FIRP BOOKLET # E120-N

TEACHING AID IN SURFACTANT SCIENCE & ENGINEERING

in English

INTERFACIAL PHENOMENA
in
DISPERSED SYSTEMS

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1.- GENERALITIES ON INTERFACIAL PHENOMENA.

1.1. DEFINITIONS

By definition, interfacial phenomena are the ones that occur at the limit between two immiscible phases, so-called surface or interface. The most relevant properties in surface science is the surface area, which is very extended in most practical applications. When one phase is fragmented into (small) pieces which are dispersed in another (continuous) phase, a so-called dispersion or dispersed system is produced. There are several kinds of dispersed systems, owing to the nature of both the fragmented and the continuous phases.

> **smoke** = dispersion of solid particles in a gas
> **cloud** = dispersion of liquid droplets in a gas
> **foam** = dispersion of gas bubbles in a liquid
> **emulsion** = dispersion of liquid drops in another liquid
> **suspension** = dispersion of solid particles in a liquid

as well as other systems of large area in which the fragments have been consolidated, such as porous media, e.g., sandstones or alumina catalysts, which are actually bicontinuous.

In many English language Surface Science textbooks, the words surface and interface are used indifferently with the same basical meaning. Here, a slight shade of meaning is introduced, with the word surface for the case of the limit between a gas and a condesed phase, i.e., solid or liquid, whereas interface will be used when dealing with two condensed phases, either two liquids or a liquid and a solid.

The scope of this booklet is aimed at the surfactant science aspects. Since surfactants are always found in a liquid solution, the systems which are to be considered here contain at least one liquid phase. Moreover, this liquid phase must be the continuous phase for the surfactant molecules to be able to move around and attain an equilibrium pattern. As a consequence, the dispersed systems to be considered here are the foams, the emulsions and the solid suspensions. There will be a gas-liquid surface and two kinds of interfaces, i.e., liquid-liquid and solid-liquid.

As discussed elsewhere (see FIRP Booklet # 201), the surfaces or interfaces are very often covered by a special kind of molecule, so-called surfactant, short for surface active agent.

According to their main role and to the kind of dispersed system they are used with, surfactants are labeled: detergent, soap, emulsifier, (de)foamer, dispersant, hydrophobant, wetting agent, corrosion inhibiter and so forth.

This non exhaustive list evidences the multiple applications of the surfactants, a kind of chemical specie which has been called "supermolecule" in a recent paper. Lets first take a look at this kind of molecule.

1.2. SURFACTANTS.

Surfactant are substances whose molecule exhibits both polar and apolar groups. The polar group contains hetereoatoms such as O, S, N, P, as part of some functional group such as carboxylate, sulfonate, sulfate, ammonium, phosphate, etc. Nonionic polar groups such as -OH or -O- (ether link) are not very polar, and thus must occur several times to form a proper polar group, i.e., as polyalcohol or polyether.

The nonpolar group is an hydrocarbon radical of the alkyl or alkyl-aryl kind, with typically 12 to 20 carbon atoms.

Fig 1 shows the molecular structure of some common surfactants. In general surfactants are classified according to their behavior in aqueous solution, as ionic or nonionic surfactants.

Those which get dissociated into a surfactant negative ion (anion) and a metallic cation, so-called counterion, are labeled anionic surfactants. Soaps, i.e., carboxylic acids Na or K salts, alkyl benzene sulfonates, i.e., the active substance in powered detergents, dodecyl or lauryl sulfate, i.e., the foaming agent in shampoos, xanthates, i.e., the collector agent in froth floatation... all belong to the anionic surfactant class, which amount to more that 50 % of the total surfactant production.

Dodecyl (ester) sulfate sodium salt

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}O^- \ Na^+$$

$C_{12}H_{25}$ —⟨○⟩— $\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}$-O$^-Na^+$

Dodecyl benzene sulfonate sodium salt

Dodecyl betaine

$C_{12}H_{25}$ - NH - CH_2-CH_2-COOH

n-dodecyl pyridinium chloride

Sorbitan Monoester

$C_{11}H_{29}$-$\overset{\overset{}{\underset{\underset{O}{\|}}{C}}}{}$-$\overset{}{\underset{\underset{H}{|}}{N}}$-$CH_2$-$CH_2$-OH

Lauryl monoethanol amide

C_8H_{17}—⟨○⟩—O$\left[CH_2\text{-}CH_2\text{-}O\right]_n$H
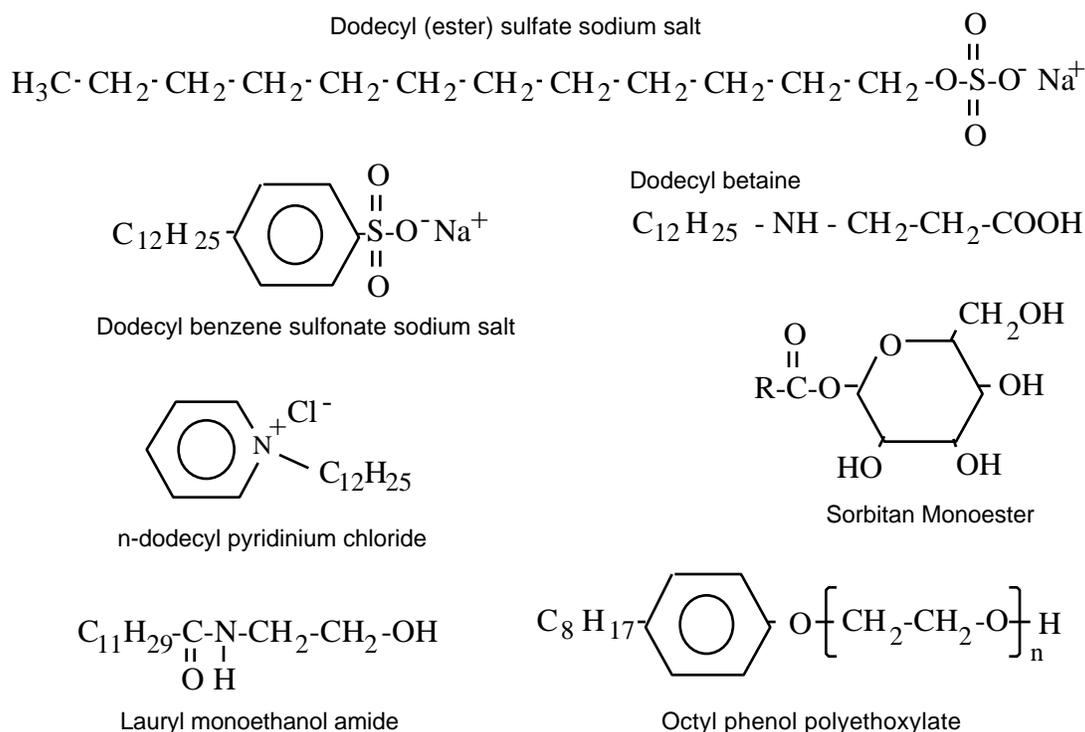
Octyl phenol polyethoxylate

Fig. 1: Some Common Surfactants

The second class in importance (40 %) gathers the nonionic surfactants, i.e., those which are not dissociated in aqueous solution. In most of these surfactants the polar group is produced by the polycondensation of ethylene oxide that result in a polyether chain. The most common surfactants are the ethoxylated alcohols, alkylphenols, acids and esters (see fig 1). Nonionic surfactants are much less sensitive to electrolytes than anionic surfactants, and they have been replacing the latter in many laundry and body care applications, when water hardness can be a problem.

Anionic and nonionic surfactants production reaches beyond 90 % of the total, and the remaining surfactant, e.g., cationic, amphoteric and polymeric ones, are only used for very special applications when cost is not a sensitive issue such as in cosmetics and body care products.

1.3. INTERFACIAL PHENOMENA -WHERE AND WHEN?

There is essentially no human activity, nor commercial, nor industrial, which can dismiss the use of cleaners, foams, emulsions or dispersions. Any time a bidimensional limit is encountered, an interfacial phenomenon is likely to happen. Since our tridimensional world is shaped by bidimensional frontiers it is obvious that interfacial phenomena are to be found everywhere.

In spite of this evidence there is no Surface Science course in the high school nor colleges curricula all around the World. Only a very few universities offer some graduate course on related topics. This is probably due to the fact that the enormous amount of knowledge accumulated in Surface Science in the past 100 years has been viewed as too disorganized to earn a full size niche in the overcrowded curricula. This is no longer true as will be seen in this booklet.

Coming back to the applications of surfactants in domestic and industrial processes, lets consider a few examples.

The human body synthesized surfactants for use in the lungs alveoli, the liver bile, the tears, the saliva, etc. where they play a leading role. Most cell membranes are made of phospholipids, i.e., a variety of amphoteric surfactants.

Industries involved in the manufacturing of health and beauty care products use extensively surfactants to condition the active agent into cream, lotion, ointment, milk, balsam, or other dispersion carriers sometimes with whimsical names such as liposome or niosome.

The cleaning and laundry activities, either domestic or industrial, make use of score of different surfactant formulations ranging from powdered detergents, to carpet dry shampoos or dry cleaning soap.

The pulp and paper industry deals with many interfacial phenomena, from the fiber dispersion processes, to the surface conditioning for cardboards or papers. In the recent years the recycling of used paper has fueled a lot of research on de-inking and ink-fiber separation processes that involve several interfacial phenomena such as detergency, dispersing action, and controlled wettability.

Most paints and inks are very complex systems that contains score of different products, among them oil droplets (resins) and solid particles (pigments, opacifiers), which make them both emulsions and suspensions.

