CHAPTER I

INTRODUCTION

Essential oils are a concentrated, natural hydrophobic liquid product obtained from a flower petal, pollen, fruit peel or root of plants. Essential oils are generally extracted by distillation or solvent extraction. They are easy volatile material, generally thermally or chemically labile in native. The essential oils are used as aroma in food, cosmetic, household cleaning products, conventional medicine, aromatherapy and aroma massage [1-7].

Essential oil can be divided into two groups according to their functionality: 1) unsaturated hydrocarbon group such as limonene, farnesene, cymene and 2) oxygenated derivatives group including: a) ketone (camphor, carvone, jasmine); b) oxides (eucalyptol, bisabolone oxide); c) esters (bornyl acetate, eugenol acetate, linalyl acetate); d) alcohols (menthol, citronellol, farnesol, geraniol); e) phenols (eugenol, thymol, carvacrol) and f) aldehydes (citral, citronellal, benzaldehyde, cinnamic aldehyde)[2-3].

Citronellal

Citronellal or 3, 7-dimethyloct-6-en-1-al ($C_{10}H_{18}O$) is an essential oil used in this study. It is an aldehyde, a colorless liquid with a very strong lemon odor, water insoluble but miscible in solvent such as acetone, ethanol, ether and chloroform. The compound is the main component in the mixture of terpenoid compounds that give citronella oils its distinctive lemon scent. It is a major isolate in distilled oils from the plants *Cymbopogon*, lemon-scented gum, and lemon-scented teatree. Citronellal has insect repellent properties, and research shows high repellent effectiveness against mosquitoes. Research shows that citronellal has strong antifungal property [4].

Figure 1.1: Chemical structure of citronellal

Essential oil is volatiles substance sensitive to oxygen, light, heat and moisture [6].

Volatile essential oils usually posses problems on initial burst, short-term durability, stability and an immiscible nature with water-based products. Many researches had tried to solve these drawbacks by innovating new technologies to improve physical and chemical stability of essential oils for easy handling. Pro-fragrance, nano/micro encapsulation or trapping into appropriate matrixes have been investigated [6-10]

Encapsulation

Encapsulation is a widely used technique to protect volatile actives and sensitive ingredients from evaporation, reaction, degradation, thus improving their long-term durability and prolonging their release time. An active substance or core material such as essential oil, fragrance, vitamin and drug, is entrapped or coated with material or a mixture of materials (wall material).

The coating material is called an encapsulant, shell, wall or carrier [4]. Encapsulants are usually protein, polysaccharides or synthetic polymers [11-17]. The size of encapsulated particles affects various physical factors such as the rate of shear, the phase viscosity, and the concentration of stabilizer needed, as well as, the design of the stirrer to be used in the process. The encapsulated particles could be prepared from various methods as follows:

Phase separation method

This technique is a general method used to prepare encapsulated particles that active materials are dissolved in organic solvent such as ethyl acetate, dichloromethane or chloroform. The mixture of drug and encapsulants are dropped into aqueous solution and the encapsulated particles are formed. The encapsulated particles are isolated by filtration. The size distributions of the obtained particles depend on many factors such as rate of stirring, active volume fraction [4], concentration of polymer/drugs and etc. Surfactant can be used to aid dispersion of particles.

Solvent displacement method

In this method, active ingredient is encapsulated into nano/micro particles by inducing the self-assembly of polymer. A solution of polymer is prepared in organic solvent and is loaded into aqueous solution containing an active ingredient under ultrasonic or stirring condition. The self-assembly is induced by dialyzing the obtained solution against water and removing of excess stabilizer is usually carried out by centrifugation [18].

Emulsion formation method

In this technique, polymers are dissolved in organic solvent (oil phase). Active substances are slowly dropped and mixed to obtain the homogenous solution. The obtained solutions are dropped into water phase containing some surfactants. The encapsulated particles are formed [13-15].

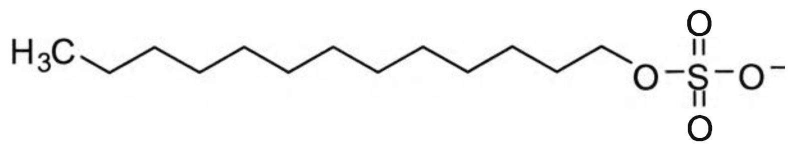
Surfactant

In a common sense, a surfactant or surface active agent is a substance that, when dissolved in water, gives a product the ability to remove dirt from various surfaces such as a human skin, textiles and other solids. In more technical terms: surfactants enable the wetting of the surface of one material with another material. Therefore, surfactants have been used to clean greasy, oily, particulate-, protein-, and carbohydrate-based stains through the enabling of wetting the surface of stains with water. They are also instrumental in removing dirt and in keeping them emulsified, suspended, and dispersed so they don't settle back onto the surface being clean.

