PHYSICO-CHEMICAL ASPECTS OF ADHESION

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1. Introduction

Adhesion of microorganisms to solid surfaces is one of the prime steps in the formation of biofilms. As regards the size of a great number of microorganisms, namely bacteria, they are quite often considered as colloidal particles (Marshall 1976). Consequently, microbial adhesion has been described in the literature in terms of DLVO theory, developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948) to explain the stability of lyophobic colloids. According to this theory, the net force of interaction arises from the balance between van der Waals forces of attraction and electrostatic double-layer forces, those having commonly a repulsive effect. However, apart from DLVO forces other types of interactions can play an important role in the adhesion process, specially hydrophobic interactions in aqueous medium and the steric hindrances in the presence of polymers. Moreover it has to be kept in mind that those "living colloids" are capable of excreting polymeric metabolites which along with external appendages can have a strong influence in the final process of adhesion.

It is relevant to note that prior to adhesion the microorganisms have to be transported to the surface of deposition. Transport mechanisms can be very different, because adhesion takes place either in quiescent waters or in turbulent flow conditions (Characklis 1981a; 1981b). The transport flux of microorganisms to the surface of deposition must be directly proportional to their bulk concentration in accordance with mass transfer theories. Therefore, in very dilute suspensions transport can be the controlling step in the overall process of deposition.

In flow systems, the effect of hydrodynamic forces has also to be stressed, because their removal action can limit the extent of biofilm growth. Some of the aspects mentioned so far will be outlined in more detail in the following survey.

2. Colloid Chemistry and Adhesion

2.1. VAN DER WAALS INTERACTIONS

The existence of attraction forces between molecules was proposed by van der Waals (1873) as a result of his studies on the deviations from the ideal-gas law. About 60 years later, with the emergence of quantum mechanics, London (1930) quantified this statement.
and Hamaker (1937) based on the pairwise principle, extended London's theory to the interaction between solid bodies.

van der Waals interactions are dependent on the geometry and on the nature (physical and chemical properties) of the interacting bodies. This last feature is included in a constant, A, named after Hamaker.

In the case of bacterial adhesion the interacting geometries are often assumed to be of the sphere/plate type and the expression for the van der Waals force ($F_W$) is:

$$F_W = \frac{AR}{6d^2}$$

(1)

where R is the radius of the spherical particle and d is the separation distance.

Those interactions are more commonly treated in terms of energy ($V_W$) rather than force, but as $F = \frac{dV}{dd}$ the energy is given by:

$$V_W = -\frac{AR}{6d}$$

(2)

Expressions for other geometries can be found in the literature (Hiemenz; Vold 1954).

2.1.1. Hamaker Constants. The Hamaker constant can be calculated from the molecular properties of the materials involved. For the interaction of two different materials 1 and 2 in vacuum the corresponding Hamaker constant can be obtained in good approximation through:

$$A_{12} = \frac{\sqrt{A_{11} \cdot A_{22}}}{\sqrt{A_{33}}}$$

(3)

If those materials are immersed in a medium 3, the interaction constant may be given by:

$$A_{132} = (\sqrt{A_{11} \cdot A_{33}}) \cdot (\sqrt{A_{22} \cdot A_{33}})$$

(4)

Several approaches have been used to calculate the $A_{ij}$ constants, most of them based on the Hamaker's assumption of molecular additivity, which is not strictly valid for condensed media interactions. Visser (1972) has an excellent review on Hamaker constants.

Lifshitz and collaborators (Dzyaloshinskii 1961), avoided the additivity principle and were able to calculate the van der Waals interactions between macroscopic bodies using the characteristic electromagnetic spectrum absorption frequencies. The resulting equation is complex and some simplifications have been tried. Israelachvili (1974) assumed that the major contribution for the dispersion interaction arises from electronic excitation in the ultraviolet frequency range and he obtained the following equation:

$$A_{ij} = \frac{3}{16\sqrt{2}} \cdot \frac{(n_0^2 - 1)^2}{(n_0^2 + 1)^{1.5}} \cdot \hbar \omega_{UV}$$

(5)

$n_0$ is the refractive index in the visible range, $\hbar$ is Planck's constant and $\omega_{UV}$ is the characteristic absorption frequency in the UV region.