The agroindustry uses surfactants to emulsify or disperse bug-killer substances for spraying applications. Many food products are conditioned as emulsions (hot dog, mayonnaise), foams (ice cream, sandwich bread), or dispersions (powered milk or chocolate).

Many interfacial phenomena are found in the chemical or petrochemical processes: separation by flotation, liquid-liquid extration, water conditioning etc. Some processes are based on the formation of a dispersed system such as emulsion polymerization.

The oil industry also makes extensive use of surfactants, from the enhanced oil recovery techniques, to the emulsion breaking in production operations. Recently a new emulsified conditioning of bitumen has been developed in Venezuela and is now sold under the tradeMark Orimulsion®, as a substitute of fuel N° 6 in thermoelectrical plants. Another heavy cut dispersion has been gaining a strong position in the world market in the two past decades, e.g., asphaltic emulsions for pavements and coating applications.

1.4. POLYPHASIC DISPERSIONS.

The expression polyphasic dispersion is somehow redundant since the word dispersion implies at least two inmiscible phases. However the expletive polyphasic remembers that the main phenomenon to be dealt with is not necessarily the situation at a liquid-liquid or other interface, but also the case of two approaching interfaces, which is a very common occurrence in dispersed systems.

The smaller the fragments of the dispersed (or discontinuous or internal) phase are, the larger is the interfacial area and as a consequence, the more important the interfacial phenomena are. If the fragments are spherical, it can be shown that the interfacial area per unit volume varies as the inverse of the fragment diameter. Thus for the submicron diameter range, the area can attain such values as several square meters per cubic centimeter. The interface-seeking surfactant molecules tend to cover this large interfacial area, generally as a monolayer.

When the dispersed systems contain a large proportion of discontinuous phase, another phenomenon becomes important, that is the approach of the interfaces of two fragments of the dispersed phase. Examples of such occurrence is the approach of two drops or two bubbles that sandwich a thin liquid film between them (fig 2.a)

In this case the situation is much more complex than in the case of a single interface since the interfacial phenomena that occur in the neighboring of the fragments produce a film drainage, i.e., a fluid flow.
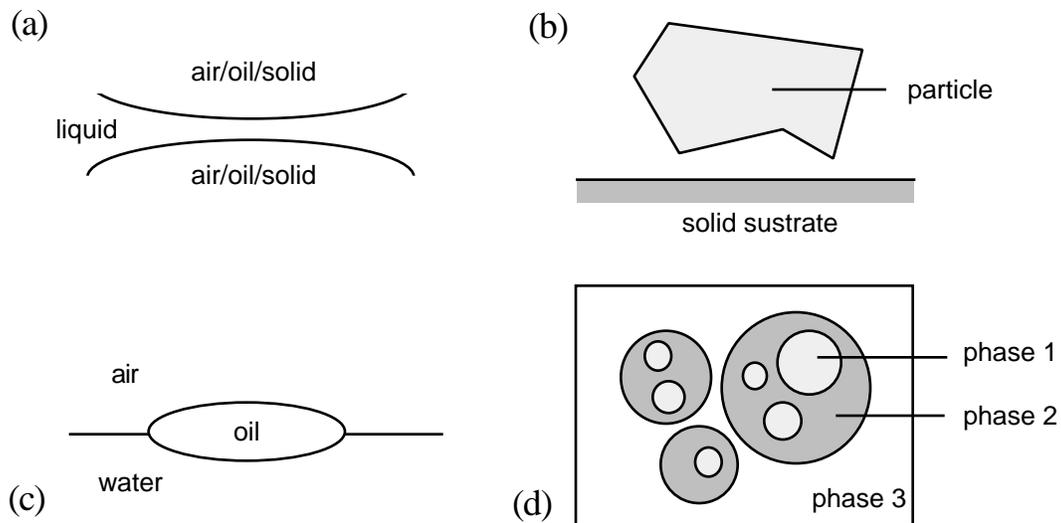
Fig. 2: The approaching of two interfaces in polyphasic systems

When the two fragments of dispersed phase approach at some close distance, Van der Waals attractive forces can become important. On the other hand if the two interfaces are different, for instance in the case of a dirt particle approaching a hair or textile fiber (fig 2-b) or a oil drop lens at the air-water interface (fig 2-c), the Van der Waals adhesive forces can be quite different from the cohesive forces, and the situation become extremely complex.

Some even more complex cases can occur, when there are two or more dispersed phases or when the drops of the dispersed phase contain even smaller droplets of another phase, as in the so-called multiple emulsions (fig 2-d).

These complex cases are very common as far as the practical applications are concerned. For instance, most tooth pastes produce an abundant foam when vigorously

brushed, becoming a continuous aqueous phase system that contains bubbles as well as talc particles and droplets of essential oil. Another example is the 2 in 1 shampoo which often contains droplets of dimethyl silicone oil. Another one is the case of the drilling muds, maybe the most complex dispersed system.

This booklet will consider most of the interfacial phenomena produced at a single interface and their combination when two interfaces are approached.

2.- PROPERTIES OF SURFACTANT SOLUTIONS.

Surfactants are molecules which possess two fundamental properties. On the one hand they tend to be located preferentially at the interface between a polar and an apolar phase. The phenomenon according to which a molecule comes from the bulk of a solution to place itself at the interface (with some specific orientation) is called adsorption, and is characteristic of many amphiphilic molecules.

On the other hand surfactant molecules in solution exhibit a tendency to self associate to produce aggregation polymer called micelles, as well as other structures.

All the properties of surfactant solutions come from one of these fundamental properties.

2.1. AMPHIPHILES

Surfactants are substances whose molecule bear both a polar and an apolar part. Such substances have been called amphiphile by Winsor which coined the word after the latin roots: *amphi* that means duality, i.e., "both sides" as in amphibian or amphitheater, and *philos* that indicates affinity or attraction, as in philosopher or philanthrope.
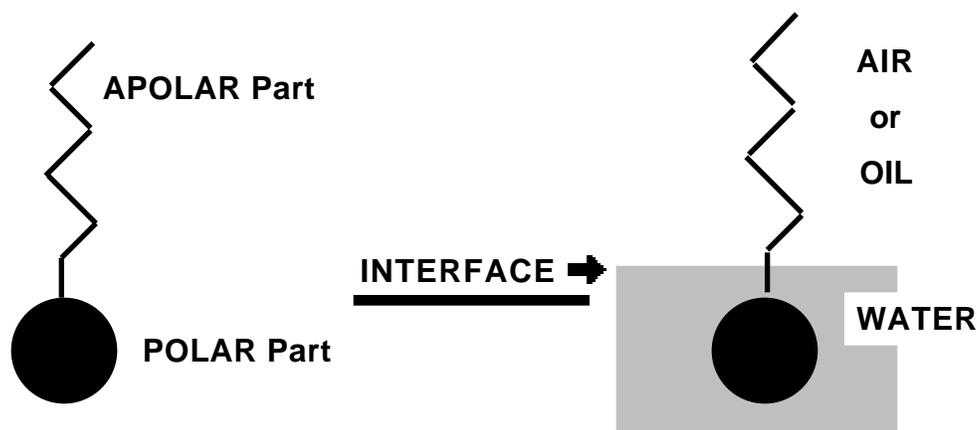

Fig. 3: Positioning of a surfactant molecule at interface

An amphiphile is a chemical substance that possesses some affinity for both the polar substances and the apolar ones. Generally speaking these affinities are referred to as hydrophilic and lipophilic (or hydrophobic) respectively since the polar solvents are in most cases aqueous solutions and the apolar phases are organic "oils".

Most amphiphilic substances are surfactants, i.e., substances that are preferentially located at a surface or interface, where the polarity changes drastically within a few angstroms of distance. Fig 3 shows a typical positioning of a surfactant molecule at

interface; the polar group is dipping inside the aqueous phase while the apolar group is outside of it, either in oil or air.

If the surfactant molecule were inside the bulk water or oil phases, one of its two affinities would not be satisfied.

It is worth remarking that the polar interaction (Debye or Keesom) are typically ten times stronger than the apolar ones (London). This is why the polar group is in general unique while the apolar part is made of a long hydrocarbon chain which contains ten or more carbon atoms. The actual surfactant thus has the shape illustrated in fig 3, with a bulky polar "head" and an elongated apolar "tail".

2.2. ADSORPTION.

When a surfactant molecule goes to the interface and locates itself there with some preferential orientation, it is said that the molecule is adsorbed. The adsorption is a spontaneous phenomenon which is driven by a reduction of the energy when the surfactant lyophobic (which "hates" the solvent) group is removed from the solvent, and when one or both affinities are satisfied respectively at a surface or at an interface.