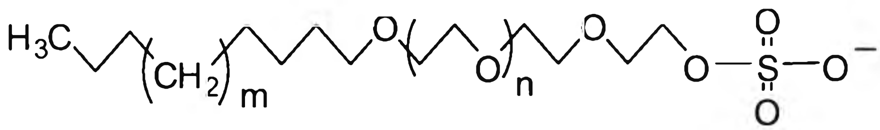
Each surfactant molecule has a hydrophilic (water-loving) head that is attracted to water molecules and a hydrophobic (water-hating) tail that repels water and simultaneously attaches itself to oil and grease. These opposing forces loosen the dirt and suspend it in the water. The mechanical agitation of the washing machine helps pull the dirt free. Surfactants are one of the major components of cleaning products and keeping the dirt in the water solution to prevent re-deposition of the dirt onto the surface from which it has just been removed. The same is true when washing your dishes or clothes. With the addition of surfactants, oil, which normally does not dissolve in water, becomes dispersible and can be removed with the wash water. There are four main types of surfactants used in laundry and cleaning products. Depending on the type of the charge of the head, a surfactant belongs to the anionic, cationic, non-ionic and amphoteric/zwitter ionic family.

Anionic surfactant

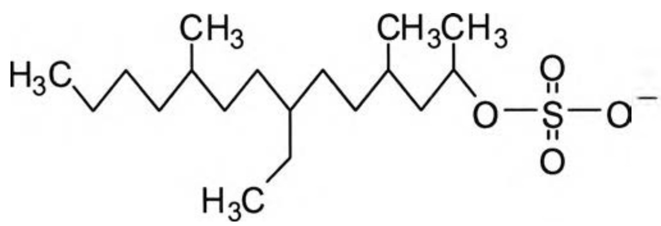
Anionic surfactant is the most widely used surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high. The surfactant is particularly good at keeping the dirt away from fabrics and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. They can react with cation in the water (calcium and magnesium), leading to partial deactivation. The more calcium and magnesium molecules in the water, the more the anionic surfactant system suffers from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrants) and more detergent should be dosed in hard water. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates (Fig 1.2). Examples of surfactant in this group are sodium lauryl ether sulfate (Fig 1.3), ammonium lauryl sulfate (Fig 1.4).



Linear Alkyl Sulfate



Alkyl Ether Sulfate



Branched Alkyl Sulphate

Figure 1.2: Chemical structure of typical anionic surfactants.

Sodium laureth sulfate, sodium lauryl ether sulfate, sodium laureth sulphate or SLES ($CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_nOSO_3Na$) (Fig 1.3) are surfactants commercially used in cosmetic, many personal care and household products (soap, shampoo, toothpaste etc.). It is synthesized by ethoxylation of dodecyl alcohol. The resulting ethoxylate is converted to an organosulfate intermediate, which is neutralized by conversion to the sodium salt.

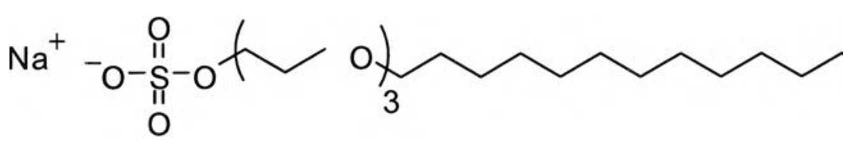


Figure 1.3: Chemical structure of sodium laureth sulphate

Ammonium dodecyl sulfate ($C_{12}H_{29}NO_4S$), ammonium lauryl sulfate, ammonium dodecyl sulfate or ALS (Fig 1.4) is very high foam surfactant. It was a good base in personal care products (shampoo, body wash etc.).

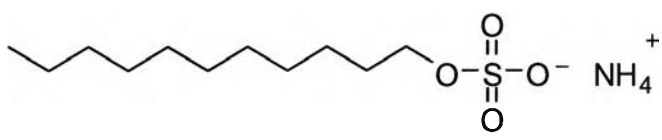


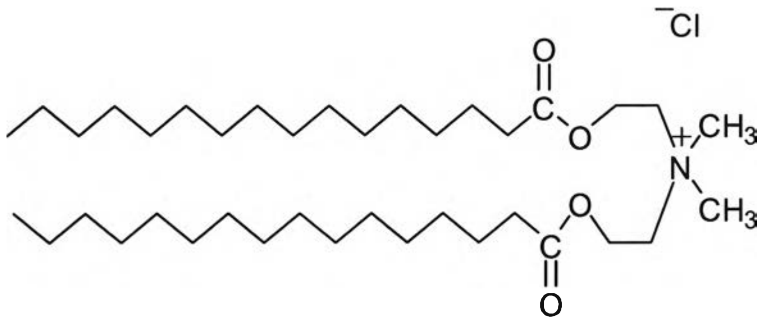
Figure 1.4: Chemical structure of ammonium dodecyl sulfate

