



CHAPTER II

BACKGROUND AND RELATED RESEARCH WORKS

2.1 The Nature of Surfactants

A surfactant or surface active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surface or interfaces of the system and altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces (Rosen, 1989). It is a polar compound consisting of an amphiphilic molecule, i.e. a molecule with a hydrophilic head attached to a long hydrophobic tail (Kouloheris, 1989). At a particular concentration (known as the critical micelle concentration, CMC) surfactant molecules become more favorable to form aggregates called micelles as shown in Figure 2.1. A surfactant can be placed in one of four classes, depending on what charge is present in the chain-carrying portion of the molecule after dissociation in aqueous solution: anionic, cationic, nonionic, and amphoteric surfactants (Jakobi and Lohr, 1987).

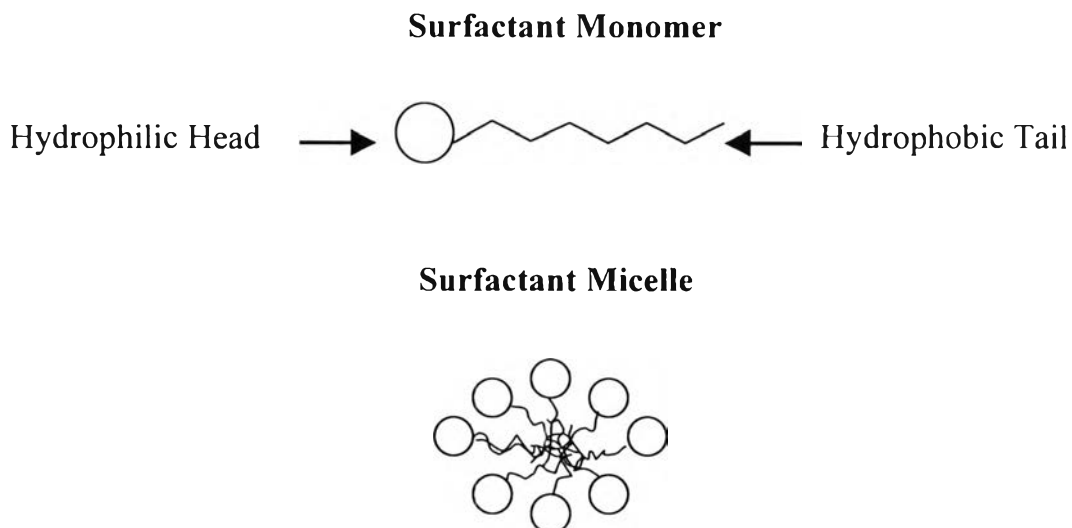


Figure 2.1 Surfactant Molecule/Ion, and a Representation of a Surfactant Micelle in a Surfactant Solution Somewhat above the Critical Micelle Concentration (adapted from Wilson and Clarke, 1994)

2.2 Surface Tension, Wetting, and Dispersion

A molecule within the body of a liquid or solid is acted upon equally by the molecular attractions of surrounding molecules. Surface tension or (excess surface free energy) arises from unequal interaction forces in the vertical direction, between molecules in the surface region and their neighbors. As shown in Figure 2.2, the number of nearest neighbors decreases in the surface. The result is molecular cohesion and orientation. This behavior is called surface tension and is responsible for the resistance of a liquid or solid to surface penetration (Kouloheris, 1989).

The wetting of solids is very important for certain processes. The ability of a liquid reagent to readily wet and react with a solid particle is related to the surface tension of both the liquid and the solid material. Wetting will take place only if

$$\gamma_{sv} > (\gamma_{lv} + \gamma_{sl}) \quad (2.1)$$

Where: γ_{sv} = surface tension of the solid under its vapor

γ_{lv} = surface tension of the liquid in equilibrium with its vapor

γ_{sl} = surface tension of the solid-liquid interface

A surfactant's ability to change the surface tension of a solid-liquid system can be used effectively in dispersion. The work of dispersion, W_d , is given by

$$W_d = -6 \gamma_{lv} \cos \theta \quad (2.2)$$

Where: γ_{lv} = surface tension of the liquid in equilibrium with its vapor

θ = contact angle of the liquid on the solid surface.