At a liquid-solid interface, the relative polarity of the solid with respect to the liquid would decide whether the surfactant adsorbs by the head or by the tail (see fig 4). When a solid is involved, other driving forces such as electrostatic attraction can play a role, and it can occur with substances different from surfactants.
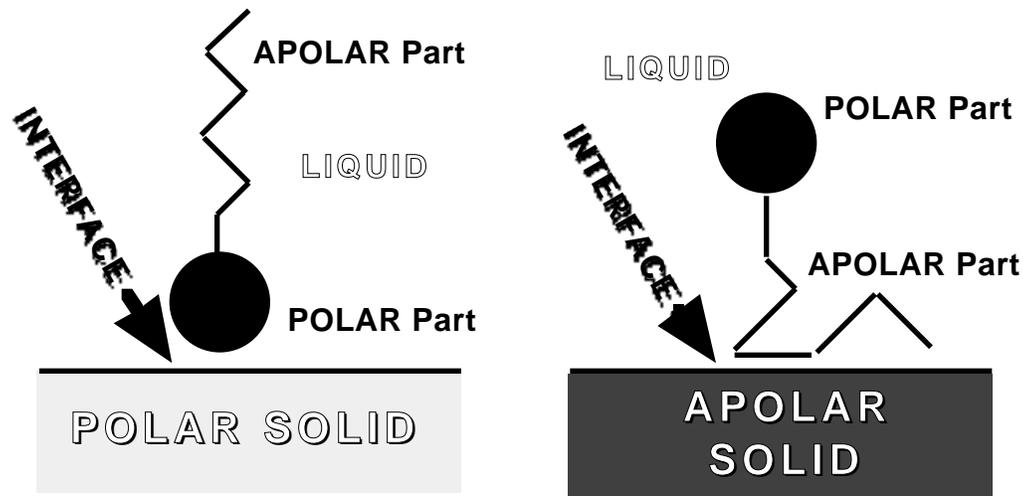
Fig. 4: Adsorption at a solid-liquid interface

Water contains both H^+ and OH^- ions which are likely to adsorb at any solid interface; the relative adsorption of H^+ or OH^- depends on both the solid nature and the ionic concentrations, i.e., the pH. As a matter of fact solid surfaces are always charged when in contact with water, unless a very specific situation so-called point of zero charge or isoelectric point is attained.

Adsorption is a dynamic phenomenon which is opposed by desorption, i.e., the transfer of a surfactant molecule to a bulk phase. The adsorption and desorption steps are often very rapid; as a consequence an adsorption-desorption equilibrium is reached after some time, which depends upon the surfactant concentration in the bulk phase.

Since the surfactant molecule has a lower free energy when it is adsorbed at interface than in the solvent bulk phase, the equilibrium is very much displaced toward the adsorbed state. In fact the interface is very rapidly covered by a monolayer of surfactant molecules. In such monolayer the molecules are arranged in some specific pattern which depends upon structural and geometrical characteristics. Typically a surfactant molecule such as a soap or a detergent requires about 30 - 50 Å^2 at interface.

When a monolayer is formed, everything happens as if the interface were coated with a thin layer of a new material. For instance a monolayer of cationic surfactant adsorbed at the water/metal interface is oriented with the head group towards the metal surface and the hydrocarbon tails towards the water bulk phase. This results in the hydrophobation of the metal surface, as if it were covered by a thin grease coating. Such phenomenon is of first importance in chemical processes such as flotation or corrosion inhibition. The degree of hydrophobation is measured by the contact angle, a geometrical concept which defines the wettability, as will be discussed later on.

This and other properties that derive from the adsorption of the surfactant are illustrated in fig 5.
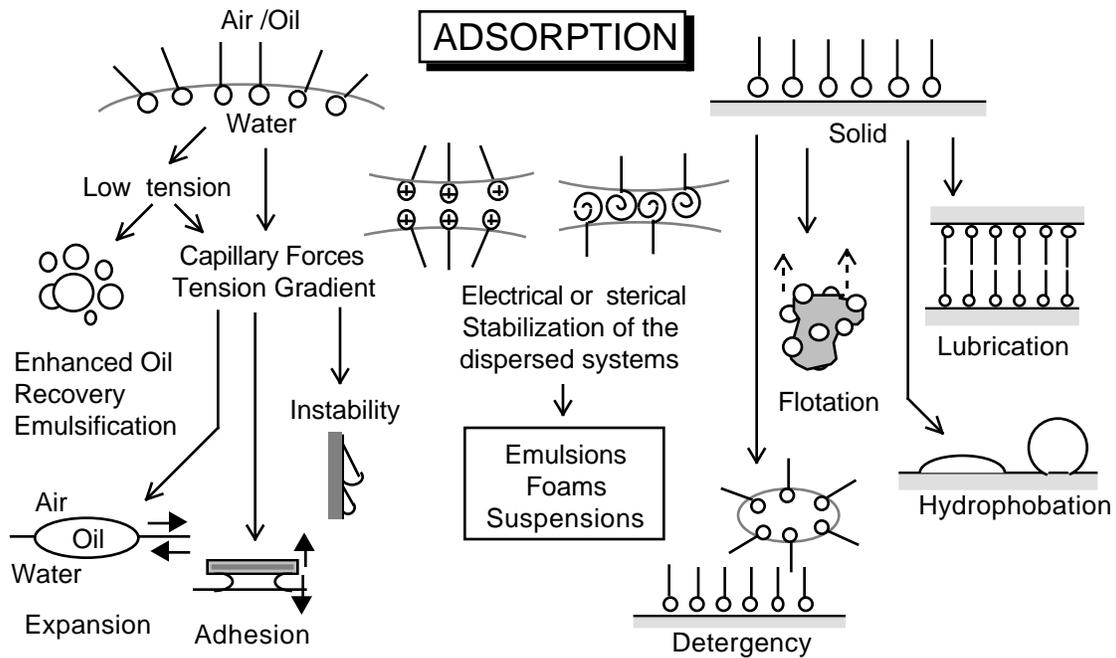
Fig. 5: Properties that derive from the adsorption of surfactant molecules at interface

2.3. SELF-ASSOCIATION.

The second fundamental property of surfactant molecules is their capability of self-association in aqueous or non aqueous solutions. The discussion here will be limited to aqueous solutions.

It has been discussed in the previous paragraph that the first molecules present in a bulk phase tend to migrate to the interface, i.e., to adsorb. The formation of an adsorbed monolayer is the first hint of the tendency of the surfactant molecules to associate.

When the surfactant concentration increases in the aqueous phase, the surfactant molecules first saturate the interface, and then accumulate in the solution. Each time a new surfactant molecule is added to the solution, the unfavorable interaction between the surfactant hydrophobic tail and the water molecules is increased. At some point the surfactant molecules start aggregating into the so-called micelles, an self-association structure in which the hydrophobe tail is removed from the aqueous environment. The concentration at which the first micelles are formed is called the Critical Micelle Concentration, which is abbreviated as CMC (see FIRP Booklet # 201). The CMC is the concentration at which the factors which favor the formation of the micelle (for instance the hydrophobic effect) start dominating the effects which oppose it.

Micellar solutions are able to solubilize different kinds of substance, and this capacity of solubilization is one of the most important properties of the surfactant solutions. Hydrophobic substances, i.e., oils, can be solubilized inside the micelles core, sometimes in very sizeable amounts. Some extreme cases are known in which the solubilized oil volume is actually larger than the aqueous solvent volume; for such situation to happen, the solution must contain a very large number of micelles and the micelles must be considerably swollen. These micelles are no longer spherical, but cigar shaped or hexagonally packed or even degraded into lamellar liquid crystals (see fig 6).
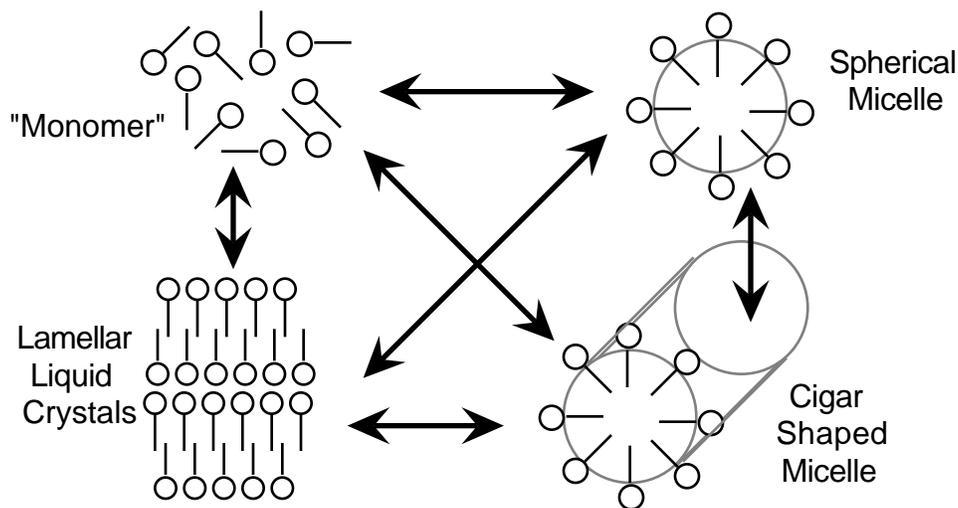

Fig. 6: Surfactant Micelles and other self-association structures

3.- INTERFACIAL PHENOMENA AT EQUILIBRIUM.

3.1. COHESION AND ADHESION.

The cohesion between the molecules of a piece of matter is due to the so-called Van der Waals intermolecular forces. These forces are the glue that keeps the material under a solid or liquid state; they have a very short range of action, and typically change as the inverse of the 6th power of the distance.

There are three kinds of Van der Waals forces: (1) Keesom forces which are produced by the interaction of a permanent dipole with another permanent dipole. (2) Debye forces which result from the interaction of a permanent dipole with an induced dipole. (3) London or dispersion forces which have no specific direction of action and are said to be nonpolar interactions, though they result from the interaction of fluctuating dipoles.

The two first forces involve polar molecules and binding energies in the few Kcal/mol range, whereas the third one occurs in all kind of molecules, specially apolar ones, with a much lower interaction energy, typically ten times lower.

