



CHAPTER II BACKGROUND AND LITERATURE REVIEW

2.1 Surfactant structures

A surfactant (a contraction of the term surface-active agent) is a substance that, when presents at a low concentration in a system, has the property of adsorbing onto the surface or interface of the system and modifying degree the surface or interfacial free energy of those surfaces or interfaces(Rosen,1988). Surfactants also have the property of forming colloid-sized aggregates in a solution called micelles at sufficient high concentrations. The lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).

Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for an organic solvent, called the lyophobic group (hydrophilic), together with a group that has strong attraction for an organic solvent, called the lyophilic group (hydrophobic), as shown in figure 2.1

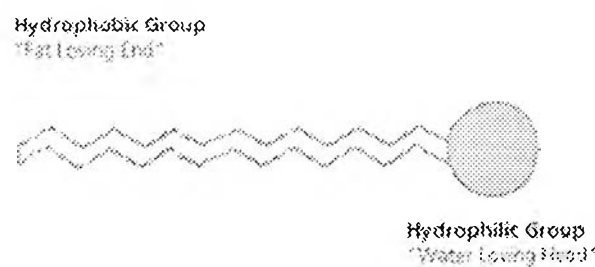


Figure 2.1 surfactant structure

The hydrophilic part may carry a positive or negative charge, giving rise to cationic or anionic surfactants, respectively, or may contain ethylene oxide chains or sugar or saccharide group, as in the case of nonionic surfactants. The hydrophobic part of the molecule is generally a hydrocarbon chain, but may contain aromatic groups (Goddard and Ananth, 1993). Depending on the nature of the hydrophilic group, surfactants are classified as:

1. *Anionic*. The surface-active portion of the molecule bears a negative charge, for example, $\text{RCOO}^- \text{Na}^+$ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkylbenzene sulfonate).
2. *Cationic*. The surface-active portion of the molecule bears a positive charge, for example, $\text{RNH}_3^+ \text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+ \text{Cl}^-$ (quaternary ammonium chloride).
3. *Zwitterionic*. Both positive and negative charge may be present in the surface-active portion, for example, $\text{RN}^+ \text{H}_2\text{CH}_2\text{COO}^-$ (long chain amino acid), $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{SO}_3^-$ (sulfobetaine).
4. *Nonionic*. The surface-active portion bears no apparent ionic charge, for example, $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$ (monoglyceride of long chain fatty acid), $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

2.1.1 Anionic Surfactant

Sodium dodecylsulphate (SDS): One of the most well-known anionic surfactant is sodium dodecylsulphate (SDS) that has a long chain alkylsulphate with a sulphate head group. The molecular shape of the bile salt exhibits a planar polarity due to spatial distribution of lateral groups in their steroid backbone. The bile salt structure results in smaller and more rigid aggregates than the micelles formed by conventional alkylsurfactants, providing highly non polar microenvironments with chiral properties. Indeed, the balance of hydrophobic and electrostatic forces in the polymer-surfactant interaction in moderate ionic strength has been shown to be sensitive to different surfactant structures being the hydrophobic component more relevant to bile salt aggregation. Sodium dodecylsulphate (SDS) is an excellent detergent (especially on particulate type soils), although it is sensitive to temperature, ionic strength, and water hardness. Figure 2.2 shows the chemical structure of SDS.

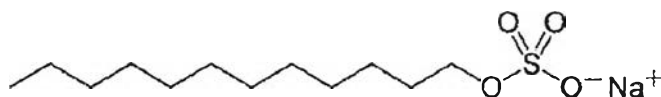


Figure 2.2 Structure of SDS

Gonzalez-Garcia *et al.* (2002) studied the free energy of the adsorption process of an ionic surfactant (SDS) from aqueous solutions onto a set of carbon black in the range of low concentrations. The results obtained in this study it can be concluded that the free energy of interaction between adsorbent and adsorbate through water results mainly from Lifshitz-van der Waals and electrostatic interactions, and its value showed a good correspondence with a combination of the model of van Oss *et al.* and the double-Langmuir equation.

2.1.2 Nonionic Surfactants

Triton® X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. It is related to the Pluronic range of detergents marketed. The pluronics are triblock copolymers of ethylene oxide and propylene oxide. The part formed from ethylene oxide is more hydrophilic than the part from propylene oxide. It is very viscous at room temperature and is thus easiest to use after being gently warmed. It is used in almost every type of liquid, paste, and powdered cleaning compound, ranging from heavy-duty industrial products to gentle detergents.