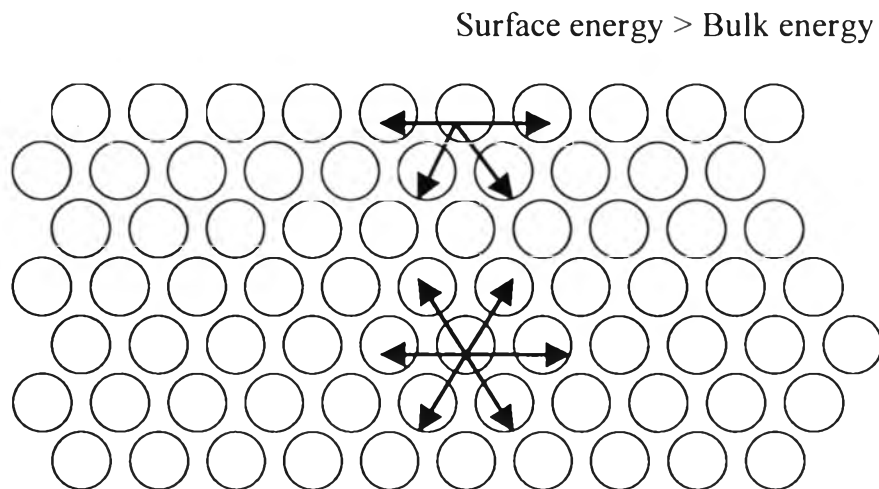


Figure 2.2 Forces on Molecules in Bulk and at Interface

2.3 Roll-back (Roll-up) Mechanism

Removal of liquid (oily) soil by aqueous solution is accomplished mainly by a roll-back or roll-up mechanism in which the contact angle that the liquid soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath (Rosen, 1989).

In the laundering process, the mechanism of soil removal from cloth fibre depends on whether the soil type is solid or liquid. Therefore, it seems reasonable to suppose that the mechanism of ink removal is dependent on the ink type. The shape of a liquid droplet or film can change during soil removal, permitting the surfactant to occupy the vacated space. Ink roll-back can occur in the deinking process since the aqueous surfactant solution preferentially wets the ink film on the polymer surface. As a result, the film rolls back to form droplets. Figure 2.3 is an illustration of how 100% ink removal occurs. In reality, however, some ink may be left behind. Such marginal roll-back has been proposed to occur in the laundering of liquid soils.