Fig 7 illustrates the difference between cohesion and adhesion; the first one is the energy required to pull apart a unit area between to faces of the same substance, while the second one is the same concept but with two different substances.
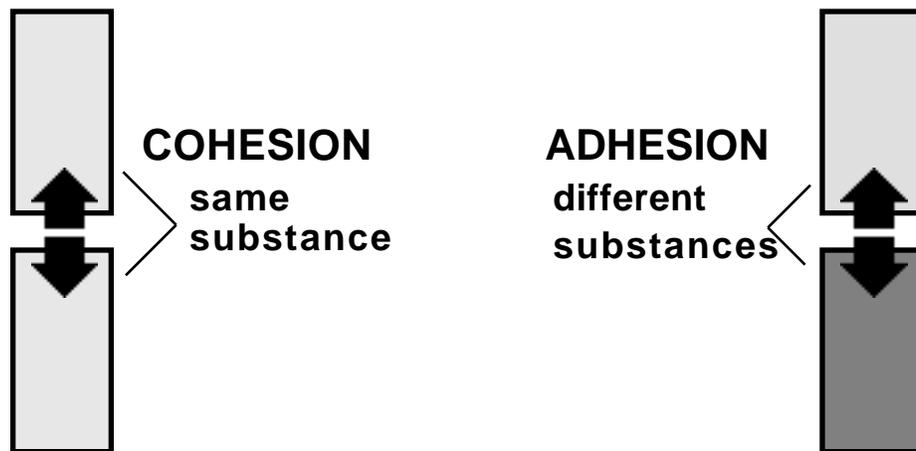

Fig. 7: Cohesion and Adhesion

The so-called "solubility parameter" gives an estimate of the cohesion forces; δ^2 is the ratio of the molar enthalpy of vaporization to the molar volume, and it has been called the cohesive energy ratio.

$$\delta^2 = \frac{H_{VAP}}{\nu_{LIQ}}$$

The adhesion between two different substances (1) and (2) is calculated by taking the geometric mean of the corresponding cohesion energies of the pure substances.

$$\gamma_{12} = \sqrt{\gamma_{11}\,\gamma_{22}}$$

This relationship illustrates the difference between cohesion and adhesion. If substances (1) and (2) have very distinct cohesion energies, as with a polar substance and an apolar one, the adhesion can be very different from the cohesion, generally much lower. On the opposite, substances of similar nature exhibit similar cohesion energies and thus a good adhesion.

An encyclopedic handbook on solubility parameters and their use has been published ten years ago by Barton (1983). This text is quite useful for people dealing with complex mixture formulation such as paints, inks or varnishes.

The cohesion/adhesion forces are the ones that determine the attractive forces between bubbles, drops or solid particles dispersed in a continuous liquid phase. These forces tend to produce the aggregation of the dispersed phase fragments, and thus they are driving forces behind the dispersion instability mechanisms.

It is worth remarking that a (mono) layer of adsorbed surfactant can substantially modify the cohesion/adhesion forces, since these forces action range is extremely short, as a matter of fact of the same order of magnitude than the surfactant layer thickness. Fig 8 illustrates the action of dispersing agents as substances that coat the solid particles and drastically change the cohesion/adhesion situation.
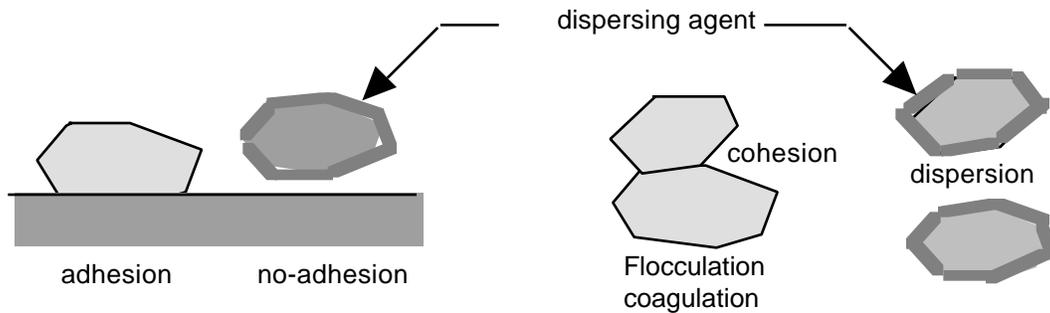

Fig. 8: The action of a dispersing agent (simbolized by ||||||)

3.2. THE THREE KIND OF REPULSION.

In presence of anionic surfactant, e.g., a soap, and a dispersed phase made of non-polar particles or droplets, the surfactant molecules adsorb at interface with their hydrophobic tails on the nonpolar phase, and their hydrophilic head towards the aqueous solution, as illustrated in fig 9 (a). The negative charges which are associated with the adsorbed anionic surfactant are essentially (and statistically) fixed at interface, whereas the counterions (Na^+) are wandering in the aqueous phase in the so-called diffuse layer of the electrical double layer (see FIRP Booklet # 610). These ions are submitted to two different opposite effects. The first one is the random molecular motion which is responsible for most diffusion process, whose result is the uniformity of concentration everywhere; the second one is the Coulomb attractive force between the adsorbed negative charges and the free moving positive charges, which prevents the cations to

wander too far away from the interface. The compromise between the two effects is that the cations are located in the aqueous solution in a layer located near the interface.

(a) ELECTROSTATIC REPULSION between CHARGED INTERFACES

(b) STERIC REPULSION between INTERFACES with NONIONIC SURFACTANTS

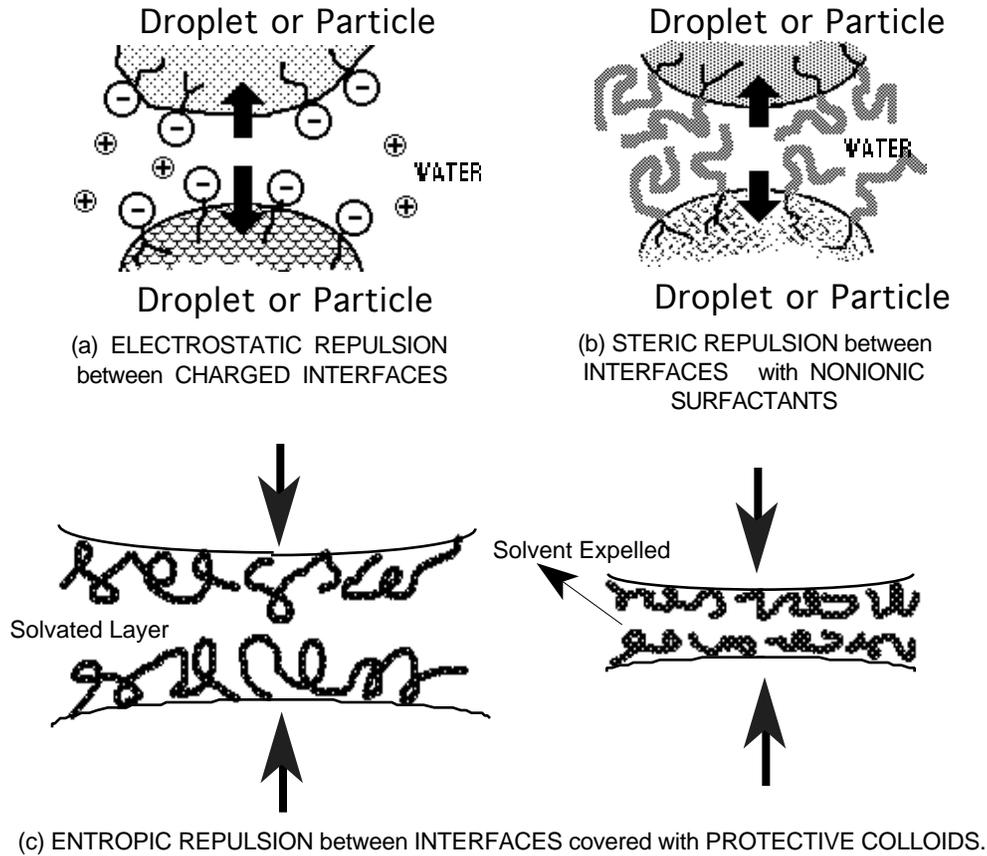(c) ENTROPIC REPULSION between INTERFACES covered with PROTECTIVE COLLOIDS.

Fig. 9: The Three kinds of repulsion

It can be demonstrated that the actual potential decreases exponentially with the distance from the interface. This decrease is characterized by the exponential "period" (a word used in radioactive decay) called the Debye length.

$$\psi = \psi_o \, e^{-x/\kappa}$$

The Debye length is typically 100 Å. Since there exist an electrostatic repulsion when the electrostatic potential effects of two approaching interface start overlapping, the typical scale at which this repulsion occurs is 500 Å or 0.05 μm. This distance might be large enough in some cases to preclude the cohesion/adhesion short range forces to enter into action. In such a case a stable dispersion is attained.

The Debye length can be shown to be:

$$\kappa = \sqrt{\frac{RT}{F^2 \sum C_i \, Z_i^2}}$$

where   is the continuous medium permitivity, C_i is the concentration of the "ith" ionic specie in the bulk phase, i.e., out of the diffuse layer, and Z_i is the ion valence, while F is the Faraday constant and R the gas constant.

This expression indicate that the Debye length should decrease with an increase of electrolyte concentration, particularly if it is due to polyvalent electrolytes. A reduction of the Debye length results in a shorter distance of potential overlapping, and thus in a higher probability for the cohesion/adhesion forces to destabilize the dispersed system.

There is a second type of repulsion, so-called steric repulsion, from the root "stereo" which is associated with the idea of volume or three-dimensional effect. Fig 9 (b) illustrates the case of this steric repulsion for a dispersed system stabilized with nonionic surfactants with long polyether hydrophilic groups, say 20 or so ethylene oxide links.