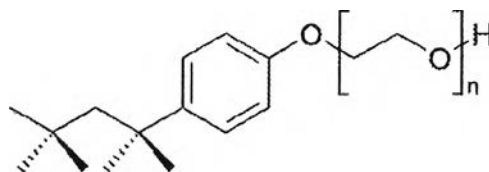


Figure 2.3 Structure of Triton X 100

Rodriguez-Cruz *et.al*, (2005) studied the influence of the different physicochemical and mineralogical properties of the soils on the adsorption of two surfactants (SDS and Triton X-100) with different structures to soils. The results obtained indicated the influence of the OM content on the adsorption of SDS and of the clay fraction content on that of Triton X-100. The mechanisms involved in surfactant adsorption were found to be different. SDS is adsorbed through hydrophobic interaction with the OM of the soil and by ligand exchange and/or electrostatic attraction with kaolinite. Triton X-100 is adsorbed by ion-dipole or hydrogen bonding of the oxygen atoms of the ethoxyl groups with the 2:1 clay minerals.

2.2 Surfactant Adsorption

The adsorption of surfactant at the solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface (2) the molecular structure of the surfactant being adsorbed (the adsorbate) (3) the environment of the aqueous phase such as pH, electrolyte content (Rosen 1989).

The adsorption isotherm for monoisomeric surfactant was first appeared in the work of Somasundaran and Fuerstenau in 1966. The schematic diagram of a typical adsorption isotherm for monoisomeric surfactant was illustrated in figure 2.4. The adsorption isotherm was divided into four distinct regions as follows:

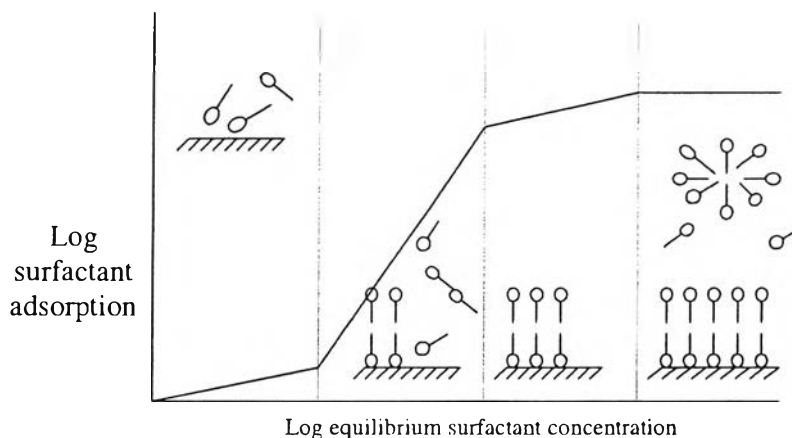


Figure 2.4 Adsorption isotherm of surfactant on an oppositely charged substrate

Region I is commonly referred to as the Henry's Law region because in this region monoisomeric surfactant isotherms are linear and have a slope of unity. In the this region, surfactant adsorption is the result of monomer interaction with the surface. There is little or no interaction between individual adsorbed surface ions.

Region II is characterized by a sharply increased isotherm slope relative to the slope in the Henry's Law region. This is a general indication of the onset of cooperative effect between adsorbed molecules. It is widely accepted that this cooperative consists of formation of micelle-like aggregates of adsorbed surfactants. These aggregates are frequently called admicelles or hemimicelles, depending on whether their morphology is viewed as local bilayers or local monolayers, and the transition point from Region I to Region II is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC). As the driving force for micelle formation is the tail-tail interactions in the micelles, so for admicelles and hemimicelles their formation is driven by hydrophobic interactions between tail groups.

Region III is characterized by a decrease in the isotherm slope relative to the slope in Region II, the change in slope may be abrupt, as shown in the schematic, or it may be gradual. An explanation for this change in the slope is that with increasing adsorption of surfactants, the surface becomes like-charged to the surfactant and the surface begins to repel the surfactant ions. However, this mechanism cannot be the explanation for the same isotherm shape for nonionic surfactant adsorption.