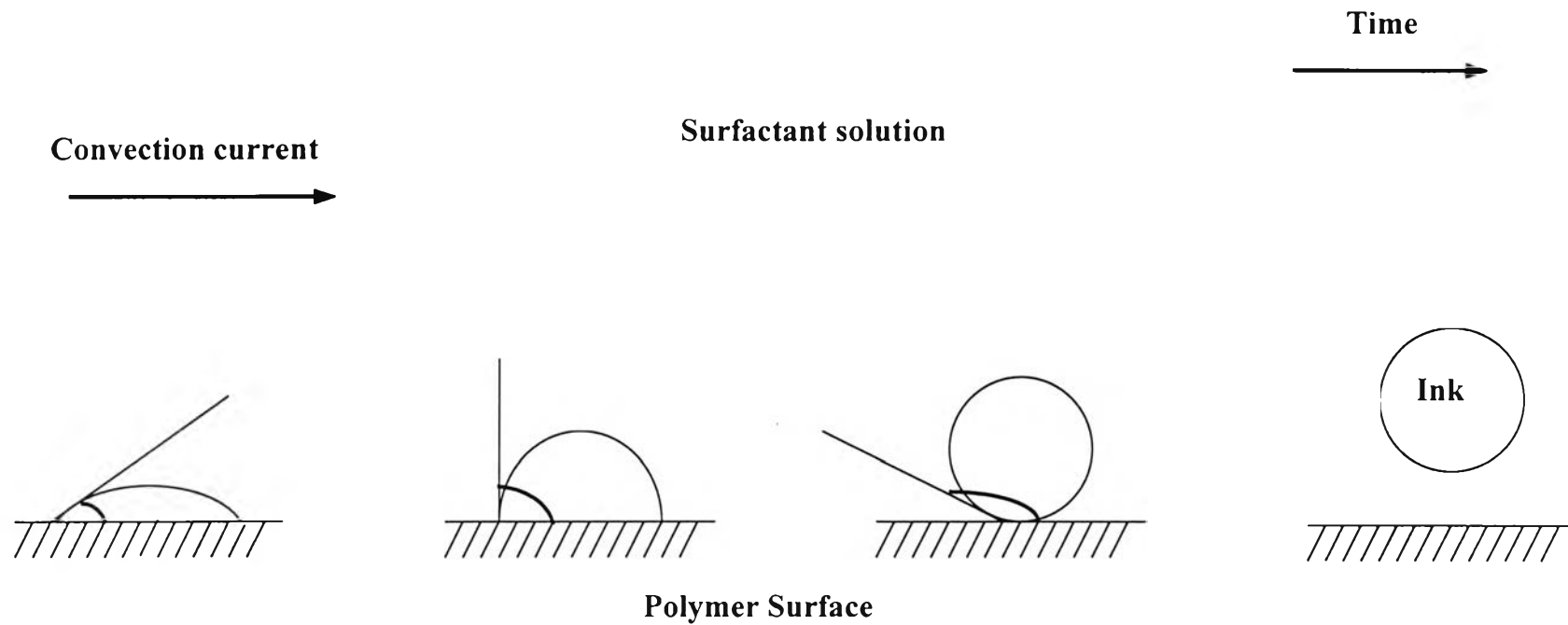


Figure 2.3 Detachment of Ink from A Polymer Surface by the Roll-up Mechanism (adapted from Borchardt, 1994)

2.4 Solubilization

If the deinking surfactant is above its CMC, ink solubilization can occur by the process illustrated in Figure 2.4.

Solubilization consists of the following steps:

- (1) Diffusion of surfactant micelles to the ink surface
- (2) Adsorption of the micelle at the ink/water interface
- (3) The ink species mix with the surfactant molecules
- (4) The micelle desorbs from the surface with ink in the interior of the micelle
- (5) The micelle diffuses into the bulk of the solution.

Step (1) and step (5) can be promoted by hydrodynamic flow of the aqueous phase during deinking, i.e. by agitation of the mixture.