However, there are still difficulties in obtaining the absorption spectra in the far ultraviolet for a great number of substances. To circumvent this problem, Van Oss and co-workers (1988) decided to calculate Hamaker constants for a series of liquids for which the values of Lifshitz-van der Waals component of the surface tension ($\gamma_{LW}$) (see 2.5) were known and for which the necessary spectroscopic data were available as well. Assuming that the equilibrium separation ($d_0$) between the interacting bodies is determined by the
balance between the Born repulsion and the van der Waals attraction they obtained the following expression:

\[ A_{ij} = \frac{LW}{\gamma_i} \cdot 32 \pi d_0^2 \]  

The average value found for \( d_0 \) is 0.136 nm, with a standard deviation of 0.007 nm (van Oss et al. 1988).

An interesting feature of the Hamaker constants is the possibility of obtaining negative values for \( A_{132} \). This happens when

\[ A_{11} < A_{33} < A_{22} \quad \text{or} \quad A_{11} > A_{33} > A_{22} \]

Consequently, the interaction between the two different materials is weaker than the interaction between each of them and the medium in which they are immersed. So, if the above conditions are fulfilled a spontaneous separation is likely to occur on account of the dispersion forces only (Visser 1975).

2.2. DOUBLE-LAYER FORCES

2.2.1. Electrostatic Double-Layer. The majority of solid bodies acquire electrical surface charge when immersed in aqueous media. Different mechanisms can be responsible for this charge acquisition (Hunter 1988), but in the case of biological systems this is generally due to ion adsorption or ionization of surface groups, phenomena that are very often dependent on the pH of the medium. At normal conditions of pH, bacteria possess a net negative surface charge. However, a charge reversal may occur at low pH values on account of the presence of some charged basic (amino) groups (Plummer and James 1961).

A charged surface immersed in an aqueous medium will promote a redistribution of ions. The ions of the same sign (co-ions) will be repelled from the surface while the oppositely charged ions (counter-ions) will be attracted. This effect along with the Brownian motion gives rise to a Poisson-Boltzmann distribution of the ions through out the aqueous phase creating a diffuse layer which, together with the solid surface, is called the electrical double-layer (Figure 1).

![Figure 1. - Electrostatic double-layer around a flat surface and a spherical particle.](image)
The electrostatic potential decreases from the charged surface through the diffuse layer, attaining a null value in the bulk.

When two charged bodies approximate, the interpenetration of their double-layers promotes the repulsion between them. This repulsive effect is the most common, because, as already mentioned for bacteria, the majority of solid bodies also acquire a net negative charge when in aqueous environments.

2.2.2. Double-Layer Interactions. The potential energy arising from the interpenetration of electrical double-layers depends on the geometry of the interacting bodies and on the electrical behaviour during the interaction. Generally, the interactions are considered to occur at constant surface potential or at constant surface charge and the most commonly used equations, for the sphere/plate type geometry, are the equation of Hogg Healy and Fuerstenau (1966) (eq.(7)) and the equation of Wiese and Healy (1970) (eq.(8)), respectively.

\[ V_{DL_{sp/pl}} = \frac{\epsilon \pi R}{2} \left[ (\psi_{o1} + \psi_{o2})^2 \ln[1+\exp(-\kappa d)] + (\psi_{o1} - \psi_{o2})^2 \ln[1-\exp(-\kappa d)] \right] \]  

(7)

\[ V_{DL}^G = -\frac{\epsilon \pi R}{2} \left[ (\psi_{o1} + \psi_{o2})^2 \ln[1-\exp(-\kappa d)] + (\psi_{o1} - \psi_{o2})^2 \ln[1+\exp(-\kappa d)] \right] \]  

(8)

\[ V_{DL}^W \text{ and } V_{DL}^G \text{ are the potential energies of interaction at constant surface potential and at constant surface charge, respectively. } \psi_{o1} \text{ and } \psi_{o2} \text{ are the surface potentials of the flat surface and of the spherical particle at infinite separation. } \epsilon \text{ is the electrical permittivity of the medium, } R \text{ is the sphere radius and } \kappa \text{ is the reciprocal double-layer thickness or Debye-Huckel parameter, given by:} \]

\[ \kappa^2 = -\frac{1000 \epsilon^2 N_A}{\kappa B T} \sum z_i^2 M_i \]  

(9)

Where \( \epsilon \) is the electron charge, \( N_A \) is the Avogadro's number, \( \kappa B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( z_i \) is the counter-ion valence and \( M_i \) is the counter-ion molarity.