Region IV is the plateau adsorption region for surfactants. Generally, the Region III/Region IV transition occurs approximately at the CMC of surfactant, and reflects the effect of micelle formation on the chemical potential of surfactant monomer, just as the formation of micelle affects the variation of surface tension with surfactant concentration. In some systems, however the Region III/ Region IV transition can be reached when the surface becomes saturated with adsorbed surfactant. For the adsorption of surfactants from aqueous solutions, this will correspond to bilayer completion for ionic surfactants adsorbed on oppositely charged surfaces, or to monolayer completion for adsorption on hydrophobic surfaces.

2.2.1 Adsorption on Hydrophobic Surface

Obviously, the nature of solid surface plays a crucial role in the adsorption of surfactants at solid-liquid interface. However, in many reports studied, the nature of the surface was not defined. Broadly, adsorbents can be divided into two classes, hydrophilic (or polar) and hydrophobic (or nonpolar). Silicates, inorganic oxides and hydroxides, natural fibers and pertinacious materials have hydrophilic surfaces, whereas the surfaces of a number of carbonaceous materials and polymers are hydrophobic. This section will review the research work on surfactant adsorption studied onto hydrophobic surface, especially carbon black.

Gonzalez-Garcia *et al.* (2004) studied the adsorption enthalpies of SDS onto a set of carbon black at low concentrations. The surfactant was found to adsorb on the carbon surface exothermically in the whole studied conditions. From the calorimetric results and the analysis of the adsorption isotherms by using the double Langmuir equation, a model of the adsorption mechanism in these systems was proposed. The adsorption of surfactant onto the carbon black was explained by two energetically distinct steps corresponding to the adsorption of SDS in two different types of porosity. The first step corresponds to adsorption in the pores where the surfactant molecule experiences some enhanced potential, without a noticeable contribution from the surface chemical composition. The second step corresponds to adsorption in pores where this enhancement is no more efficient.

Rao and He (2005) studied the adsorption behavior of mixed surfactant: anionic surfactant (sodium dodecylbenzenesulfonate, SDBS) and nonionic surfactant (an alcohol ethoxylates with 12 carbons and 9 oxyethyl groups $A_{12}E_9$) mixtures from synthetic detergents on soils. The result showed that saturated adsorption amount of SDBS and $A_{12}E_9$ on soils decreased when $A_{12}E_9$ was added into the soil firstly compared with that secondly, possibly resulting from the screening of $A_{12}E_9$ to part adsorption sites on soils and the hydrocarbon chain-chain interactions between SDBS and $A_{12}E_9$. With the increase in pH in the mixed surfactant solution, the adsorption amounts of SDBS and $A_{12}E_9$ on the soils decreased. The reduction of ion strength in the soils resulted in the decrease in the adsorption amounts of SDBS more than that of $A_{12}E_9$ on the soils.

2.3 Wetting Phenomena

Wetting is the displacement of air from liquid or solid surface by water or an aqueous solution. Wetting can be examined by measuring the contact angle of a drop of surfactant solution sitting on the substrate surface. Complete wetting means that the contact angle between a liquid and solid is zero, or so close to zero that the liquid spread easily over the solid surface while non-wetting means that the angle is greater than 90° , so that the liquid tends to ball-up and run off the surface easily (Garbassi *et al.*, 1994). Wetting, especially wetting of solids by surfactant solutions, is a key phenomenon in many applications such as oil recovery, coating, painting, and detergency. Mostly, the addition of surfactants to water can enhance the ability of aqueous solution to wet and spread over solid surface. However, the presence of surfactant does not always enhance wettability; it depends on several parameters including molecular structure of the surfactant, and the nature of solid surface (Rosen, 1988).

Simoncic and Rozman (2007) investigated influence of structure and concentration of surfactants on the modification of wettability of cotton fabric. Two anionic surfactants: SDS and sodium dioctylsulfosuccinate (SDOSS) and a nonionic surfactant, Triton X-100 (TX100) were used. The results showed that the surfactant penetration rate into the studied fabric samples depended on the structure and concentration of the surfactant as well as the surface properties. All three surfactants, Triton X-100 causes the highest wetting power, followed by SDOSS and SDS. It is related to their chemical structure, where the branch hydrophobic group of TX100 causes much higher diffusion rate in a comparison with SDOSS and SDS, which contain straight hydrophobic alkyl chains. The results also showed that the surfactant adsorption onto cotton surface, which depended on attractive interactions between surfactants and cotton surface, known as the adhesion tension.