Cationic surfactant

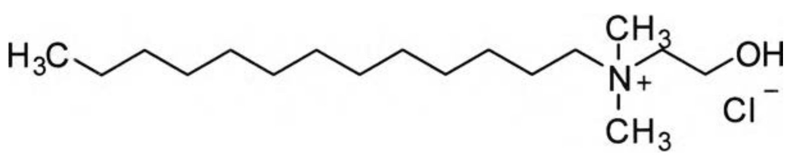
In solution, the head of cationic surfactant molecule is positively charged. There are 3 different categories of cationic surfactant, each with its specific application:

(1) Cationic surfactant for use in fabric softeners and detergents with built-in fabric softener (cationic surfactants provide softness). Their main use in laundry products is in rinse added fabric softeners. Esterquats (Fig 1.5) is one of the most widely used cationic surfactants in rinse added fabric softeners.

(2) Cationic surfactant for use in laundry detergents. Cationic surfactants (positive charge) helps improving the packing of anionic surfactant molecules (negative charge) at the stain/water interface. This helps to reduce the dirt/water interfacial tension in a very efficient way, leading to a more robust dirt removal system. They are especially efficient at removing greasy stains. An example of a cationic surfactant used in this category is the mono alkyl quaternary system (Fig 1.5).



Esterquat



Mono Alkyl Quaternary system

Figure 1.5: Chemical structure of typical cationic surfactants.

(3) Cationic surfactant for disinfection in household and bathroom cleaners. Cationic surfactants contribute to the disinfecting/sanitizing properties (Fig 1.5). Examples of surfactant in this group are di(hydrogenated tallow)dimethyl ammonium chloride (Fig 1.6) and ditallow dimethyl ammonium chloride (Fig 1.7).

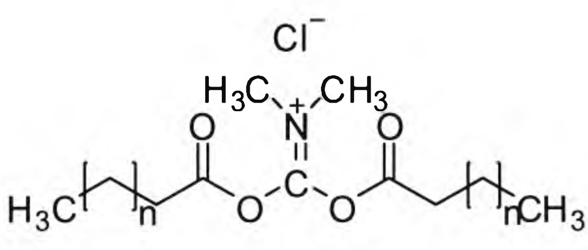


Figure 1.6: Chemical structure of di(hydrogenated tallow)dimethyl ammonium chloride

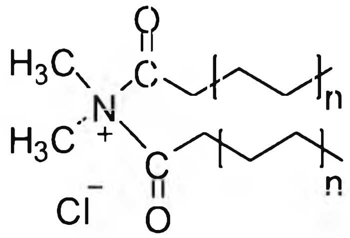
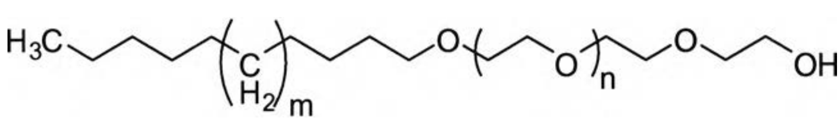


Figure 1.7: Chemical structure of ditallow dimethyl ammonium chloride

Non ionic surfactant

This group of surfactant does not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers, thus are popularly used in laundry products, household cleaners and hand dishwashing liquids. Most laundry detergents contain both non-ionic and anionic surfactants as they complement each other's cleaning action. The most commonly used non-ionic surfactants are ethers of fatty alcohol (Fig 1.8). Examples of surfactant in this group are nonyl phenol ethoxylate (Fig 1.9), polyoxyethylene (20) sorbitan monooleate (Tween 80) (Fig 1.10).



Non Ionic Surfactants

Figure 1.8: Chemical structure of typical non ionic surfactant.

Nonylphenol ethoxylate (NP 6), 4-(2,6-dimethylheptan-4-yl) phenol or nonoxynols ($C_{15}H_{24}O$) (Fig 1.7) are mixtures of nonionic surfactants used as detergents, emulsifiers, wetting agents, defoaming agents. Nonylphenol 6 is the compound with approximately 9 repeating ethoxy groups.

