



CHAPTER II

LITERATURE REVIEW

2.1 Surfactants Characteristics

A surface-active agent, surfactant, is a substance that can adsorb onto the surfaces or interfaces of the system, which can be occurred in liquid-liquid phase, gas-liquid phase and liquid-solid phase, and reduce a marked degree the surface or interfacial free energies of those surfaces or interfaces even the concentration of system is low. Due to the remarkable properties of surfactants to affect the properties of interfaces, surfactants are widely studied and for various applications such as detergents, the drilling muds, pharmaceuticals and flotation agents. At sufficient high concentration, surfactant is able to form the colloid-sized aggregates, called micelle, in solution. The lowest surfactant concentration at which the first micelle occurs, called the critical micelle concentration (CMC) (Rosen, 2004).

A characteristic molecular structure of surfactants, called an amphipathic structure, consists of a lyophobic group (hydrophilic), which has very strong attraction for the water, together with a lyophilic group (hydrophobic), has strong attraction for the organic solvents. The amphipathic structure of the surfactant shows the orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it, in additions, this structure can reduce the surface tension between liquid and air phases.

Surfactants are divided into four groups according to the charged of their head group as:

- Anionic surfactant: The surface-active portion bears a negative charge e.g. amine salts, sodium and potassium salts of coconut oil fatty acids.
- Cationic surfactant: The surface-active portion of the molecule bears a positive charge e.g. acylated diamines and polyamines and their salts.
- Nonionic surfactant: The surface-active portion bears no apparent ionic charge e.g. sulfated polyoxyethylenated (POE) alkylphenols and alkylphenol ethoxylates.

- Zwitterionic surfactant: Both positive and negative charges may be present in the surface-active portion e.g. imidazoline carboxylates.

2.2 Surfactants Adsorption at the Solid/Liquid Interface

Adsorption of surfactants at the solid/liquid interface is basic phenomenon in industry and agriculture, e.g. to control stability and floatability, detergency and the surface treatment of fibers, removal of trace amounts of surfactants from waste water and boundary lubrication of metal to concentrate valuable ores. Behavior of surfactants is different on hydrophobic surfaces (e.g. Teflon) compared to hydrophilic surfaces (e.g. metal oxides).

The surfactants adsorption at the solid/liquid interface was related to chemical potential (Huang *et al.*,1996), consequently, it depended on these parameters (Rosen, 2004):

- The structural groups on the solid surface (the adsorbent).
- The structure of the surfactant being adsorbed (the adsorbate).
- The condition of the aqueous phase, for example; pH, electrolyte content, additives and temperature.

2.2.1 Mechanisms of Surfactant Adsorption

Rosen (2004) divided the mechanisms of surfactant adsorption onto solid surfaces as shown below:

- Ion exchange: The replacement of counterions adsorbs onto the surface from the solution by similarly charged surfactants.
- Ion pairing: The ions of surfactant solution are adsorbed onto the oppositely charged sites unoccupied by counterions.
- Acid-Base interaction: The adsorption process occurs by hydrogen bond producing between the surface and adsorbate.
- Adsorption by polarization of π electrons: The adsorption forms the attraction between electron-rich aromatic nuclei of adsorbate and positive sites on the adsorbent.

- Adsorption by dispersion force: This mechanism is done by London-van der Waals dispersion forces acting between adsorbent and adsorbate molecules, and generally increases with the increasing molecular weight of the adsorbate.
- Hydrophobic bonding: The attraction occurs between a hydrophobic group of adsorbed molecule and a molecule present in the solution.

2.2.2 Adsorption Isotherm

Results from adsorption experiments are usually expressed in the form of adsorption isotherm, which is plotting of the amount of surfactant adsorbed per unit mass or unit area of the solid adsorbent versus the equilibrium concentration of the adsorbate. This isotherm correlates the concentration of adsorbate at the interface to the equilibrium concentration in the liquid phase (Rosen, 2004), for describing the adsorption at the solid/liquid interface or the extent of the solid surface that is covered by the adsorbate molecules at the given condition (Paria and Khilar, 2004).