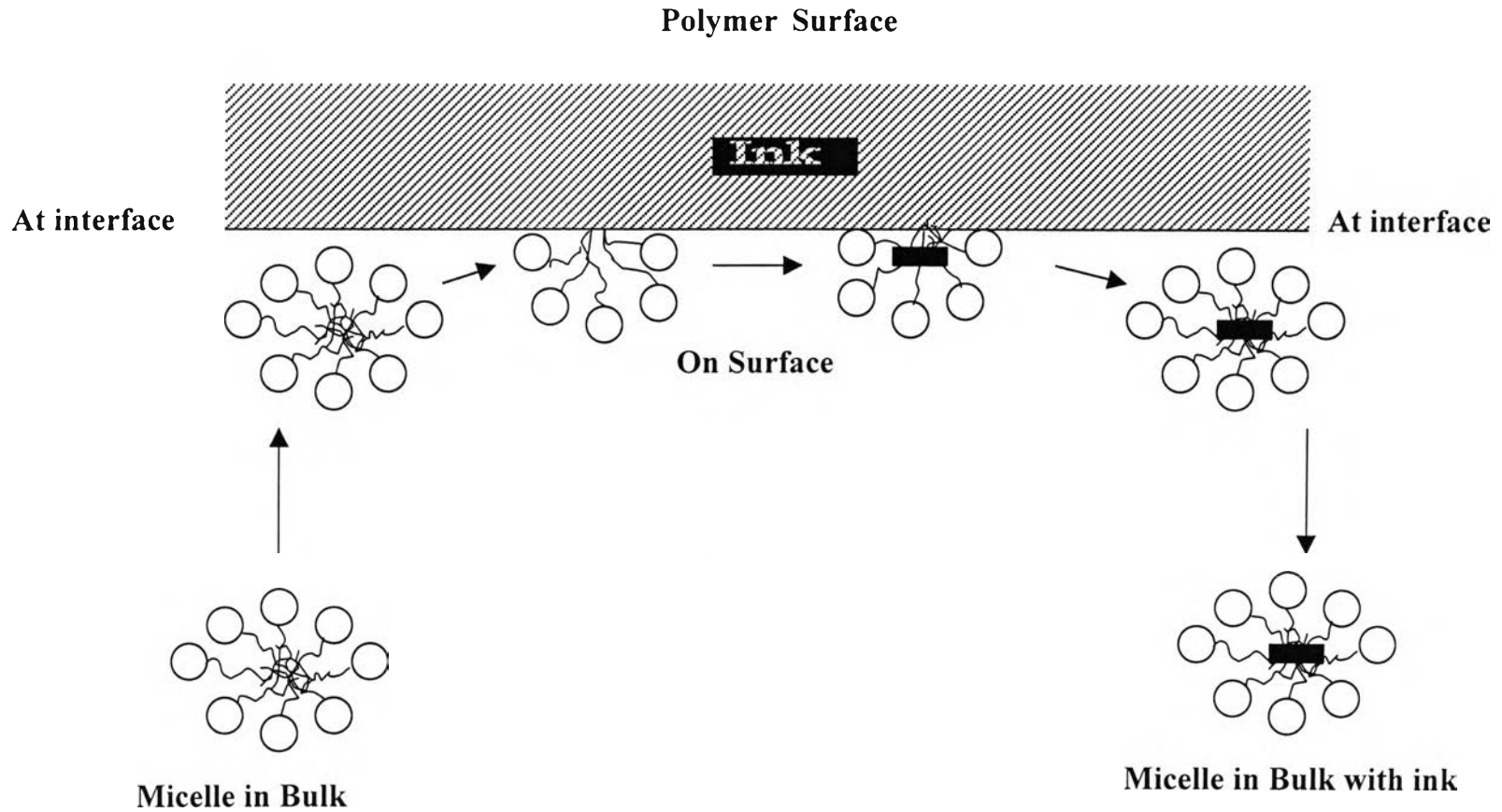


Figure 2.4 Detachment of Ink from a Polymer Surface by the Solubilization Mechanism (Adapted from Borchardt, 1994)

2.5 High-Density (Linear) Polyethylene

Linear polyethylene can be produced in several ways, including radical polymerization of ethylene at extremely high pressures, coordination polymerization of ethylene, and polymerization of ethylene with supported metal-oxide catalysts. Commercial production of polyethylene, using the second and third routes named, began 1957 and reached a volume of 5 billion lb/ yr. in 1979; its 1982 volume was about 4.8 billion lb, at list prices of \$ 0.45 - \$ 0.50 per lb, heavily discounted (Billmeyer, 1984).

2.6 Literature Review

The plastic recycling field has seen an increasing number of dedicated researchers in both commercial and university laboratories due to factors, i.e. the dependency of natural raw materials such as oil and natural gas, environmental and municipal solid waste considerations. As plastic film containing print can only be reused for low grade applications such as garbage bags, deinking (removal of ink) techniques using water and different types of surfactants have been carried out by some researchers to produce clear films.

Ellis and Teeters (1997) discussed the deinking of polyethylene packaging films printed with desired multicolor labels of commercial flexographic water-based ink by the use of aqueous solution and alumina beads at pH 10. They also established a standard method for deinking and a method for quantifying ink removal. Critical surface tension values for plastic films were obtained by measuring the contact angle of the plastic film using a variety of liquids and a Wilhelmy plate technique to determine the surface tensions of nine different inks. Attenuated total reflection (ATR) FTIR spectroscopy and an optical scanning method were used to quantify the ink removal. It is well known that low surface tension liquids wet the substrates

that have higher critical surface tension values. They concluded that there is a relationship between the deinking of plastic film and the critical surface tension of the solid substrate. It was also found out that higher pH solutions were required to deink plastic film having multiple layers of ink.