2.3.1 Contact angle

Contact angle is the angle between the solid surface and the tangent of liquid droplet. The measurement of contact angle is the most rapid and convenient way of characterizing surface properties such as wetting, hydrophobicity, and surface/interface tension. The contact angle Θ that the liquid makes when it is at equilibrium with the other phases in contact with it is related to the interfacial free energies per unit area of those phases. When the liquid is at equilibrium with the other two phases, gas and solid substrate, the diagram of the contact angle as shown in figure 2.5 (Rosen 1988).

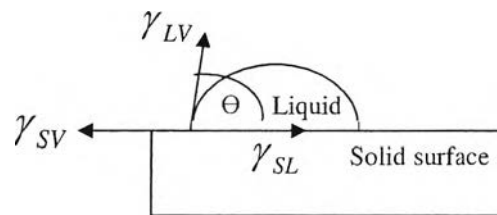


Figure 2.5 Contact angle

$$\gamma_{LV} \cos \Theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

Equation (1) is generally called *Young's equation* which the contact angle (Θ) is related to the interfacial free energies per unit area of the liquid-vapor (γ_{LV}), solid-vapor (γ_{SV}), and solid-liquid (γ_{SL}) interfaces.

Cippriano *et al.*, (2005) studied the surface tension and adsorption properties of hexadecyl imidazolium (Im BF_4) surfactant adsorbed on a clay surface. The results showed that the Im BF_4 surfactant adsorbed onto mica surface and produced a hydrophobic surface, similar to the behavior of cetyl trimethyl ammonium bromide (CTAB). However, the hydrophobic surface was formed at a lower concentration for the Im BF_4 surfactant than the CTAB surfactant. The surface tension data suggested that Im BF_4 was more surface active and less soluble than the CTAB.

2.4 Electrical Double Layer

At any interface, there is always an unequal distribution of electrical charges between the two phases. This unequal distribution causes one side of the interface to acquire a net charge of a particular sign and the other side to acquire a net charge of the opposite sign, giving rise to a potential across the interface and the so-called *electrical double layer*. A major problem for investigation has been the determination of the exact distribution of the neutralizing charges (counterions) in the solution surrounding a charged surface, since this distribution determines the rate at which the electrical potential will change with distance from the charged surface. Stern suggested the model, which divided the solution side of the double layer into two parts: (1) a layer of strongly held counterions, adsorbed close to the charged surface on fixed sites (to correct the basic defect of the Gouy-Chapman model), and (2) a diffuse layer of counterions similar to that of their model (figure 2.6 and 2.7) (Rosen 1988).

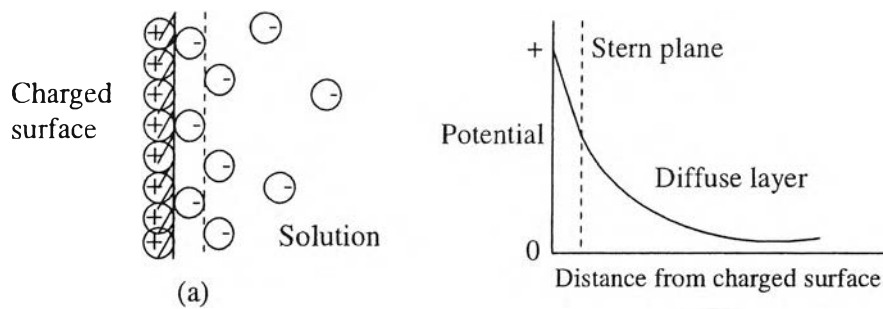


Figure 2.6 Stern model of the electrical double layer (a) Distribution counterions in the vicinity of the charged surface. (b) Variation of electrical potential with distance from the charged surface.

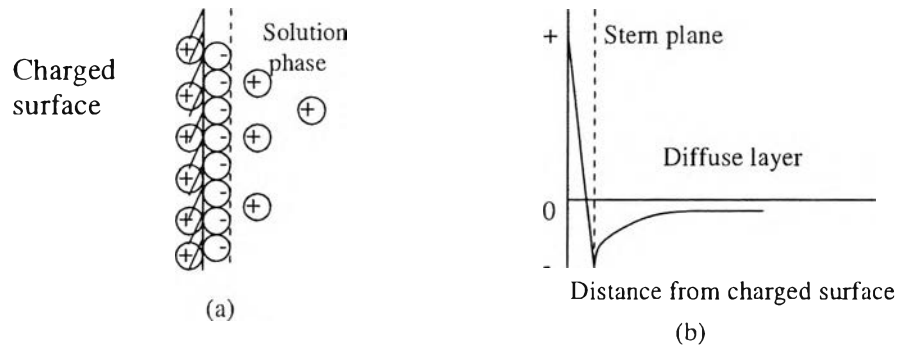


Figure 2.7 Stern model of the electrical double layer, showing reversal of the sign of the charged surface caused by adsorption of counterions in the Stern layer.