The HHF and HW equations are based on the linearization of Poisson and Boltzmann equations and are only valid for surface potentials \(<25 \text{ mV}\), although they can be used without significant errors for potentials until \( 60 \text{ mV} \) (Rajagopalan and Kim 1981).

The condition of constant surface potential may only be fulfilled if the surface charge is created by the adsorption of "potential determining ions", while the situation of constant surface charge arises when the charge is originated by isomorphic substitutions inside the lattice (Rajagopalan and Kim 1981).

The intermediate situations, where neither the charge nor the potential are kept constant, occur when the surfaces acquire electrical charge due to the ionization or dissociation of surface groups (Rajagopalan and Kim 1981), which seems to be the most common case for biological systems.

In such situations, Gregory (1975) considers that the best approximation is given by the equation of Bell Levine and McCartney. Kar et al. (1973) derived an expression for the interaction between a surface at constant charge and a surface at constant potential.
Frens and Overbeek (1972) assume that the condition of constant potential is impossible during an interaction, only the charge can be kept constant. A similar consideration is also given by Weaver and Feke (1985).

Lyklema (1980), introducing the concept of double-layer relaxation, assumed that both situations of constant potential and constant charge are extreme cases. The real situation is determined by the relaxation rate of the different double-layer regions (e.g. diffuse layer and/or Stern layer).

Although there is such a controversy, most of the authors utilize the HHF equation on account of its simplicity.

An important point to be noted is that it is still impossible to determine the exact values of the surface potentials. Those values are replaced in the equations by the corresponding zeta potential values (Hunter 1988).

2.3. DLVO THEORY

According to this theory, the total potential energy of interaction \( V_T \) is obtained summing up the energy due to van der Waals interactions \( V_W \) and the energy arising from double-layer interactions \( V_{DL} \):

\[
V_T = V_W + V_{DL}
\]

(10)

Conventionally, the repulsive interactions are positive and the attractive interactions are affected by a minus sign. This makes possible to speak about the "depth" of the minima of energy and the "height" of the energy barrier. Therefore, in the most common case, where only the van der Waals forces are attractive a possible profile for the total potential energy of interaction is given in Figure 2.

The interacting bodies will attain the maximum stability in the primary minimum of energy. The possibility of existing two energy minima enables to explain adhesion in terms of reversibility and irreversibility. In a situation of reversible adhesion the stabilaz:J.tion occurs in the secondary minimum of energy. In these circumstances the microorganisms are still
capable of Brownian motion and can be removed by washing. In irreversible adhesion the primary minimum is attained, all Brownian motion ceases and a simple washing procedure is not enough for the removal of the deposited materials.

As can be seen from the equations concerning the energies of interaction the energy profile is influenced by several parameters. The effect of the different parameters on the energy profile was shown by Ruckenstein and Kalithod (1981). The most common example shown is the effect of the ionic strength. An increase in the ionic strength lowers the energy barrier favouring adhesion.

2.4. OTHER FORCES

There is now experimental evidence of other types of forces acting at short or intermediate distances, being attractive or repulsive, which can play an important role in the process of adhesion.

2.4.1. Hydrophobic Interactions. Hydrophobic interaction is generally so called when being attractive, while its repulsive counterpart is commonly referred to as "hydration pressure". These interactions are of polar nature and can have a magnitude up to two decimal orders higher than the components of DLVO theory (van Oss et al. 1988). Van Oss and collaborators (1987) considered that those forces are based on electron donor-electron acceptor (Lewis acid-base) interactions (section 2.1) between polar species in polar media (e.g. water) and are responsible for almost all the anomalies found in the interpretation of interfacial interactions in polar media.