Although a polyether chain of such a length is never straight but rather folded, this results in a bulky hydrated head group layer on the aqueous side of the interface, with a thickness in the range of 100 Å or more. When two interfaces are approached, these "protective" layers bump one against the other, and the actual distance between the drop or particle surface can never reach the minimum required for the cohesion/adhesion force to take over. This kind of steric stabilization is probably responsible for the stability of water-in-oil emulsions in the crude oil production, where the steric repulsion comes from the bulky hydrophobic groups of the asphaltene or resin materials that are the natural surfactants.

A third stabilization mechanism, which results in some kind of repulsion, has been called entropic repulsion. It is typical of the use of polymeric surfactants or macromolecules which are referred to as protective colloids in many recipes. Fig 9 (c) illustrates this effect in the presence of an adsorbed polymeric material chain. This kind of adsorbed substances are not completely lying down on the surface or interface; in reality they are in contact with the interface through several functional groups and the rest of the macromolecules is solvated (by solvent molecule) in the liquid phase. Thus the surface is actually covered by a layer that often contains much more solvent than protective colloid (see Fig 9 (c)). When the two interfaces are approached, there is no really steric repulsion upon contact of these layers since they are not compacted. However when the interfaces get closer and closer, a larger and larger amount of solvent molecules is expelled from the layers, resulting in a more organized positioning of the polymer, and a lesser amount of freedom of motion, that is a lower entropy. Since an entropy decrease can not happen spontaneously, this mechanism can occur only at the expense of the cohesive/adhesive forces that it opposes.

In commercial detergents this stabilization mechanism is often provided by carboxy methyl cellulose, an agent which avoids the redeposition of removed dirt.

In many cases the repulsion is not provided only by one of the previous mechanism but by two of them, a very common case when high-molecular-weight surfactants are used.

3.3. DLVO THEORY

Half a century ago, Derjaguin and Landau in Russia, and Verwey and Overbeek in Holland, independently and simultaneously proposed a theory to interpret the known phenomena related to the stability of lyophilic colloids, i.e., systems with small dispersed fragment with no affinity for the dispersing continuous phase. In their honor the theory is now recalled as DLVO theory, and its application range has been extended qualitatively to systems containing fragments of matter up to the 10 μm range, that is at least 100 times larger than the bigger colloids.

This theory assumes that when two interfaces are approaching, as it happens in any dispersed system when two fragments of matter get close enough, then the overall

force can be calculated as the combination of the attractive Van der Waals forces and the repulsive electrostatic Coulomb forces.

There is no space here to discuss in details the different expressions of these forces (see FIRP Booklet # 614), and it is only necessary to take for granted that these expressions depend upon the approaching interface geometry and the intrinsic nature of the forces, i.e., the Debye length value on the electrostatic repulsion side, and the Hamaker constant as far as the Van der Waals forces are considered.

Fig. 10 indicates the variations of the overall resulting force as a function of the distance between approaching interfaces. At infinity, which may means only a few microns in many cases, the force is nill. At a extremely short distance, i.e., essentially zero, the two interfaces are in contact and the force is always repulsive. Extremely short range repulsion depending on the inverse of the 12th power of the distance have been proposed for this "compressibility" repulsion.
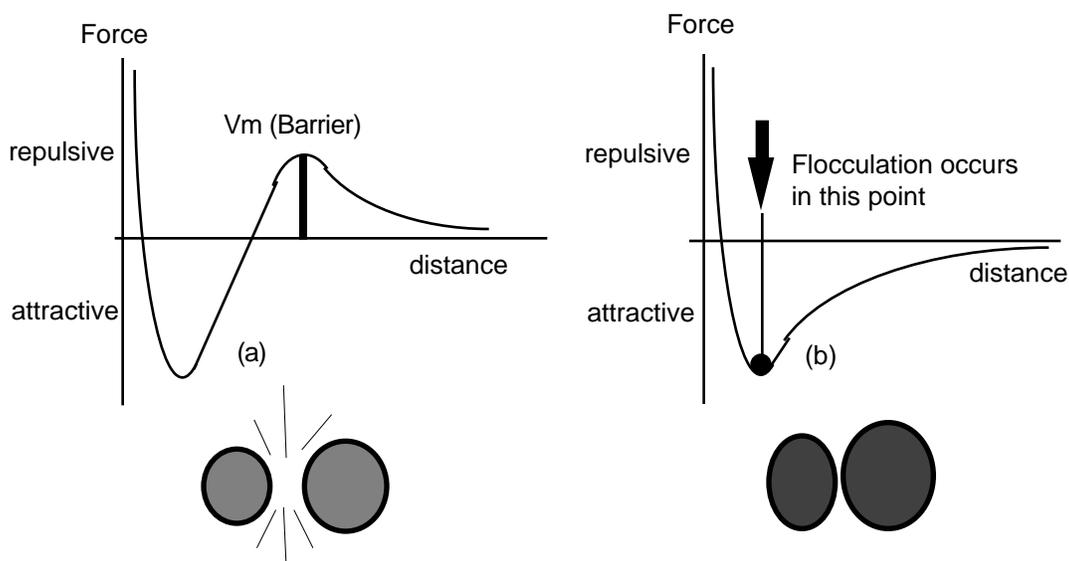

Fig. 10: Attractive-Repulsive overall resulting force as a function of the distance between particles

Depending on the case the force balance can be repulsive (fig. 10-a) or attractive (fig. 10-b) at intermediate distance, which can be as short as 100 Å. The occurrence of cases (a) or (b) is commanded by the nature of the fragmented material, the solvent, the state of the interface (charge, adsorbed surfactant) etc.

In case (a), the force is always repulsive from long distance down, and there is a maximum repulsive force referred to as barrier Vm in fig 10-a. If this barrier happens to be superior to the Brownian motion thermal agitation (which is typically 10 kT), then the kinetic energy of the fragments is not large enough to offset the barrier, and the repulsive force will impede the two interfaces to get close enough for the overall force to be attractive. A high barrier is thus associated to a stable dispersed system.

In the case of fig. 10-b, the force is attractive at all distances and the approach proceeds until the curve minimum is reached, where the most stable state is encountered. By the way this also happens in fig. 10-a case, provided that the energy barrier is overcome.

Depending whether this minimum occurs at short or very short distance, a matter of very few Å indeed, the situation is called floculation, coagulation or aggregation. Often the word floculation is kept for a "long" distance low energy minimum, while coagulation

or aggregation is used when the interfaces are actually in contact with an attraction energy similar to the cohesion/adhesion energy. Fig. 11 has been prepared to summarize the role of the repulsion barrier and the potential minimum in the practical cases of interest.
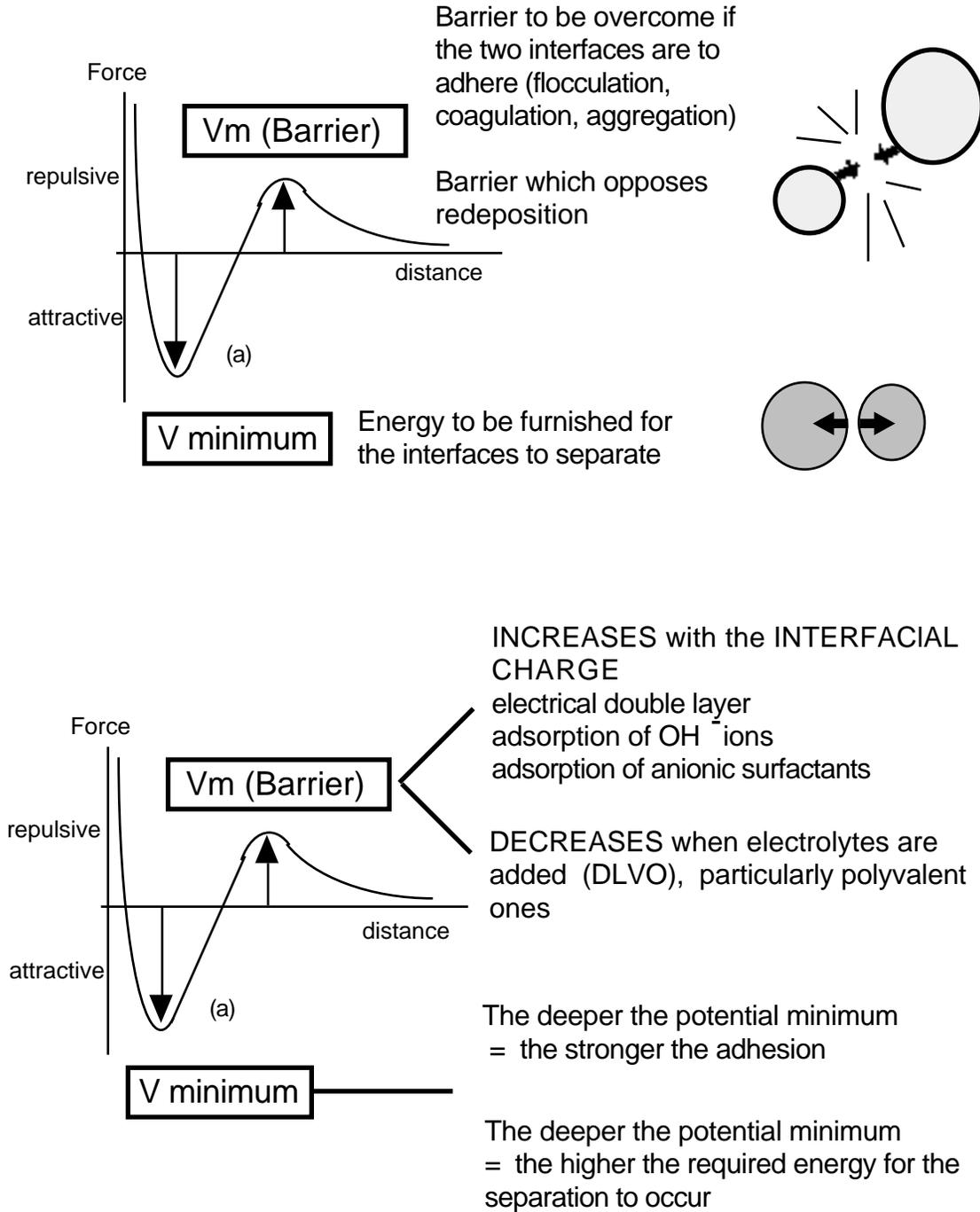

Fig. 11: Physical meaning of the different concepts involved in the DLVO theory.