2.2.3 Adsorption on Hydrophobic Surface

Gupta *et al.* (2005) studied the adsorption behavior of anionic, cationic and nonionic surfactants at the solid-liquid interface. From the anionic surfactant adsorption isotherm, the adsorption attained for sodium dodecylbenzene sulfonate (SDBS) solution was higher than that of sodium dodecyl sulfate (SDS) solution which was ascribed to the greater CMC/C_{20} value (the higher CMC/C_{20} denoted the adsorption was facile more than micellization.). Furthermore, carbon black possessed a large number of π electrons; it offered aromatic properties to carbon black. The aromatic ring of SDBS attached itself to the surface of carbon black thus resulting in higher adsorption of SDBS in comparison to SDS which did not contain an aromatic ring. For cationic surfactants, their maximum adsorption value was higher than both of the nonionic and anionic surfactants (except SDBS) since carbon black surface had negative charge which was confirmed by measuring the zeta potential. For nonionic surfactants, their alkyl chain attached to carbon black surface and ethylene oxide (EO) chain extended into aqueous phase in order to

provide the steric stabilization to carbon black particles. Thus, the amounts of surfactant adsorbed and the stability of dispersion increased in the order: nonylphenol ethoxylates (NP) 40 EO < NP20 < 4-octylphenol polyethoxylate (Triton X-100) as the number of EO units (hydrophilic) decreased.

Soria-Sánchez *et al.* (2010) clarified the adsorption behavior of a series of nonionic surfactants (Triton X-114, Triton X-100, Triton X-165 and Triton X-305, where the ethoxylation degree was increasing in the series) on carbon materials (non-microporous graphite surface and mainly microporous activated carbon). At maximum adsorption, similar trends were observed for all adsorbents. An increasing of the oxyethylene length caused a decreasing in the adsorbed amounts. In the case of surface area, the adsorbed amounts of surfactants molecules on graphite were higher than on activated carbon, which was attributed to the inaccessibility of micelles to smaller micropores of the activated carbon.

2.2.3.1 Modification of the Bundles of Nanotubes to Individual Carbon Nanotube

Most carbon nanotubes (CNTs) are naturally found in bundles or ropes through van der Waals force, which is able to attract each of CNTs into the clusters. These bundles change both the mechanical and electrical properties, namely the one-dimensionality character of the bundles is lower than the isolated CNTs. The alteration of one-dimensionality character effects to study the unique properties of CNTs in order to achieve a desired product, thus, debundling of CNTs are necessary condition. The main approaches of unbundles CNTs can be divided into three groups (Tasis *et al.*, 2004):

- The covalent attachment of chemical groups onto π -conjugated structure of CNTs, such as sidewall halogenation of CNTs (Mickelson *et al.*, 1998 and Peng *et al.*, 2003), hydrogenation (Pekker *et al.*, 2001), cycloadditions (Chen *et al.*, 1998 and Holzinger *et al.*, 2001), radical additions (Khare *et al.*, 2004), electrophilic additions (Tagmatarchis *et al.*, 2002), additions of inorganic compounds (Nunzi *et al.*, 2004), ozonolysis (Banerjee and Wong, 2004), mechanical functionalizations (Barthos *et al.*, 2005), plasma activation (Chen *et al.*, 2001), nucleophilic additions (Chen *et al.*, 2005) and grafting of polymers (Qin *et al.*, 2004 and Zhu *et al.*, 2004).

- The non-covalent adsorption of various molecules onto the MWCNTs surface, such as polymer composites (Tang and Xu, 1999 and Sabba and Thomas, 2004), interactions with biomolecules and cells (Keren *et al.*, 2003) and surfactants (O'Connell *et al.*, 2002).

- The endohedral filling of their inner empty cavity, such as encapsulation of fullerene derivatives and inorganic species (Sloan *et al.*, 2000), encapsulation of biomolecules (Davis *et al.*, 1998) and encapsulation of liquids (Werder *et al.*, 2001).