Based on the works of several investigators van Oss et al. (1988) proposed an equation for the calculation of the free energy ($\Delta F^{AB}$) associated with this type of forces, for the parallel flat plate conformation. Using the approach of Derjaguin (Hogg et al. 1966) it is possible to obtain the equation for the sphere/plate type geometry:

$$\Delta F^{AB}_{SP/pl} = 2\pi R A \Delta F^{AB}(d_0) \exp\left(d_0 - d\right)/\lambda$$

(11)

Where $\lambda$ is the correlation length pertaining to water molecules, $d_0$ is the equilibrium distance and $d$ is the distance. This equation is valid for $d_0 > \lambda$. For pure water the value of $\lambda$ is around 0.2 nm, but at higher ionic strengths is related to the dimensions of the hydrated ions, having values up to 1.2 nm (van Oss et al. 1988). $\Delta F^{AB}(d_0)$ is the free energy at the distance of equilibrium and can be calculated through the electron acceptor ($\gamma^+$) and electron donor ($\gamma$) parameters of the polar components ($\gamma^{AB}$) of the surface tension of the interacting bodies (van Oss et al. 1987).

The polar component of the free energy of interaction between materials 1 and 2 immersed in a medium 3 is expressed by (van Oss et al. 1987):

$$\Delta F^{AB}_{123}(d_0) = 2 \left[ \sqrt{\gamma^+ \gamma^-} \left( \sqrt{\gamma^+ - \gamma^-} \sqrt{\gamma^+ - \gamma^2} + \sqrt{\gamma^+ \gamma^2 - \gamma^- \gamma^2} \right) \right. \nonumber$$

$$\left. - \sqrt{\gamma^+ \gamma^-} \sqrt{\gamma^+ \gamma^2 - \gamma^- \gamma^2} \right]$$

(12)

$\Delta F^{AB}$, as expressed by equation (11), has the dimensions of energy (joule) and so it is suggested that it can be introduced, as a third term, in equation (10). This means that the DLVO theory is extended, in order to contemplate the hydrophobic interactions.

2.4.2. Steric Forces. This type of forces is considered to arise between polymer coated surfaces. The potential energy of interaction between two uncharged polymer coated
surfaces is complex, but essentially comprises contributions from three additive terms (Vrij 1976; Napper 1977; Scheutjens 1982):

1. a mixing term related to the polymer segment concentration in the interacting zone;
2. an elastic term related to the loss of configurational entropy of the polymer chain;
3. an adsorption or bridging term, being important at low coverages.

The situation becomes even more complex when the surface layers are charged or are polyelectrolytes.

It is expected that those forces may be relevant in biological systems, where the existence of macromolecules (e.g. glycoproteins, polysaccharides, lipopolysaccharides, etc.) are quite common. The adsorption of these macromolecules, which may be neutral polymers or polyelectrolytes, can occur before any appreciable microbial adhesion takes place, giving rise to the so called surface conditioning. However, in the present state of the art it does not seem possible to quantify steric forces, on account of their complexity.

2.5. SURFACE FREE ENERGY APPROACH

According to Absolom et al. (1983), bacterial adhesion is possible if the process causes the free energy to decrease:

$$\Delta F_{ad} < 0$$ (13)

The change in the free energy of adhesion ($\Delta F_{ad}$), when electrical charge interactions are neglected, can be determined by:

$$\Delta F_{ad} = \gamma_{sb} - \gamma_{sl} - \gamma_{bl}$$ (14)

with

- $\gamma_{sb}$ - interfacial tension substratum-liquid phase
- $\gamma_{sl}$ - interfacial tension substratum-liquid phase
- $\gamma_{bl}$ - interfacial tension bacteria-liquid phase

There are different approaches for the calculation of the interfacial tension values, because there are distinct insights on the nature of the surface tension. However, all those approaches are based on Young's equation (Fowkes 1967), that correlates the contact angle ($\theta$), formed by a liquid drop on a solid surface with the interfacial free energies of the three contacting phases:

$$\cos\theta \gamma_{lv} = \gamma_{sv} - \gamma_{sl}$$ (15)

Where I stands for liquid, v for vapour and s for solid.

