepper particles; this was only successful in the case of the superhydrophobic weighing scoop (bottom right image).

1.3. Adsorption

In a biphasic system, if one compound present in one of the phases is able to move within this phase (solute in a liquid phase, polymer chain above the glass transition temperature, *etc.*), and if this compound reduces the interfacial tension by establishing favourable interactions with the two phases, then it will accumulate in the surface domain. Adsorption refers to this accumulation of a compound at the interface and must be distinguished from absorption (which designates the penetration of the compound within a phase).

Figure 1.6 presents the concentration profile of a solute that adsorbs at the interface between two immiscible phases α (liquid) and β (liquid, solid or gas). The hatched area represents the amount of solute that can be considered as attached to the interfacial area, in other words, the adsorbed amount or surface excess Γ. This adsorbed amount is evaluated taking into account a position of the interfacial plane that was defined by making sure that the solvent itself does not present any surface excess. Here, the decrease in solvent concentration is linear in the interfacial area, and therefore, the surface plane is localized at the position where the concentration is half the one found in the bulk of phase α [1].

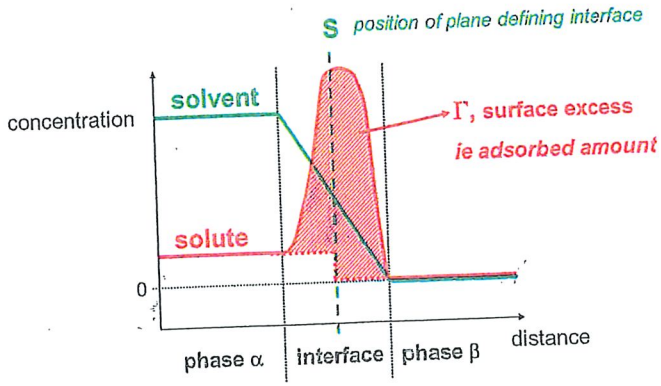

FIG. 1.6. – Scheme of concentration profiles of a solvent and a solute both present in a phase α, in contact with a phase β. The interfacial area separating these two phases is depicted. The red hatched area represents the solute surface excess, which is associated to the interface. The broken green line gives the position of the plane defining the frontier between the two phases. By convention, the position of this plane is such that there is no surface excess of the solvent itself.

The preferential occupation of the surface by a compound present in one of the two phases is illustrated in figure 1.7. A drop of detergent (washing-up liquid) was deposited in the middle of a water surface on which pepper had been previously dispersed. The amphiphilic detergent molecules tend to spontaneously accumulate at the interface (*i.e.*, to get adsorbed), pushing the pepper

particles out to the edges of the recipient. This highlights the concept of surface pressure Π, which results from the difference between the surface tension γ_0 of water (whose molecules are bound through hydrogen bonds) and the surface tension γ of a detergent aqueous solution. The latter is lower because of the weaker interactions, of the van der Waals type, that act between the aliphatic chains of the detergent:

$$\Pi = \gamma_0 - \gamma \tag{1.5}$$

This surface pressure provokes the displacement of pepper particles towards the recipient walls. In the same way, a small piece of a floating polymer sheet is propelled on the surface of water if a drop of detergent is placed behind it.

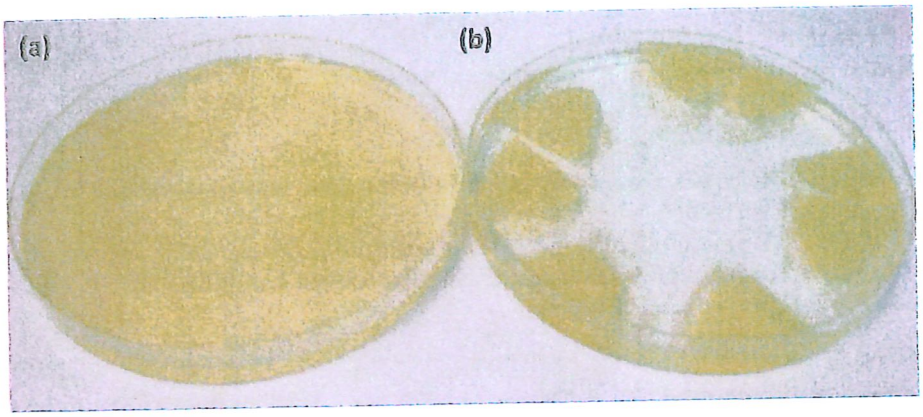

FIG. 1.7. – Water surface on which pepper was dispersed, (a) before and (b) after depositing a drop of liquid detergent in the middle of the recipient.