2.4.1 Zeta potential

A term often associated with the electrical double layer is the *zeta potential*, or electrokinetic potential. This is the potential of a charged particle as calculated from electrokinetic phenomena. It is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other.

Point of Zero Charge (PZC) is a pH of zero zeta potential and it is also called the isoelectric point (IEP). At a pH lower than PZC, the surface has positive charge resulting in the preferable adsorption of anionic surfactants while the adsorption of cationic surfactants occurs above the PZC.

Gallardo-Moreno *et al.*, (2004) carried out zeta potential measurements carbonaceous materials; carbon blacks and activated carbons in a SDS solution. Although both studied solids had different zeta potential when they were suspended in pure water, the relative change of zeta potential at the maximum surfactant adsorption for each solid was found to be proportional to the area amount adsorbed. These results indicated that the adsorption of anionic surfactant on the surface with the ionic head to be exposed to the solution.

Kaya and Yukselen, (2005) determined the zeta potential of kaolinite, montmorillonite, and quartz powder in the presence of alkali, alkaline earth, hydrolysable metal ions with anionic, cationic and nonanionic surfactants in a

systematic manner. The results indicated that the anionic surfactant was found to produce negative zeta potentials. The cationic and nonionic surfactants produce both positive and negative zeta potentials depending on soil type and ion present in the system. The zeta potential of kaolinite and quartz powder with surfactants showed similar trends; however, the absolute magnitude of the zeta potential of quartz powder is higher than that of kaolinite.

2.5 Types of Soils

Soils can be defined as unwanted substances that cause a garment or fabric unclean. Soils, in general, are either colorless or colored also water soluble or insoluble in water. Soils can be divided into three categories as follows:

2.5.1 Oily and Greasy soils

Oily soils mean soil only composed of nonpolar hydrocarbons such as diesel and motor oils. These materials are usually liquid and highly hydrophobic, and which means that they do not mix with water. However, these oils are very soluble in many organic solvents and particularly in halogenated hydrocarbons. They are quite easily removed by dry cleaning. Greasy soils mainly refer to triglycerides and their derivatives: mono- and diglycerides, fatty acid. They are more polar but not polar enough to be dissolved by water.

2.5.4 Proteins and Starchy Soils

Protein and starch are polymeric materials that can resist conventional cleaning. They act as glue for other soils, making cleaning more difficult. A typical example is macaroni and cheese. These soils are effectively removed by enzymatic cleaning. Proteolytic and amylolytic enzymes are currently used for this purpose in modern automatic laundry detergents.

2.5.3 Particulate Soils

Solid particles such as clay, alumina, silica, iron, and other metal oxides are present in particulate soils, deposited mostly from air suspensions (dust). They are soluble neither in water nor in inorganic solvents. They usually exhibit a

large surface area, on which the oils and greases adsorb very strongly. Particulate soils contribute significantly to the difficulty of removing oily and greasy soils because they contribute to their rigidification and, sometimes, they act as catalyst in the oxidation/crosslinking of unsaturated triglycerides. Since they are not water soluble, the particulate soils can be redeposited on the surfaces that have been cleaned. It is accordingly important to keep such soils effectively dispersed in the washing liquid (Lang, 1994).

2.6 Carbon Black

Any of a group of intensely black, finely divided forms of amorphous carbon, usually obtained as soot from partial combustion of hydrocarbons, used principally as reinforcing agents in automobile tires and other rubber products but also as extremely black pigments of high hiding power in printing ink, paint, and carbon paper. The arrangement of carbon atoms in carbon black has been well established by x-ray diffraction method. Carbon black can have a degenerated graphitic crystalline structure. Figure 2.10 shows the three dimensional order of graphite as compared to the two dimensional order of carbon black. From the x-ray data, carbon black consists of well-developed graphite structure platelet roughly parallel to one another but random in orientation with respect to adjacent layers.