Among the modification methods, the non-covalent adsorption is particularly attractive, since the adsorbed molecules do not change the chemical and electrical properties of CNTs. Therefore, the CNTs structures are maintained after the modification. Especially, a wide variety of surfactants (anionic, cationic, nonionic) as the adsorbed molecules is kept an eye from many scientists due to its low cost, simple experimental procedure and commercial availability e.g. hexadecyltrimethyl ammonium bromide (CTAB) (Bai *et al.*, 2011), sodium dodecyl sulphate (SDS) (Islam *et al.*, 2003), sodium dodecylbenzene sulfonate (SDBS, NaDDBS) (Bystrzejewski *et al.*, 2010 and Tan *et al.*, 2008), Tween 20 and Tween 80 (Rastogi *et al.*, 2008) and Triton X-series (Bai *et al.*, 2010). The mechanism of surfactant adsorption on MWCNTs is the hydrophobic tail of surfactants interacted with the CNTs surface through van der Waals forces (π - π stacking) or hydrophobic interaction, while the hydrophilic head groups are oriented toward the aqueous phase.

Islam *et al.* (2003) reported that SDS surfactant did not have benzene ring to interact with the graphic structure of CNTs. Thus, SDS showed a lower adsorption than SDBS (both have a 12-carbon alkyl chain). Moreover, SDBS had the higher adsorption compared to Triton X-100, the head group of Triton X-100 was polar and larger than that of SDBS which made the lower packing density. In terms of chain interaction, SDBS had a longer alkyl chain (12 carbons) to lie flat on the graphitic structure of SWCNTs than Triton X-100, that is, the longer chain length could improve surfactant energetically. They also speculated that the tubes were stabilized by hemimicelles as depicted in Figure 2.1. From Figure 2.1, the alkyl chains of a surfactant molecule adsorb flat along the length of tube instead of the diameter.

tail length and benzene ring factor. However, the presence of benzene ring in the tail group of Triton X-100, had the shortest chain length of the four, exhibited the higher dispersion power in comparison to Tween 80 which had the greater hydrocarbon tail length and none the aromatic ring, they concluded that the benzene ring factor enjoyed reigning status compared to the tail length factor.

Bai *et al.* (2010) investigated the adsorption of a series of surfactants with a same hydrophobic functional group but different hydrophilic polyethoxyl chain lengths on MWCNTs and the dispersion of MWCNTs in aqueous phase. They found that the capacity of surfactant adsorption increased with decreasing hydrophilic chain length follow the trend: Triton X-114 > Triton X-110 > Triton X-165 > Triton X-305. It was ascribed to the hydrophobic and π - π interactions between the MWCNTs and surfactants. Furthermore, the stabilization of MWCNTs in water could be enhanced by surfactant adsorption and decreased with the increasing hydrophilic fraction ratio of the X-series surfactants.

Tan *et al.* (2008) elucidated the adsorption of anionic surfactant (SDBS) and nickel on MWCNTs which the adsorption mechanism depended on chemical interaction. Π -Stacking interactions of the aromatic rings on the graphitic structure were able to enhance the capacity of surfactant adsorption as well as of other highly benzene molecules.

Yu *et al.* (2007) studied the sonication-driven dispersion process of MWCNTs in aqueous SDS (sodium dodecyl sulfate) solution. The UV-vis absorbance of the dispersion showed that the increasing sonication time resulted in an increasing area below the absorbance which implied to the increasing amount of dispersed MWCNTs. They expected that the bundle ends of MWCNTs were frayed by the high local shear during the sonication process. Besides, it was able to overcome the van der Waals forces in the MWCNTs agglomerates. This became the space for SDS adsorption which can prevent the reaggregation of MWCNTs by electrostatic repulsion.