Neumann et al. (1974) assume a single component surface tension and derived an "equation of state" for the calculation of $\gamma_{sv}$ and $\gamma_{sl}$.

Busscher (1984) considering the existence of a polar ($\gamma^P$) and a dispersion ($\gamma^D$) component of the surface tension, proposed the following equation for the calculation of the surface tension of the solid substratum ($\gamma_s = \gamma^P_s + \gamma^D_s$).
$$\cos \theta = -1 + \frac{2}{\gamma_1} \left( \gamma_{s}^{d} \gamma_{f}^{d} \right)^{1/2} + \frac{2}{\gamma_1} \left( \gamma_{s}^{p} \gamma_{f}^{p} \right)^{1/2} \cdot \pi e$$

(16)

The spreading pressure, defined as the difference between the free energy of the solid in the air ($\gamma_s$) and the free energy in the presence of vapour molecules ($\gamma_{sv}$) of the liquid used in contact angle measurements ($\pi e = \gamma_s - \gamma_{sv}$). Having determined $\gamma_s^{d}, \gamma_s^{p}$ and $\pi e$, by means of a least square fitting of the data obtained using a defined series of liquids, it is possible to calculate $\gamma_{ij}$ (or generally $\gamma_{ij}$) through:

$$\gamma_{ij} = \gamma + \gamma^{-2} \left( \gamma_{i}^{d} \gamma_{j}^{d} \right)^{1/2} - 2 \left( \gamma_{i}^{p} \gamma_{j}^{p} \right)^{1/2}$$

(17)

More recently, van Oss et al. (1987) considered that the surface tension ($\gamma$) of a given substance comprises a component arising from the Lifshitz-van der Waals interactions ($\gamma_{LW}$) (of the London + Keesom + Debye varieties) and a component due to polar interactions ($\gamma_{AB}$) of the type electron acceptor-electron donor, similar to Lewis acid-base (AB) interactions, which include the special case of hydrogen donor-hydrogen acceptor interactions.

The surface tension can then be expressed by:

$$\gamma = \gamma_{LW} + \gamma_{AB}$$

(18)

with

$$\gamma_{AB} = 2 \sqrt{\gamma^{+} \cdot \gamma^{-}}$$

(19)

Where $\gamma^{+}$ and $\gamma^{-}$ are the electron acceptor and the electron donor parameters, respectively. $\gamma_{LW}^{+}$ and $\gamma_{LW}^{-}$ can be determined by contact angle measurements (van Oss et al. 1988).

In certain circumstances, the thermodynamic approach has been used with some success to explain bacterial adhesion (Bellon-Fonraine et al. 1990).

2.5.1. Substratum Wettability. One of the liquids that is commonly used in contact angle measurements is water. The data obtained with water reflect a special feature of solid surfaces, that is named wettability. The degree of wettability of a surface is variable, it can be low or high and, in accordance, surfaces can be divided into hydrophobic or hydrophilic.

Baier (1973), based on experience with some biological systems, predicted that minimal bacterial adhesion in aquatic habitats should occur on substrata within a critical surface tension range of 20 to 30 mN/m. Those values pertain to low energy (or hydrophobic) surfaces and so, maximal adhesion should be expected on high energy (hydrophilic) substrata. However, Fletcher and co-workers (1979 and 1984) observed a different trend in some situations and in others they could not find any generic pattern of attachment according to surface wettability. They have expressed the substrata hydrophobicity in terms of work of adhesion ($W_A$), obtained via the Young-Duprê equation:

$$W_A = \gamma_y (1 + \cos \theta_F) + \pi e$$

(20)

Where $\theta_F$ is the equilibrium contact angle for water. For adhesion to occur between hydrated species water must be displaced as the two surfaces move closer. $W_A$ represents the work that is necessary to displace the water molecules.
With such conflicting results the concept of wettability, alone, does not seem to be a good approach to predict bacterial adhesion.

It must be stressed that although the surface energy and the colloid-chemical approaches are often considered as separate entities, there are strong connections between them, as was shown by Pethica (1980).