Generally, adsorption finds its origin in weak interactions (van der Waals forces, electrostatic interactions, hydrogen bonds, hydrophobic interactions) acting between the surface and the adsorbate. This process is referred to as physisorption. Adsorption may, however, also result from the formation of covalent bonds between the compound and the surface, which is then called chemisorption. Depending on the case, adsorption may be considered essentially reversible, as for gas molecules on a solid, or may be largely irreversible, as for proteins on a solid. In the first case, desorption, *viz.*, the reverse process, constantly competes with adsorption, in a dynamic equilibrium, while in the second case, desorption is very limited [2].

In the case of reversible adsorption, the process may be described based on the Langmuir model [1]. This model rests on several hypotheses: adsorption is considered fully reversible, and the surface is constituted of a defined number of adsorption sites, which are all equivalent and can each be occupied by an adsorbed moiety. This typically corresponds to the case of chemisorption. Adsorption can then be considered as a chemical equilibrium, leading to the

formation of a particle-site complex (s-p) starting from the free adsorption site (s) and the free particle (p) (ion, molecule):

$$s + p \leftrightarrows s\text{-}p \tag{1.6}$$

An equilibrium constant K can be associated to this chemical equilibrium:

$$K = (s\text{-}p) / (s)\ (p) \tag{1.7}$$

The fraction Θ can then be defined by dividing the number of occupied sites ($n_{s\text{-}p}$) to the total number of sites (n_{total}), *i.e.*, to the sum of occupied ($n_{s\text{-}p}$) and free (n_s) sites:

$$\Theta = n_{s\text{-}p} / n_{total} = n_{s\text{-}p} / (n_{s\text{-}p} + n_s) \tag{1.8}$$

Langmuir equation is finally deduced by combining equations 1.7 and 1.8, and by assimilating activities to concentrations:

$$\Theta = C / ((1/K) + C) \tag{1.9}$$

With C, the equilibrium concentration of the adsorbate in the phase in contact with the surface.

It should be noted that in the case of adsorption onto a solid, with adsorption sites s, from a liquid phase containing the solvent l and the solute p, equation 1.6 is rather written as follows:

$$s\text{-}l + p \leftrightarrows s\text{-}p + l \tag{1.10}$$

Since the activity of the solvent in the liquid phase can be considered constant in a sufficiently diluted regime, the resulting equation will be similar to equation (1.9) [1].

Langmuir equation is represented in figure 1.8 under the form of a graph of the evolution of the fraction Θ of occupied sites as a function of the concentration C of the adsorbate. At high concentrations ($C >> 1/K$), Θ tends asymptotically to 1 (all sites are occupied, or in other words, the maximum adsorbed amount is reached). At low concentrations ($C << 1/K$), $\Theta \sim KC$ and the graph can be assimilated to a straight line with a slope equal to K. Moreover, half of the sites are occupied ($\Theta = 0.5$) at a concentration equal to 1/K. Starting from experimental data (adsorption isotherm), the model leads to the determination of the constant K, which gives indication of the tendency to form s-p complexes (Eq. (1.6)), thus describing the affinity of the adsorbate for the interface.

It is tempting to apply the Langmuir model to many situations in which data related to the adsorbed amount were experimentally determined. Quite often, there will be a good, if not excellent, agreement between the mathematical model and the data. As for every modelling approach, hypotheses that were made to develop the model should however be kept in mind. As far as protein adsorption is concerned, the assumption of reversibility is usually not met and applying the Langmuir model is subject to caution. Drawing a plot according

to the Langmuir model is however convenient to compute an apparent affinity, and to highlight a saturation behaviour at high concentration. In the case of the adsorption of ions, the expression can be adapted, taking into account the fact that K varies with the local electrical potential, and thus with the adsorbed amount. There are other models to describe adsorption, whose presentation is however falling outside of the scope of this introduction chapter.