In some very particular cases, the potential versus distance curve is even more complex, as indicated in fig. 12.
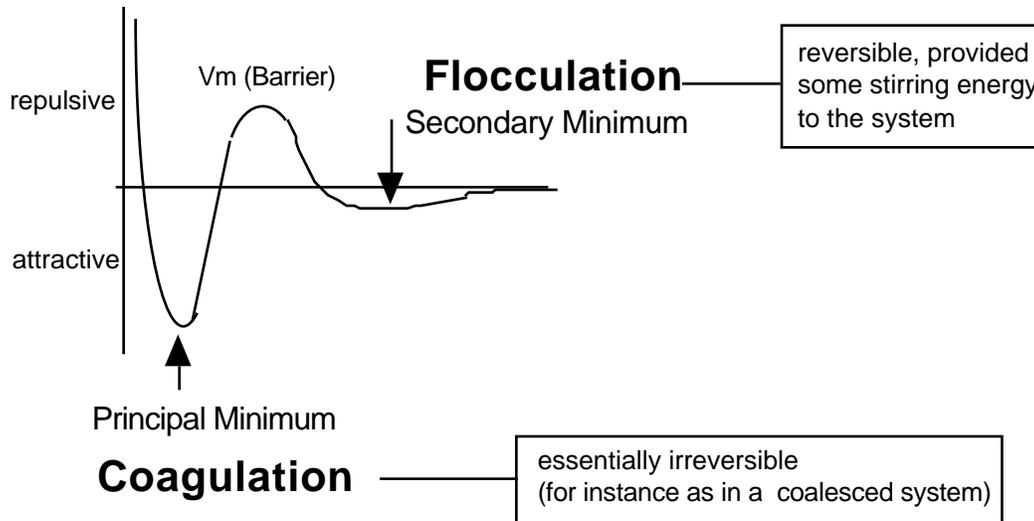

Fig. 12: Case when there exists a barrier and secondary minimum

In this case there are two minima separated by a maximum. The farther minimum is shallow and at some "long" separation distance. When two particles get close, the potential is slightly attractive and the particles become stuck together at the secondary minimum, which is said to correspond to a floculation. Since the attractive energy that corresponds to this minimum is weak, a weak energy input such as a hydrodynamic stirring is generally strong enough to separate again the two particles. As a consequence floculation is essentially a reversible phenomenon.

On the contrary the principal minimum is associated with a short distance and a very strong attractive energy. The associated situation is termed coagulation, and it is essentially irreversible, since the energy input to reverse it is of the same magnitude that the one which was supplied to the system to make it dispersed in the first place.

If the dispersed phase is a fluid, the bubbles or drops generally coalesce as an instant consequence of the coagulation. If the dispersed phase is solid, then the particle size starts growing upon coagulation. In any case coagulation results in an alteration of the dispersed system which is generally viewed as instability.

On the other hand floculated systems are in some weakly metastability, and can be returned to a stable system with little energy input.

3.4. WETTABILITY AND CONTACT ANGLE.

When the system contains three phases, the binary interactions are used to describe the physico chemical situation. The interfacial or superficial free energy (or tension) is a measurement of the adhesion forces between two phases. When three phases are present, the relative extension of the interfacial area of each binary contact is also an indication of the match between each binary. In microscopic terms, these concepts are rendered through a property called wettability, which essentially applies to solid surfaces.

The wettability is the property that indicates the affinity between a solid and a fluid phase, and the contact angle is the experimental and practical way to quantify the concept of wettability.

Fig. 13 shows a typical situation in which a drop of fluid 2 is deposited on a solid (flat) surface, while all the rest of the space is occupied by fluid 1. For instance fluid 1 may be a gas , and fluid 2 a liquid.
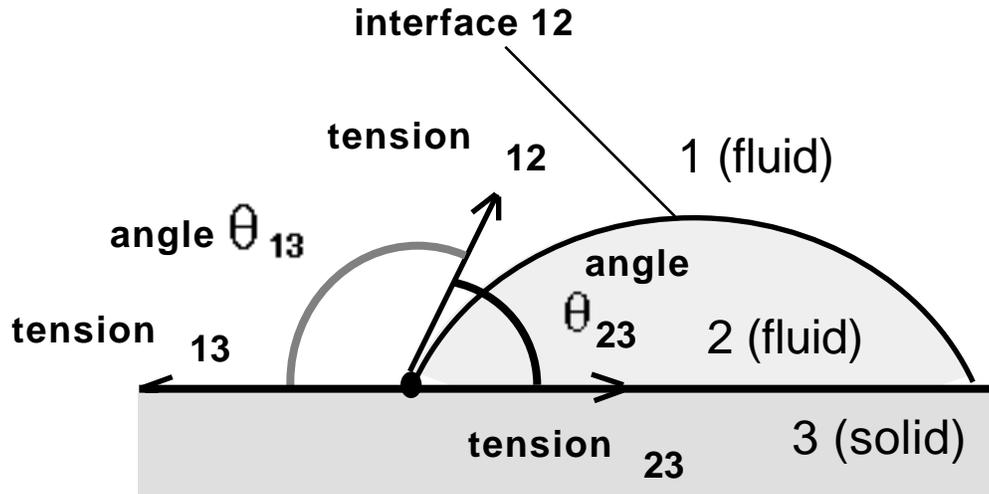

Fig. 13: Wettability and Contact Angle

The mechanical equilibrium at the three phase contact line requires that:

$$\gamma_{12} + \gamma_{23} + \gamma_{13} = 0$$

where γ's are the surface or interfacial tensions, which are expressed in this case as vectors tangent to the respective surface. In the case shown in fig. 13, the solid has a flat surface, and the vertical component of any net force can be absorbed by the solid. The only significant motion can occur along the solid surface, and the horizontal force balance can be written:

$$\gamma_{13} = \gamma_{23} + \gamma_{12} \cdot \cos \theta_{23}$$

where θ_{23} is the contact angle between fluid 2 and solid 3.

If this angle is very small (near zero) the fluid 2 drop lens extends all over the solid surface and displace fluid 1 contact. It is said that fluid 2 wets the solid surface. On the contrary, if the contact angle is larger than 90°, then the fluid is said not to wet the surface. In fig. 13 case, it is thus obvious that fluid 2 wets the solid surface, while fluid 1 does not.

Fig. 14 shows a typical case of detergency action. On the left drawing a drop of oily or greasy dirt (fluid 2) is wetting the solid surface (3), while water (fluid 1) does not wet it. When a detergent is added to the aqueous phase the change in the interfacial

tensions make the solid to be wettable by the water (1). As a consequence the contact area of the oily drop decreases, and the drop is said to roll up, a situation which favors its remotion from the solid surface by any proper mechanical stirring.
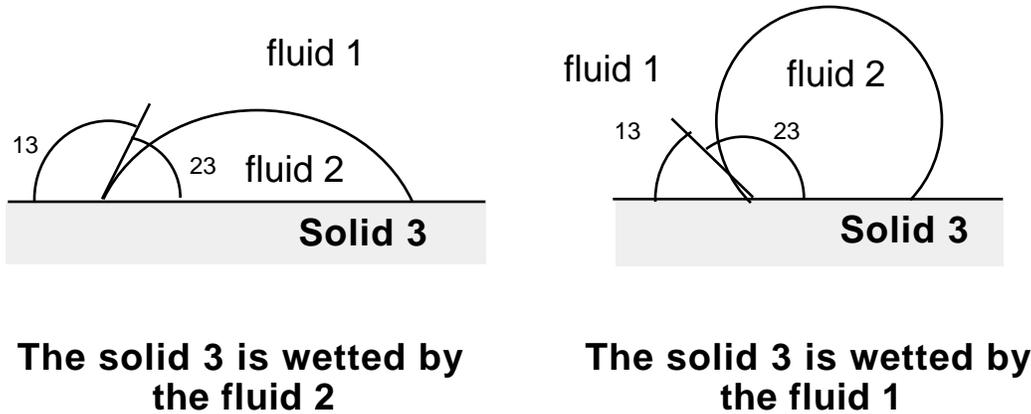

Fig. 14: Different cases of wettability

In others applications such as froth flotation the opposite is sought, i.e., a change of the solid surface from water wet to air wet or hydrophobic.

4. NON EQUILIBRIUM INTERFACIAL PHENOMENA.

The previous sections dealt with situations in which forces or potentials oppose each other until an equilibrium is reached. No consideration was made of the time scale nor the way the changes are occurring, because only physico chemical or thermodynamics phenomena were discussed. It is now time to address the case where the kinetics is responsible for the phenomena of interest.