Matarredona *et al.* (2003) investigated the interactions of SDBS with single-walled carbon nanotubes (SWCNT) by varying the surfactant concentration, pH and sonication time, and also developed a simple-model for the SWCNT - SDBS interaction. The adsorption isotherms of SDBS on SWCNT

indicated that the interaction between the surfactants and the SWCNT was mostly hydrophobic in natural condition, and the Coulombic forces of attraction or repulsion became a central role only at pH values far from the point of zero charge (pH_{pzc}). Their expected model was a monolayer of adsorbed surfactant in which the headgroups of SDBS directed outward to the aqueous solution while the tails remained in contact with the surfaces of SWCNT as illustrated in Figure 2.2. Furthermore, they also found that the concentration of added surfactant and sonication time were the key factors in the dispersion of SWCNT due to the fact that the increasing feed concentration of SDBS or time of sonication resulted in the higher amount of suspended SWCNT.

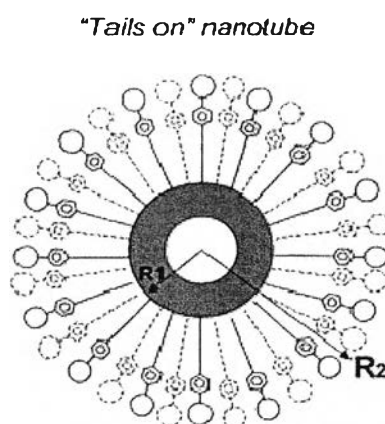


Figure 2.2 Model for the surfactant-nanotube interaction (Matarredona *et al.*, 2003).

Geng *et al.* (2008) studied the effects of surfactant treatment of MWCNTs on the thermo mechanical, mechanical and electrical properties of MWCNTs – epoxy nanocomposites. A non-ionic surfactant, $\text{OP}(\text{EO})_{10}$ was successfully used to improve the dispersion of MWCNTs, as given in Figure 2.3 which showed the $\text{OP}(\text{EO})_{10}$ molecule and micelle, and the corresponding interactions with MWCNTs. The alkyl chain length (red color) acts as the hydrophobic group, while the other side is the hydrophilic section (Figure 2.3 a). At CMC, the interface between the MWCNTs surface and surfactant solution becomes saturated (Figure 2.3 b), and above the CMC the $\text{OP}(\text{EO})_{10}$ molecules begin to form micelles (Figure 2.3 c). Since, at very high surfactant concentration, the larger the

micelle size, the stronger the steric repulsion induced by micelles, it was effectively able to disentangle the MWCNTs agglomerates (Figure 2.3 d).