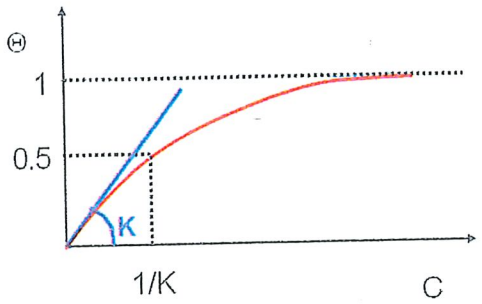

FIG. 1.8. – Evolution of the fraction Θ of occupied sites as a function of the equilibrium concentration C of the adsorbate, as described by the Langmuir model. K is the equilibrium constant of the association reaction between the adsorption site and the adsorbed particle.

1.4. Charged surfaces

1.4.1. Concepts

Electrostatic interactions play a very important role in many processes and are notably among the weak interactions which are at the origin of physisorption. They find their origin in the presence of electrical charges at interfaces. Almost all surfaces bear electrical charges [1]. This can be attributed to: (i) acid-base reactions at interfaces, with the deprotonation of acidic function that generates negative charges, or to the protonation of basic functions that generates positive charges; (ii) the selective dissolution of an ion constitutive of a salt: there is electro-neutrality within an ionic crystal, but the crystal surface may be enriched in one of its constituting ions if the tendency to be dissolved in the surrounding liquid is not the same for the different constituting ions; (iii) structural defaults of a solid, as is the case for so-called "swelling" clays (smectites), in which substitutions of Si^{4+} by Al^{3+}, or of Al^{3+} by Mg^{2+}, generate the presence of negative charges at the surface, compensated by mobile alkaline ions between the sheets of these clays; (iv) the preferential adsorption of ions which modify the intrinsic electrical potential of the surface, as illustrated by the accumulation of phosphate ions at the surface of a variety of metals. It should be noted that a surface

can simultaneously bear positive and negative charges. In such case, it is said to be "zwitterionic". This is generally the case for biological surfaces.

With a view to modelling and understanding interactions between two charged surfaces, taking into account the intensity and distance over which electrostatic interactions are at play, the distribution of ions in solution at the proximity of a charged solid surface must be described, as well as the variation of the electrical potential, as a function of the distance to the interface. In a first approach, it can be considered that the surface charges are entirely compensated by opposite sign ions located in the immediate vicinity of the interface. In such case, the potential varies linearly, from a value equal to the intrinsic surface potential Ψ_0 at the level of the interface, to a value of zero beyond the plane where the counter-ions are localized. Figure 1.9 illustrates this model, called the Helmholtz model, or the parallel-plate capacitor model [1, 2]. This model can be considered simplistic as it depicts a very ordered and frozen situation, not likely to be compatible with the tendency of systems to be disordered.

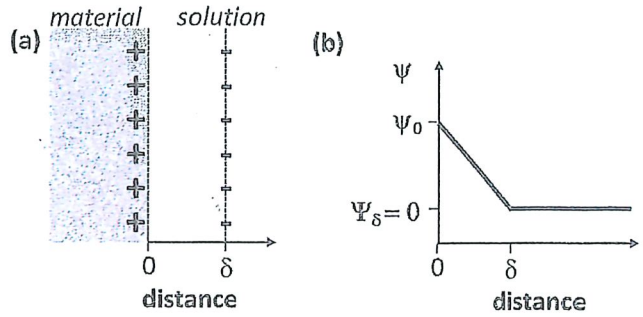

FIG. 1.9. – (a) Representation of a charged solid surface in contact with a solution containing ions, according to the Helmholtz model: counter-ions with a sign opposite to the surface charges are aligned at a distance δ along the surface plane to compensate the surface charge. (b) Evolution of the electrical potential Ψ as a function of distance according to the model depicted in (a).