Since the neighborhood of the interface is a non homogeneous region, a convective fluid flow can drain away some substances, and produce a physico chemical unbalance. It is known that a system tends spontaneously to oppose any change, so the unbalance generally generates some potential that induces some motion to reestablish an equilibrium situation.

When two dispersed fragments of matter (particles, bubbles, drops) are separated by a thin film of continuous phase, the approach of the two fragments and the film tangential drainage are associated in the sense that there is a coupling between the two mechanism which must be considered in some simultaneous fashion.

There are two types of non equilibrium effects: those which are related to the presence of the electrical double layer at interface and which are named electrokinetic effects, and those which are related to transport driving forces which arise generally from a gradient in temperature or concentration. The most important non-equilibrium phenomena are shortly described in the following paragraphs.

4.1. STREAMING POTENTIAL.

It is known that there is a double electrical layer at most interfaces, particularly in the presence of an ionic surfactant. This double layer takes its name from the fact that the surfactant ions are adsorbed, and somewhat motionless at interface, whereas their counterions are free-moving in the liquid phase. When there is a fluid flow near the interface, the ions which are in the diffuse layer are swept away with the bulk phase motion; a charge separation builds up as the counterions are dragged away, and an electrostatic potential, so-called streaming potential arises. The resulting electrical field produces a force that tends to bring back the ions to their original location (see fig. 15).
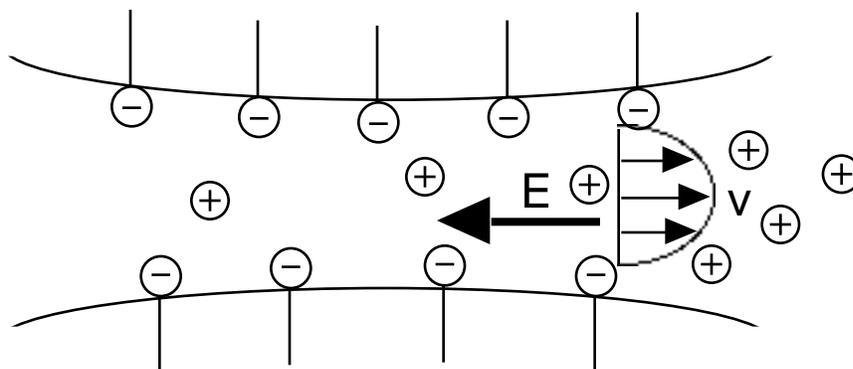

Fig. 15: Streaming Potential

The streaming potential is the electrokinetic effect that results in a situation in which a fluid motion induces the generation of an electrostatic field. There are three other electrokinetic phenomena in which fluid motion and electrical potential are coupled (see FIRP Booklet # 611).

In the electrosmosis, an imposed electrical field induces a fluid flow through a porous plug of large surface area. In the two previous electrokinetic phenomena the solid phase is stationary and the fluid phase is the moving one. In the two following phenomena small solid particles are susceptible to move with respect to a stationary fluid phase.

In the sedimentation potential, the motion of small particles under the effect of gravity induces the formation of an electrical potential. In the electrophoresis, the application of a potential across a cell, which contains suspended particles, results in the particle motion. This last effect is used as an analytical technique to separate proteins, as well as other macromolecules and colloids. It can be used also to measure the surface potential, or more exactly the so-called zeta potential, which is the potential at the surface of shear.

4.2. ELECTROVISCOSITY EFFECT - APPARENT VISCOSITY.

The streaming potential creates an electrical field that applies a force on the displaced ions to get them back into their original position. These ions are generally solvated, i.e., associated with solvent molecules, so that the force is also exerted on the solvent, whose motion is slowered. On the other hand some solvent molecules can get associated with the adsorbed surfactant species; these molecules form some kind of jellyfied layer that does not move with the liquid flow.

Both previously outlined effects tend to restrain the thin liquid film drainage, and result in an apparent increase of the liquid phase viscosity.

These effects are important only when the distance between the interfaces is of the same order of magnitude than the Debye length (electroviscous effect) or the motionless solvent layer. Thus these effects are expected to take place when the film thickness is extremely small, say in the 100 - 500 Å range, that is late in the drainage process. These effects are thought to be responsible for the long term stability of some high internal phase ratio dispersions. As a matter of fact it can be shown, provided that the films are resistant to perturbation, that the apparent increase of viscosity can be hundred fold or more, an increase which directly enhances the dispersion stability by the same factor.

4.3. INTERFACIAL VISCOSITY.

The superficial or interfacial viscosity is the two-dimensional equivalent to the bulk viscosity; it is the conductivity of momentum perpendicularly to the direction of motion on the surface or interface.

Interfacial viscosity is related to the (lateral) interactions of molecules located at interface with one another. Macromolecular surfactants are known to produce a high interfacial viscosity, as well as high MW molecules with functions that favor lateral interactions.

Since each adsorbed molecule is interacting with both the solvent molecules and its neighboring adsorbed molecule, a fluid phase motion produces a pull on the adsorbed molecule which is transferred to the neighboring molecules through the interfacial viscosity effect (see fig. 16).
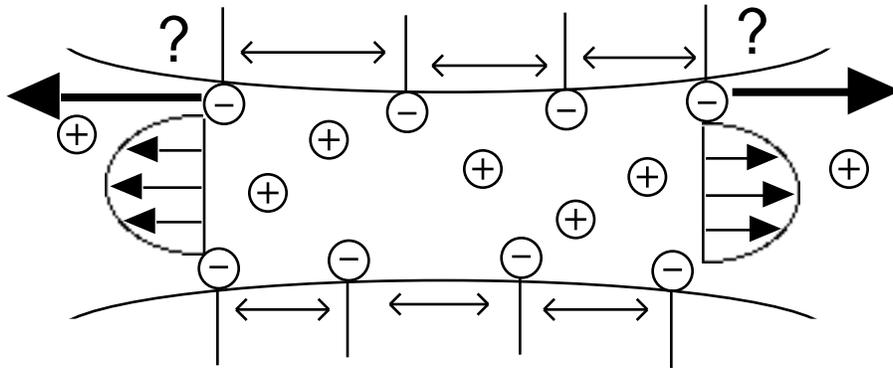
Fig. 16: Interfacial Viscosity Effect

If the adsorbed molecules form a very well structured lattice, i.e., an almost polymeric layer, this could result in the "freezing" of one or more layers of solvent molecules, with the resulting restriction in the fluid motion. Asphaltenes are known to produce such rigid coating after a water-in-crude emulsion is kept in rest for a few days.

The theory indicates that there are actually two surface viscosity parameters, one that traduces the classical shear effect while the other has to do with the elongation of the surface area. In any case the surface on interfacial viscosity is very difficult to measure, and it is a property which is not currently controlled in most practical applications. (Edwards et al).

4.4. MOTION INDUCED BY CAPILLARITY.

Laplace equation of capillarity indicates that there is a difference of pressure between the two sides of a curved interface.

$$P = \frac{2}{R}$$

where   is the superficial or interfacial tension and R the mean curvature radius.

As a consequence the pressure is different in approaching bubbles or drops, if they have a different size. This effect can be important in foam, since the difference of pressure between two bubbles can drive a gas diffusion transport through the interbubble thin film. As a matter of fact this is one important decay mechanism which applies to long life foams. Theoretically it could be important in emulsions as well; actually this is not the case because the diffusion coefficient of oil through water or water through oil are so much lower that the effect is neglectible.

Most high internal phase ratio fluid-fluid dispersions (foams and emulsions) do not exhibit spherical bubbles or drops but rather polyhedrical ones. The interbubble or interdrop films have a central flat structure and exhibit some thickening when they join (see fig. 17), in a location called Plateau's border. Since the interface exhibit a concave curvature at the Plateau's border, the pressure is lower and a motion from the flat zone to the border is induced, which tends to thin even more the film (Ivanov, 1988).

This film thinning phenomena have been described by Derjagning through the so-called disjoining pressure concept, which is useful to discuss some practical problems.

The thin film drainage might produce the electrokinetics and interfacial viscosity effects mentioned in the previous paragraph, as well as others.

For instance, when the film liquid drains under the action of the capillary pressure and under the action of gravity, the liquid tends to move downwards; then the film located at the top of the dispersed system becomes necessarily thinner, while the ones which are located below change according to the balance between two effects: the feeding of liquid coming from drainage of films located above, and the depletion of liquid by downward drainage. Since this is a non-equilibrium process the actual composition of the moving fluid can change with time, a very complex situation that is not trackable quantitatively but can be very well understood qualitatively by people familiar with the chromatography mechanism.

Differences in concentration or temperature are responsible for a very important phenomenon so-called tension gradient, because it results from a difference in tension from place to place at interface (see fig. 18).

The difference in concentration can occurs in different ways, either because a high local surfactant concentration in the bulk phase results in a higher adsorbed concentration, or because the surface is extended quickly as in the formation of foam.

Since a small difference in adsorbed surfactant concentration can produce a large difference in surface or interfacial tension, this tension-gradient effects induce extremely strong forces at interface (Levich, 1962). Because of the continuity with the bulk phase, particularly when the bulk phase is located in a thin film, the interfacial force also produces a displacement in the bulk phase, which can result in the formation of ripple, tears and film breakage. In any case the motion is always from the low tension region (high surface pressure or high surfactant concentration) towards the high tension region.

Local difference in temperature have been shown to produce similar effects, which can be detrimental for instance in paint coating applications.