Gecol (1998) observed the use of different surfactant solutions for the deinking of a mixture of polyethylene plastic films printed with water-based ink by the flexographic process at various pH levels. Surfactants, in general, are environmentally innocuous compared to organic solvents. A back-scatter image of the surface containing both clear and printed parts of the plastic film was taken with a Scanning Electron Microscope (SEM) to view the surfaces layer by layer. Transmittance Electron Microscope (TEM) micrographs clearly indicated ink aggregates of approximately 2-5 μm in size in the re-extruded printed plastic film. The physical properties of plastic film after re-extrusion were also determined and compared with clear and printed plastic film. In her paper, she discussed the removal of water-based inks from plastic film using either water or selected surfactants with the use of porcelain beads as abrasive under a variety of conditions and compared the degree of deinking with that of clear, printed, and deinked plastic samples. The results of her research showed that deinking with only water was minimal at high pH values such as 11 or 12 since the binder in water-based ink is more soluble in water at higher pH. By adding abrasive material to the water, the deinking level rose by a factor of approximately three. Furthermore, deinking with the use of surfactants at other pH levels indicated the relative effectiveness of surfactants in the deinking process. Finally in her research, she concluded that cationic surfactants are the only effective surfactants either below or above their CMC at various pH levels and anionic surfactants are the least effective surfactants, which is only slightly better than water for deinking.

Gecol (1998) investigated the use of nonionic surfactants of varying structure for deinking of a mixture of polyethylene plastic film containing water-based printing inks because nonionic surfactants are often less expensive and more biodegradable than cationic and amphoteric surfactants. In her study, a number of experiments were carried out to find the effectiveness of deinking for different types of nonionic surfactants. A scale-up experiment, using a Denver flotation cell or TMI distintegrator, was also developed. Based on her investigations, it was shown that the Hydrophilic Lyophilic Balance (HLB) value and the cloud point are useful parameters for characterizing the effectiveness of nonionic surfactants. She reported that the cloud point of the nonionic surfactant should be slightly above the process temperature for optimum deinking. The results of her research showed that cutting the plastic film into smaller sizes and soaking them in surfactant solution for a certain period of time prior to agitation has a positive impact on deinking. It was also shown that an ethoxylated amine, AM(EO)₅, provides flexibility for setting the process pH to either acidic, neutral or basic pH levels compared with other nonionic surfactants.

Gecol (1998) studied the use of selected surfactants on the removal of water-based inks from a mixture of polyethylene plastic film and the effect of added calcium ion concentration and length of surfactant hydrophobe in this research. She conducted several deinking experiments on a commercial polyethylene plastic film printed with water-based ink using different types of surfactants in the presence of hardness ions (calcium ions) at various pH levels. The electrostatic properties of ink particles in the washing bath were also observed. The study of zeta potential measurements of ink particles in surfactant solution showed the possibility of surfactant adsorption on ink particles. Surfactant adsorption depends on electrostatic properties, surface heterogeneity, and chemical interaction between surfactant and ink surface. The results of her experiments showed that anionic surfactants or fatty acid

soaps in the presence of calcium ions at alkaline pH levels are nearly as effective for deinking as cationic, nonionic, and amphoteric surfactants alone. But adding calcium ions decreases the effectiveness of cationic and nonionic surfactants for deinking. Furthermore, she investigated the effect of carbon chain length of ionic surfactants and concluded that an increase in carbon chain length enhances deinking. It was hypothesized that calcium probably forms a bridge between the negatively charged ink and the anionic surfactant head group. On the other hand, it might compete for adsorption sites with cationic and nonionic surfactants.

In this study, Gecol (1998) conducted deinking tests on solvent-based printing inks from both commercial plastic packaging materials and plastic films exhibiting individual colors (yellow, pink, rouge, green, gold, black, and violet) using surfactants under a variety of conditions. Several experiments were done to study the effectiveness of deinking on a mixture of polyethylene film printed with solvent-based inks. In addition, a scale up deinking experiment was performed and the results showed that deinking of plastic film using surfactant solution is technically feasible. In her experiments, it was also found that cationic surfactants are the most effective surfactants for the removal of solvent-based ink from plastic film and a process pH of 11.5 or above is required for complete deinking. Finally, it was concluded that deinking of solvent-based inks requires more severe conditions, such as a very high pH and a more restricted choice of surfactant, than water-based inks.