2.7 Mechanisms of Particulate Soils Removal

Particulate soils almost always occur with other soils such as oily and greasy soils. The particulate soils contribute to the toughness of the soil deposit, and the grease acts as cement, binding the particle together. The first step, just after wetting, is to attack the oily-greasy component. The particulate soils are then made available. The best way to clean particulate soils is to use a surfactant that adsorb efficiently at the water-solid particle interface, to reduce the interfacial tension and, accordingly, to reduce the adhesion forces binding the particle together. This can be achieved with an anionic surfactant, in which case the surface of solid particles is made more negative and electrostatic repulsion can occur between adjacent particles.

Since particulate soils are not water soluble, they have a tendency to redeposit in the later stages of the washing operation.

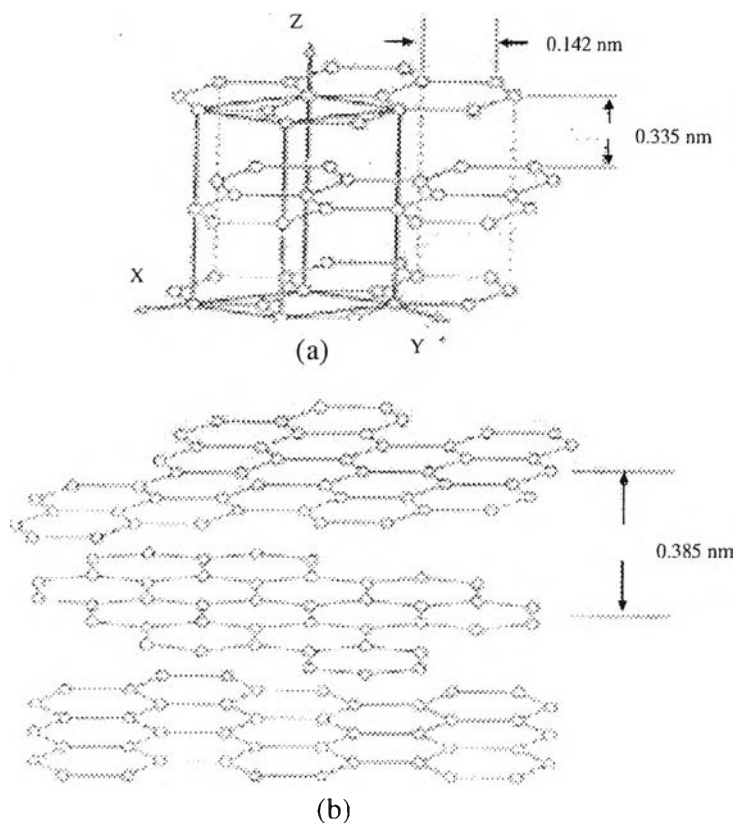


Figure 2.8 Atomic structure models of (a) graphite, and (b) carbon black (Baker et al., 1992)

Roosmalen *et al.*, (2003) studied particulate soil removal in dry-cleaning with high-pressure carbon dioxide by using surfactants. Various anionic and amine based surfactants were investigated to enhance the removal of particulate soils in dry-cleaning with high-pressure CO₂. The results showed that the addition of anionic surfactant has a distinct positive influence on the removal of particulate soil, especially when using dodecyl sulfate sodium salt (DSS). However, when the anionic surfactant was used, the addition of a co-solvent gave a pronounced negative effect on the particulate soil removal. In the case of the amines, the secondary amine was the most suitable amine for the particulate soil removal when no co-solvent was used.

2.8 Soil Redeposition

Once the soil has been detached from the substrate, it is either “solubilized” inside the micells or dispersed as a suspension in the washing liquid. Both emulsion and dispersions of solids are not stable, and they often redeposit on the cleaned items or on parts of washing machine. The redeposition can be assessed by measuring the loss of reflectance (whiteness) of white fabrics after several cumulative washes with soiled items.

There are two basic ways to stabilize the dispersion in an aqueous liquid and to prevent (or delay) redeposition: electrostatic repulsion and steric stabilization.

2.8.1 Electrostatic Repulsion

If the particles are electrically charged, electrostatic repulsion can create an energy barrier to flocculation/coagulation, represented by ΔE as shown in Fig. 2.9. Electrostatic repulsion drops with the square of distance. Its magnitude depends on the amount of charged on each particle, the dielectric constant of the solvent, and the ionic strength. If the latter is low, the distance at which the electrostatic repulsion is perceived (Debye length) is relative long (on the order of 1 μm in water); if the water contains an electrolyte (>0.01 mole, as NaCl), the Debye length is reduced, as well as the energy barrier ΔE . It is not a good idea to rely on electrostatic repulsion to prevent redeposition because ionic strength is not a good parameter under our control. Stains can include a significant amount of electrolytes, and builders, contained in most detergents, are electrolytes.