In other case, this tension gradient is beneficial. For instance the so-called Gibbs elasticity which favors the formation of stable foam films is due to a proper tension

gradient which heals any film thinning during the foam formation. Since the tension gradient can be eliminated either by surface transport or by adsorption from solution, both the surfactant type and concentration are found to influence the amount of foaming, i.e., the foam stability during the first instants.
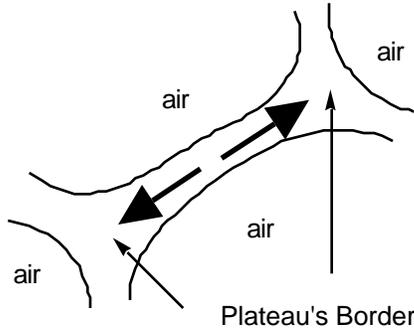

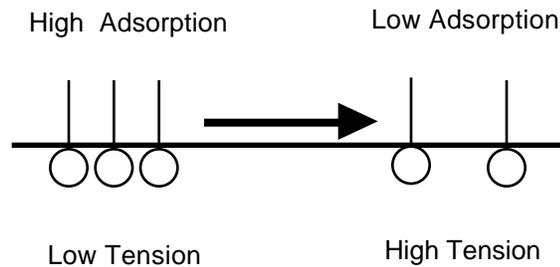Fig. 17: Drainage toward Plateau's Border   Fig. 18: Movement induced by a tension gradient

5. DETERGENCY.

Detergency is the generic name to describe several phenomena that result in the removal of dirt from a solid substrate. Dirt actually means a solid particle or a liquid drop of an undesirable substance. There are many cases depending upon the dirt and substratum characteristics, and the involved phenomena.

The two most important mechanism are discussed in the following sections.

5.1. WETTABILITY CHANGE.

This mechanism applies to an apolar, e.g., greasy, liquid drop located on a substrate, which is in most cases a polar one.

Fig 19 illustrates the change in wettability; on the left drawing the oil droplet wets the solid surface, e.g. the   contact angle is less than 90°; meanwhile the contact angle with water is much larger than 90°.
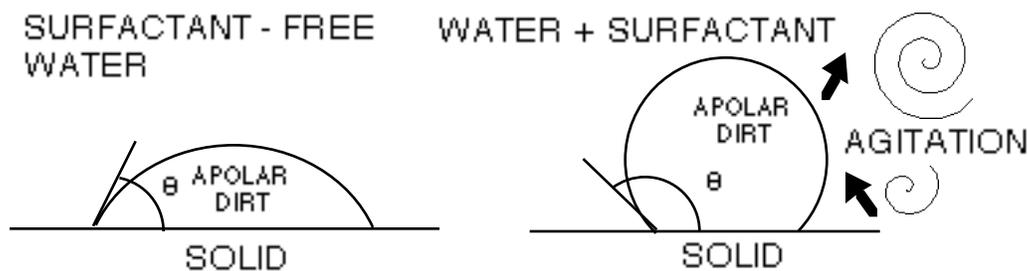

Fig. 19: Change in wetability and the rolling mechanism

When some detergent is added to the aqueous solution, one of the effects is to increase the water-wettability of the substratum, particularly by solubilizing contaminating hydrocarbons or other hydrophobic substances. The interfacial free energy of the water-solid interface is substantially decreased, in general much more than the oil-water tension. As a consequence the contact angle of the oil phase with the solid changes to a value much over 90°.

The contact area between the dirt drop and the substrate decreases substantially and the drop protuberance on the solid surface increases, a condition that favors its removal by the eddies produced by the mechanical stirring of the washing machine.

This rolling mechanism is often accompanied by some micellar solubilization, which does not play however but a secondary role.

5.2. ADHESION OVERCOMING.

This second mechanism applies to the deposition of a solid dirt particle on a solid substrate. According to the discussion on cohesion/adhesion, the removal is more difficult when the dirt and the substrate are both polar substances.

The role of the detergent here is to reduce or offset the adhesion, i.e., the attractive forces between the dirt particle and the substrate.

Fig. 20 illustrates the different stages of this mechanism. First the surfactant molecules penetrate, by diffusion, in the gap located between the dirt particle and the solid surface. This could be a quick process if the surfaces are rough, or a long lasting one if the geometries are matching very well. This stage is generally known as soaking.

(a) stuck particle

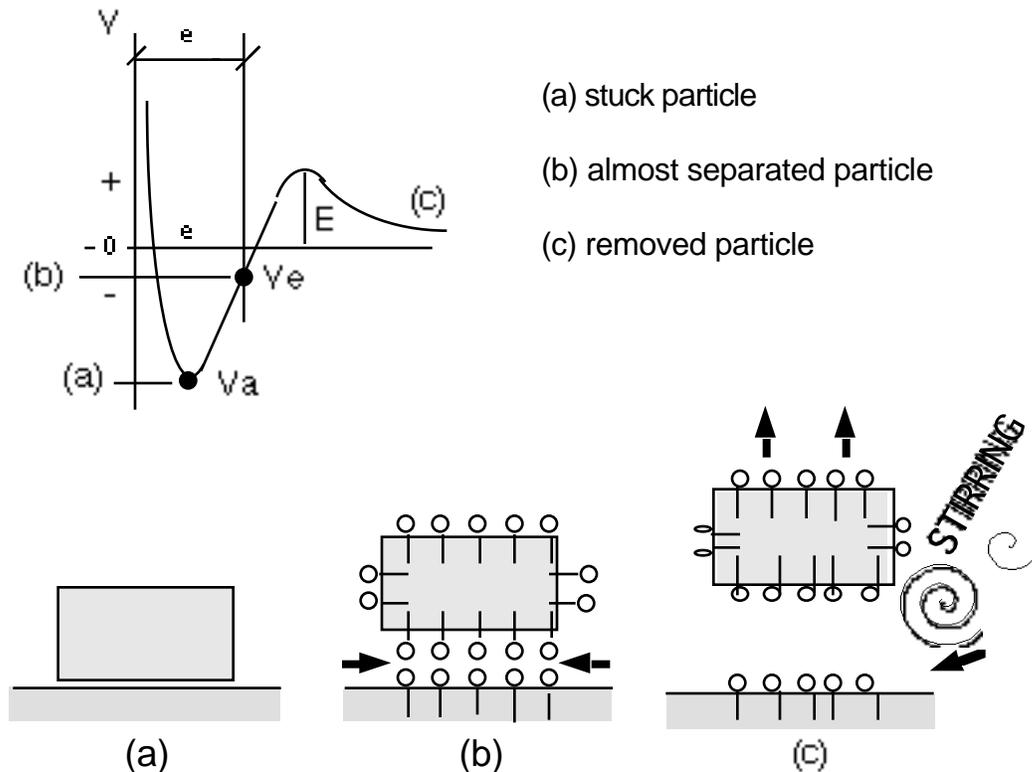(b) almost separated particle

(c) removed particle

Fig. 20: Adhesion Destabilization

The gap passes from a distance (a) without adsorbed surfactant to a distance (b) with the surfactant slightly pulling apart the two interfaces. Actually both (a) and (b) are very short distances, which are not very significant on the macroscopic scale. However the potential energy curve allows to pinpoint the difference. At distance (a) the attractive forces, i.e., Va, are extremely strong, actually too strong to be overcome by any mechanical stirring. When the surfactant molecules slightly open a gap to a distance e (b), the condition is completely different. In fig. 20 case, the attractive energy in (b), i.e., Ve, is very small, so that the mechanical stirring energy of the washing operation is enough to overcome it and to produce the removal of the dirt particle.

In some cases, the force at distance e can even be repulsive, i.e., the dirt can be removed by the sole soaking.

In any case it is important that the removed particle does not redeposit elsewhere, as will be discussed in the following section.

5.3. DISPERSION STABILIZATION.

The situation dealt with previously in the case of a dirt particle and a solid substrate applies as well for two dirt particles or two dispersed fragments of matter in the general case. It applies also to the removed dirt particle that may be likely to redeposit elsewhere on the solid surface. In all these cases the distance between one particle and the other particle (or the interface) is originally large, i.e., infinity in the reference frame of fig. 20. When the interfaces approach, the potential to be overcome is the energy barrier E, that is quite independent from the adhesion energy Va. Actually E can be enhanced by the presence of adsorbed substances, surfactants or polymers so-called colloid protectors, that result in one of the repulsion types discussed in section 3.2. In most cases the kinetic energy that animates the particles or droplets is the Brownian motion, or the sedimentation or Arquimedes pull, i.e., a low level energy that can be easily inhibited by a barrier in the 30 kT range.

Other mechanisms, so-called non-DLVO ones, can be combined, particularly if a high electrolyte content preclude the use of an electrostatic repulsion: steric repulsion with bulky head or tail groups, or entropic repulsion, or both.

If the energy barrier can not be set to a high enough value, the kinetic processes of film drainage can be slowed down through one of the following effects: electroviscosity and interfacial viscosity increase, as well as an increase in the bulk phase viscosity or a decrease in the fragment size.

Some substances such as lignosulfonates or carboxy methyl cellulose provide several effects at the same time and are used extensively, alone or combined with real surfactants.

5.4. OTHER PHENOMENA.

Some other phenomena can take place in the detergency processes, which are more or less important depending on the particular case.

The combination of a physico chemical effect and an efficient short scale stirring, such as ultrasonic vibration, can result in the emulsification of the dirt, an effective mechanism on some cleaning processes.

Microemulsification and extreme micellar solubilizations are too specific to be used in a laundry formulation process; however they can exhibit magic-like performances when they are fine tuned for a particular application. It is worth remarking that nowadays systems with solubilization exceeding 30 g of oil per g of surfactant are known, even with edible oils.

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