3. Adhesion in Flowing Systems

Most of the studies on biofilm formation deal with systems exposed to little or no fluid motion. However, there are situations, like in industrial processes where there is significant fluid flow.

The fluid velocity seems to have two opposite effects on biofilm formation. An increase in fluid velocity increases the shear stress exerted on the deposited microorganisms which can promote their detachment. On the other hand, it makes possible an increase in the mass transfer rate of nutrients to the surface, which may be responsible for a higher biofilm growth. It has been reported that biofilms formed under higher velocity conditions may adhere more firmly to surfaces than the ones developed at lower velocities (How et al. 1982; Duddrige et al. 1982; Vieira et al. 1986), probably this is due to a stronger cohesion promoted by the higher shear stresses and to a higher production of extracellular polymers (in a more adverse environment) making the deposit more "stickier".

Some authors assume that the removal effects of hydrodynamic forces on deposited materials can only be explained if a short range repulsive force is considered in conjunction with DLVO theory, in order to make possible a finite primary minimum in the energy profile (Figure 3) (Ruckenstein and Kallay 1981; Ruckenstein 1978; Kallay et al. 1986). Otherwise, only a force of infinite magnitude could promote the re-entrainment of deposited particles. A similar reasoning was suggested by Hamaker (1937), when studying the re-pelletization (defloculation) of colloidal particles.

![Figure 3. - Total potential energy profile considering the effect of Born repulsion.](image-url)
The short range force considered so far, is the Born repulsion. For the sphere/plane conformation, when \( R \gg d \), it can be expressed by:

\[
V_{BR_{sp}} = \frac{A d_0^3 R}{168 \, d^7}
\]

However, Frens and Overbeek (1972) consider that it is not possible for the superficial atomic orbitals of two coagulated particles to interpenetrate to give rise to a Born repulsion. Although they have considered that it is highly improbable that a Brownian collision could bring two particles closer than twice the distance between the particle surface and the outer Helmholtz plane of the electrical double-layer.

4. Microbiological Aspects

Beyond all the forces mentioned above, that can be involved in the adhesion process, an additional difficulty arises in studying microbial adhesion, because living systems are being concerned. This condition of living organisms is expressed by the ability to reproduce, grow and produce extracellular polymers and external appendages and, in some cases, to move independently.

4.1. EXTERNAL APPENDAGES

The external appendages are present in a great number of bacteria and are commonly divided into three different types:

1. flagella - very fine threads with an helical structure protruding from the cytoplasm through the cell wall, responsible for bacteria motility;
2. pilus or fimbriae - very fine threads, shorter than flagella. One cell may have several of these structures appearing like tufts;
3. stalks and prostaticae - filiform or blunt extensions of the cell wall and membrane that can occur in one or more sites on the cell surface, respectively.

The latter two types of appendages are not involved in motility and are commonly considered as specialized attachment structures (Kent and Duddridge 1981; Paerl 1975; Handley et al. 1991). In many prostaticae and especially in stalks there is a disc in the end, called the "hold-fast", which has been referred to in the literature as the preferential attachment structure of diatoms (Characklis and Cooksey 1983).

The attachment through these filamentous structures can be interpreted as a means to favour adhesion, because it reduces the effective radius of interaction and concomitantly lowers the energy barrier, as predicted by DLVO theory. However, it must be noted that, although present, they are not always involved in the adhesion process (Characklis and Cooksey 1983).

4.2. EXTRACELLULAR POLYMERS

The second major means of microbial attachment is thought to be the extracellular polymers. Extending lengths of polymers attached to cell surfaces can interact with vacant bonding sites on the surface - polymer bridging - and as a result the cell is held near the surface. Possible mechanisms for polymer bridging have been suggested (Characklis and Cooksey 1983; Kent and Duddridge 1982) but they are not yet fully understood.
4.3. ION BONDING

Inorganic ions may also affect microbial attachment to surfaces. In the case of Ca\(^{2+}\) and Mg\(^{2+}\), claims have been made that they are fundamental for an efficient adhesion of aquatic bacteria (Marshall and Stout 1971; Fletcher and Floodgate 1973). Different mechanisms have been proposed for the role of divalent cations in the process of bacterial adhesion, namely the formation of a cation bridge between the negatively charged bacteria and the substratum (Fletcher and Floodgate 1973) and the precipitation of polymer, mediated by the cation, between the cell and the substratum (Rutter 1980). More recently, Van Oss et al. (1987) proposed that Ca\(^{2+}\) can depress the monopolar electron-donor parameter of the surface tension of the interacting species, depressing their capacity for mutual repulsion and their degree of hydration, resulting in a decrease of the hydration pressure.