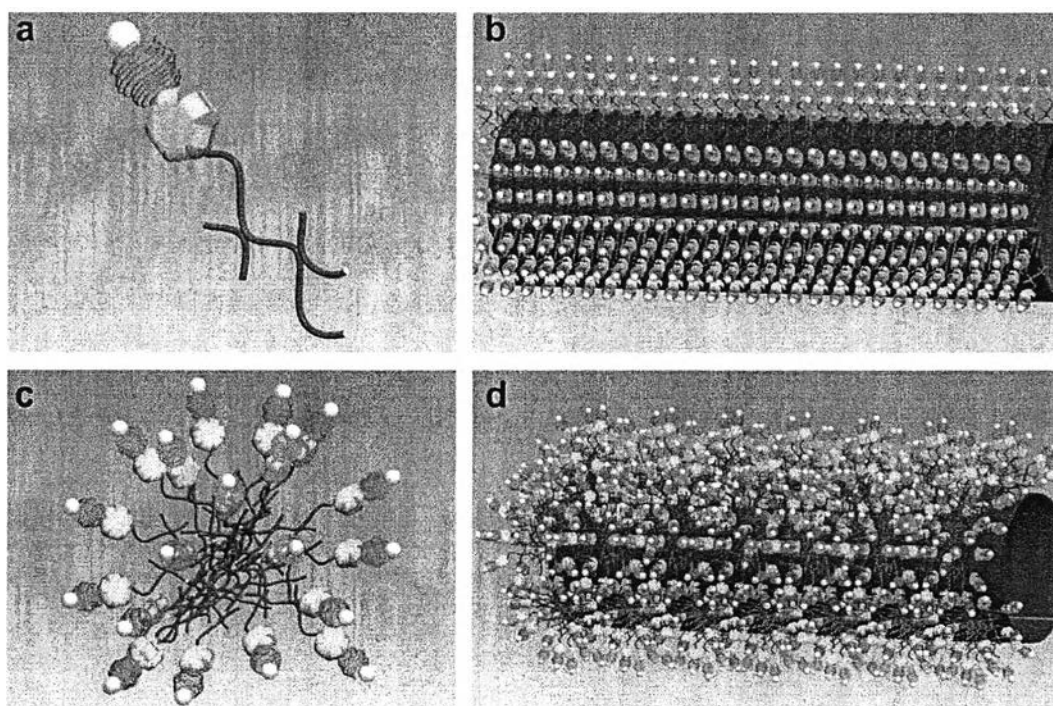


Figure 2.3 Schematics of (a) single OP(EO)₁₀ molecule; (b) a MWCNT wrapped by OP(EO)₁₀ molecules (1 CMC); (c) a OP(EO)₁₀ micelle; (d) a MWCNT wrapped by OP(EO)₁₀ micelles (10 CMC) (Geng *et al.*, 2008).

2.3.4 Point of Zero Charge

Point of zero charge or pH_{pzc} is the pH at which that surface has a net neutral charge. Surface will have positive charge at solution pH values less than the pH_{pzc} and thus be a surface on which anions may adsorb. On the other hand, that surface will have negative charge at solution pH values greater than the pH_{pzc} and thus be a surface on which cations may adsorb.

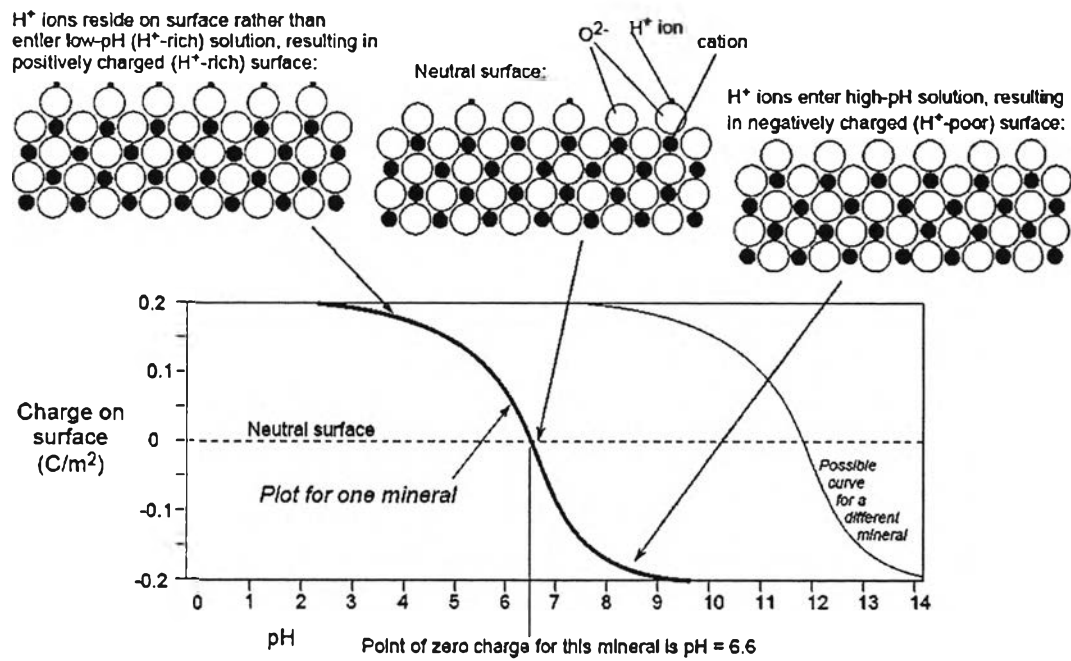


Figure 2.4 An explanation of point of zero charge of one mineral (Railsback, 2006).