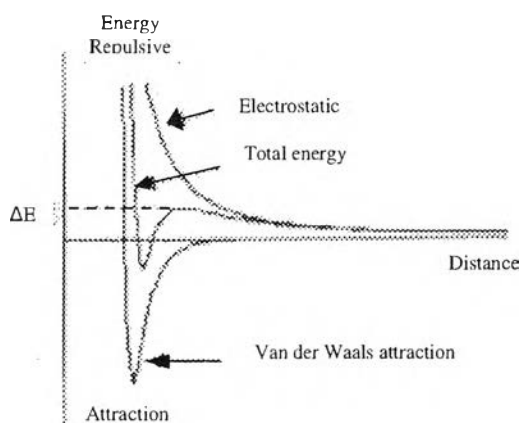


Figure 2.9 Energy profile in the presence of electrostatic repulsion. (Jacobi, 1987)

2.8.2 Steric stabilization

Steric stabilization offers a better potential for the control of redeposition. The principle is to deposit a large molecule (a surfactant or a polymer) on the surface of the particle or of the substrate to be protected from redeposition.

Figure 2.10 illustrates the adsorption of polymeric material on a solid particle. Some polymer segments called *trains* stick to the surface (thanks to van der Waals or electrostatic interactions), and other segments called *loops* interact with water. The *tails* of the molecule usually interact with water. This process is dynamic: the trains can desorb and the loops can adsorb.

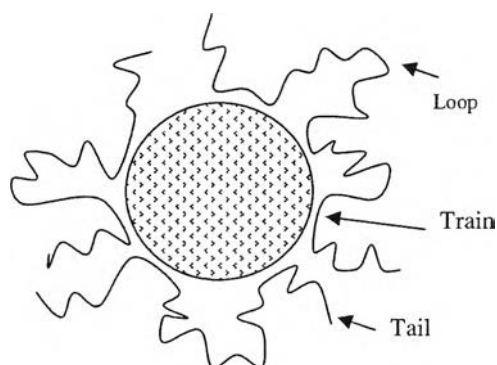


Figure 2.10 Polymer adsorbed on a solid particle (Lang, 1994)

The antiredeposition agent must exhibit the right balance between water solubility and adsorption efficacy. If the water solubility is too high, the proportion of loops is too high and the adsorption is not efficient; on the other hand, if water

solubility is too low, there are almost no loops and the molecule is deposited as a thin layer on the surface of the particle.

The result of the expansion of the loops in the water phase is an increase of the effective volume of the particle. If two particles come together, the loops of their adsorbed polymers begin to interact. In the interaction volume, the polymer concentration becomes too high, resulting in an osmotic pressure (water molecules want to enter the interaction volume and pull the particles apart). There is also an entropic effect: compression significantly reduces the configurational entropy of the polymer. The net result is illustrated in Fig. 2.11. At a distance significantly longer than the onset of van der Waals attraction, a new energy barrier, corresponding to the compression of polymer loops, develops to prevent flocculation.

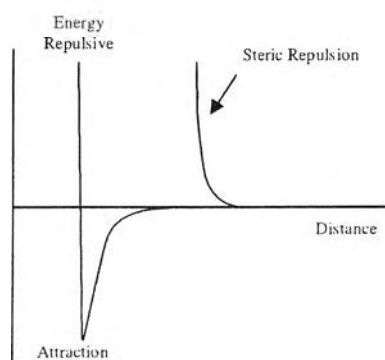


Figure 2.11 Energy profile in the presence of steric repulsion. (Lang, 1994)

The control of redeposition is significantly more complex than this theoretical approach would lead one to believe. The adsorption efficacy depends on the nature of the surfaces, on the composition of the water phase, on temperature, and so on. The use of polymer adsorption for suspension stabilization is very delicate. Particularly when too small an amount of a high molecular weight polymer is used, interparticle bridging can occur, speeding up the flocculation. To prevent redeposition on cotton fabrics, carboxymethylcellulose appears to be the most efficient material. On polyester fibers, hydroxyethyl- or hydroxypropylcellulose gives better results.