The effect of other cations is complex, because some favour adhesion and others do not (Duddrige et al. 1981; Daniels 1972), possibly by affecting the adhesive properties of the extracellular polymers. However, these results cannot be interpreted straightforward, since the ions may affect cell metabolism and viability (Vieira et al. (b)).

5. Conclusions

The explanation of microbial adhesion have been tried in terms of colloid chemistry theories, specially DLVO theory, which only takes into account long range forces. However, there is now the possibility of quantifying other types of forces, namely hydrophobic interactions, and they must be associated to DLVO forces in order to have a better defined energy profile. Nevertheless, even doing this, it is not possible to have a fully characterised picture of the adhesion process of microorganisms They have to be regarded as "living colloids" with their adaptable and varied nature, being capable of very special types of interactions. Therefore, much more has to be known!

Nomenclature

\[ \Delta F_{ad} \] - change of free energy of adhesion (J/m\(^2\))
\[ K_B \] - Boltzmann constant (J/K)
\[ e \] - electrical charge of electron (C)
\[ \Delta F_{AB} \] - change of free energy associated to hydrophobic interactions between a sphere and a flat plate (J)
\[ \Delta F_{123} \] - polar component (acid-base) of the surface free energy between bodies 1 and 2 in medium 3 (J/m\(^2\))
\[ \Delta F_{ad} \] - change of free energy of adhesion (J/m\(^2\))
\[ K_B \] - Boltzmann constant (J/K)
\[ M_i \] - counter-ion molarity (mol/dm\(^3\))
\[ N_A \] - Avogadro's number
\[ n_o \] - refractive index in the visible range
\[ R \] - radius of particle (m)
\[ T \] - absolute temperature (K)
\[ V_{BR} \] - potential energy associated with Born repulsion (J)
\[ V_{tot} \] - total potential energy of interaction (J)
\[ V_{VW} \] - potential energy associated to van der Waals interactions (J)
\[ V_{DL} \] - potential energy due to double-layer forces (J)
\[ V_{DL}^W \] - potential energy due to double-layer forces at constant surface potential (J)
\[ V_{DL}^\sigma \] - potential energy due to double-layer forces at constant surface charge (J)
\[ W_A \] - work of adhesion (J/m²)
\[ z_i \] - valence of ion i
\[ \varepsilon \] - electrical permittivity (F/m)
\[ \gamma_{ij} \] - interfacial free energy between bodies i and j (J/m²)
\[ \gamma_{bi} \] - interfacial free energy between bacteria and a liquid phase (J/m²)
\[ \gamma_{sb} \] - interfacial free energy between a solid surface and bacteria (J/m²)
\[ \gamma_{sl} \] - interfacial free energy between a solid surface and a liquid phase (J/m²)
\[ \sigma_p \] - polar component of the surface tension (J/m²)
\[ \sigma_d \] - dispersion component of the surface tension (J/m²)
\[ \sigma_{AB} \] - acid-base component of the surface tension (J/m²)
\[ \gamma_{LV}^W \] - Lifshitz-van der Waals component of the surface tension (J/m²)
\[ \gamma^+ \] - electron acceptor parameter of the \( \sigma_{AB} \) surface tension component
\[ \gamma^- \] - electron donor parameter of the \( \sigma_{AB} \) surface tension component
\[ \hbar \] - Planck's constant (J.s)
\[ \lambda \] - correlation length of water molecules (m)
\[ \psi_{ei} \] - electrical potential of surface i (V)
\[ \omega_{AV} \] - characteristic absorption frequency in the UV range (rad/s)
\[ \sigma_s \] - spreading pressure (J/m²)
\[ \theta \] - contact angle (degree)

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