More sophisticated models describing ion distribution close to a charged surface were developed [1, 2]. Gouy-Chapman model, coupled to Debye-Hückel approximation for surfaces with a weak electrical potential, have led to a so-called "diffuse double layer" representation of the interface. Without entering into details, it is considered here that both ions with an opposite and an identical charge compared to the surface can be found at its vicinity, with, however, an overrepresentation of counter-ions, and an underrepresentation of co-ions, compared to the bulk of the solution (Fig. 1.10a and Fig. 1.10b). The evolution of the electrical potential Ψ as a function of distance x is described by the following equation:

$$\Psi = \Psi_d \exp(-x\kappa^{-1}) \qquad (1.11)$$

With Ψ_d, the potential at the origin of the diffuse double layer, and κ^{-1}, the Debye length. This evolution is represented in figure 1.10c. It should be noted that, when $x = \kappa^{-1}$, $\Psi / \Psi_d = \exp(-1) = 0.368$. In other words, the Debye length is the distance from the surface at which only about one third of the initial potential is remaining. The Debye length is inversely proportional to the square root of the ionic strength I of the medium, which is a function of the concentration and the valency of the ions. Hence, the higher the salt concentration, the shorter the distance over which the surface charge is compensated, and the shorter the distance over which electrostatic interactions are effective. Moreover, for a given concentration, a multivalent salt will screen the surface charge over a shorter distance compared to a monovalent salt. Debye lengths typical of aqueous media with different salt concentrations are summarized in table 1.2.

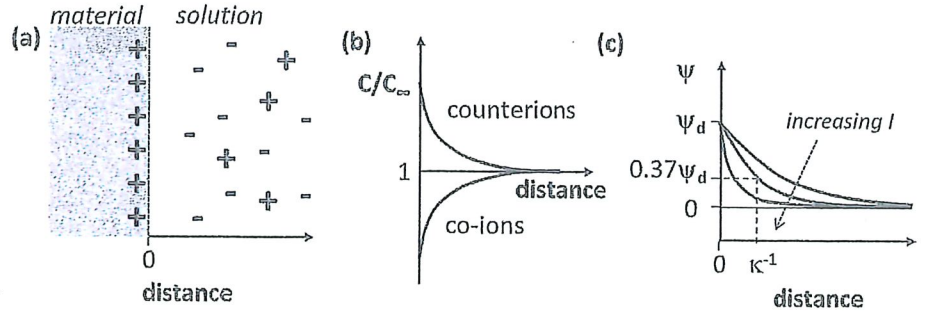

FIG. 1.10. – (a) Scheme of a charged solid surface in contact with an ion-containing solution, according to the diffuse double layer model: counter-ions (with a charge opposite to the one of the surface) and co-ions are respectively over- and underrepresented close to the surface in comparison with the solution bulk, as also shown by their concentration C profile in (b), with C_∞ the concentration in the solution bulk. (c) Evolution of the electrical potential Ψ as a function of the distance, according to the model illustrated in (a) and (b), and depicted for increasing ionic strengths I values.

TABLE 1.2. – Debye length in aqueous media with different ionic strengths.

Ionic strength I (M)	κ^{-1} (nm)	Relevant aqueous medium
1	0.3	seawater
10^{-1}	1	culture medium, biological fluid, industrial water
10^{-3}	10	tap water
10^{-5}	100	mountain lake
10^{-6}	300	distilled water

To both take into account the tendency of systems to be disordered, on the one hand and the peculiar affinity of some ions for surfaces, on the other, charged interfaces will finally be better described based on a global approach which combines Helmholtz model with the double diffuse layer theory. This is illustrated in figure 1.11. A first linear decrease of the potential is provoked by the accumulation of high affinity ions very close to the surface, in the so-called Stern layer. The remaining potential is then screened by ions from the diffuse double layer. In practice, electro-kinetic methods are usually applied to determine the surface electrical potential. The measured potential, called the ζ potential, corresponds to the potential at the shear plane between the surface and the solution, which is considered to be close to the potential at the origin of the double diffuse layer, *i.e.*, at the level of the Stern layer. A surface with a ζ potential equal to zero is said to be at its isoelectric point (iep). It should be noted that this does not necessarily corresponds to the point of zero charge (pzc), which is defined by the situation in which $\Psi_0 = 0$ V. Indeed, if ions are adsorbed in the Stern layer, the potential measured at the shear plane may substantially differ from the one intrinsically related to the surface.

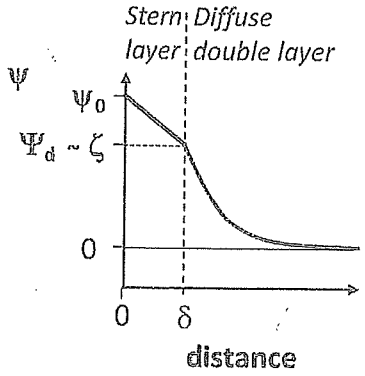

FIG. 1.11. – Evolution of the potential with the distance from a solid surface in contact with an ion-containing solution, according to the global model. Ions are found in the Stern layer, then a diffuse double layer screens the remaining charge. The Ψ_d potential at the origin of the diffuse double layer may be assimilated to the ζ potential which can be determined experimentally based on electro-kinetic methods.

1.4.2. *Interactions between charged surfaces*

When two charged surfaces get closer to each other, the observed behaviour will depend on the different interactions that may occur, and in particular on electrostatic interactions. For two surfaces of the same kind, thus bearing the same electrical charge, the contribution of electrostatic interaction will be repulsive. Such surfaces will only adhere if other interactions are strong enough

to compensate the effect of electrostatic repulsion. If a suspension of charged particles is considered, this suspension will be stable if electrostatic repulsion outweighs attractive interactions, and in particular if it plays a role at sufficiently long distance to prevent shorter distance forces (such as van der Waals forces) to act. The coagulation of the suspension can be triggered by decreasing the contribution of electrostatic repulsion. On the one hand, a pH change may alter the surface electrical potential. On the other hand, adding salts to the medium may reduce the distance over which electrostatic repulsion is effective. This is illustrated in figure 1.12. A suspension of gold particles was synthesized by reduction of a gold salt in presence of citrate [8]. Such particles are negatively charged. The original suspension at pH 4 is stable and exhibits a red colour, corresponding to particles with a diameter of about 20 nm. There is indeed a direct relationship between the size of gold particles and the suspension colour [9]. The colour is left unchanged when KCl is added to the suspension, which remains stable. In contrast, the addition of $CeCl_3$ provokes an immediate modification of the colour of the suspension, which becomes purple-blue. The estimated diameter of the obtained aggregates is of about 60 nm. Moreover, the suspension is unstable, and a blackish deposit form in a few hours, leaving a totally transparent supernatant. This illustrates the concept of Debye length. In a medium with a low ionic strength, gold particles are repulsive to each other due to the negative charges of the citrate groups. When a trivalent salt is used, the higher ionic strength provokes a contraction of the diffuse double layer (thus a decrease of the Debye length), and electrostatic repulsion between particles becomes restricted to a very short distance. In such case, van der Waals forces can provoke particle aggregation, followed by sedimentation.

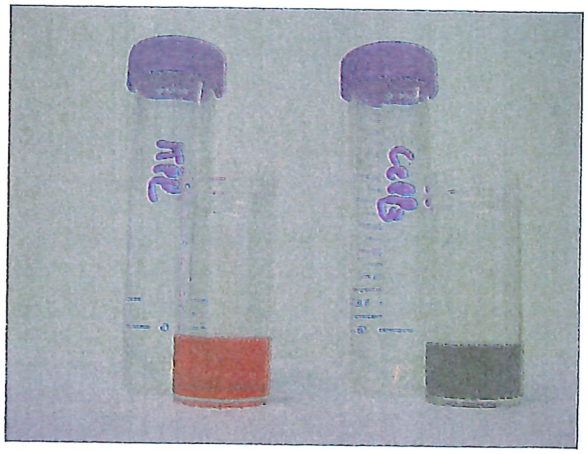

FIG. 1.12. – Suspensions of gold colloids bearing citrate groups at their surface, after the addition of a few drops of (left) a KCl solution, (right) a $CeCl_3$ solution. The purple-blue suspension obtained after adding $CeCl_3$ becomes transparent, with a blackish deposit, after a few hours, while the red suspension obtained in presence of KCl is stable. This experiment was performed based on reference [8].

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