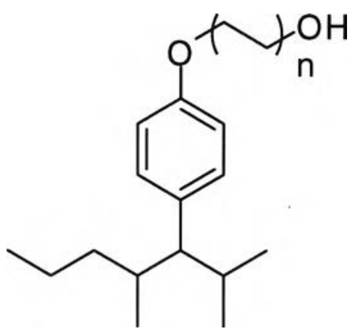


Figure 1.9: Chemical structure of nonylphenol ethoxylate

Polyoxyethylene (20) sorbitan monooleate or Tween 80 ($C_{64}H_{124}O_{26}$) (Fig 1.8) is an emulsifier derived from polyethoxylated sorbitan and oleic acid. It is used as emulsifier in food, manufacture of medication e.g. eye drops.

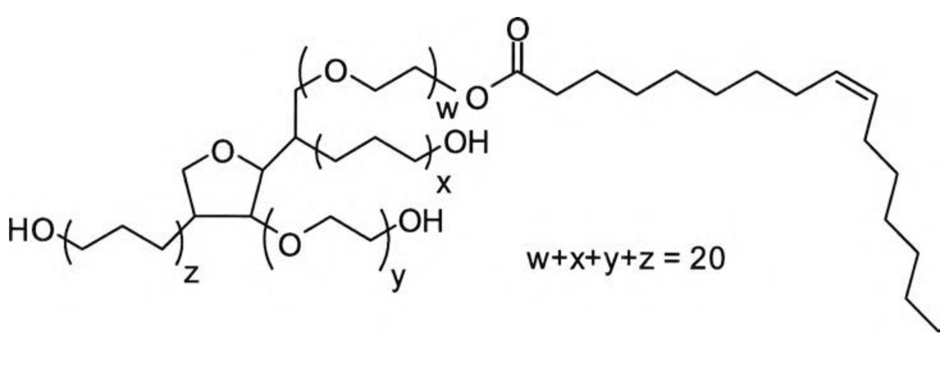
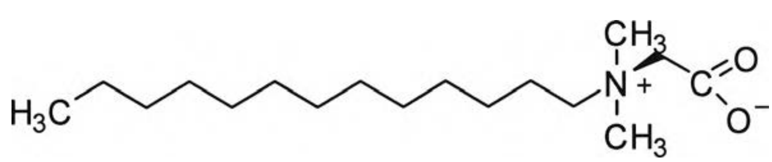


Figure 1.10: Chemical structure of polyoxyethylene (20) sorbitan monooleate

Amphoteric/zwitter ionic surfactant

Surfactants in this group are very mild, making them particularly suited for use in personal care and household cleaning products. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties. An example of an amphoteric/zwitterionic surfactant is alkyl betaine (Fig 1.11) [12].



Alkyl Betaine

Figure 1.11: Chemical structure of typical amphoteric/zwitterionic surfactant.

Controlled release

Controlled release is a mechanical which administer drug, fragrance, or other active agents were encapsulated in polymeric material or natural matrixes to release at a specific rate and specific condition. The releases of active agents are depending on four important factors including initial loading of active agent in the polymer, the solubility of the active agent in the solvent, the equilibrium partitioning of the active agent between polymer and solvent and diffusion barriers. The advantages of controlled release including 1) decreased the losing of active agent between production processes at high temperature, 2) separate active agents from incompatible component to protect degradation of fragrance, 3) posses controllable release rate and 4) increased stability of fragrance storage under several conditions. The stability of encapsulated spheres is depending on chemical structure, volatility and polarity of fragrance, type of coating material and mechanical and condition of encapsulation. The mechanical of release based on solvent effects, such as diffusion, melting, pH, degradation and particle fracture [4, 9-10].

For controlled release by diffusion, diffusion is a major mechanism of fragrance from encapsulation matrix. The vapor pressure of volatile agents on each side of matrix is the important driving force influence diffusion. The principle steps of this technique in the release of volatile substance from system by diffusion of volatile agent to the matrix surface. The volatile components were transported away from the matrix. The factors effect to diffusion of fragrance throughout from encapsulating materials depends on degree of swelling.

This technology now spans many fields and includes pharmaceutical, food and agricultural applications, cosmetics, and household products [18].

Literature reviews on controlled release of essential oil

In 1999, K. Hong and S. Park prepared melamine resin microcapsules containing fragrant oil by oil in water emulsion technique and studied thermal properties. The obtained melamine microcapsules possessed a great surface smoothness (Fig 1.12). The particles size was below 10 μm with narrow size distribution. The obtained melamine resin microcapsules were stable at high temperature up to 420°C. The resultant melamine resin microcapsules possessed thermosetting wall [19].

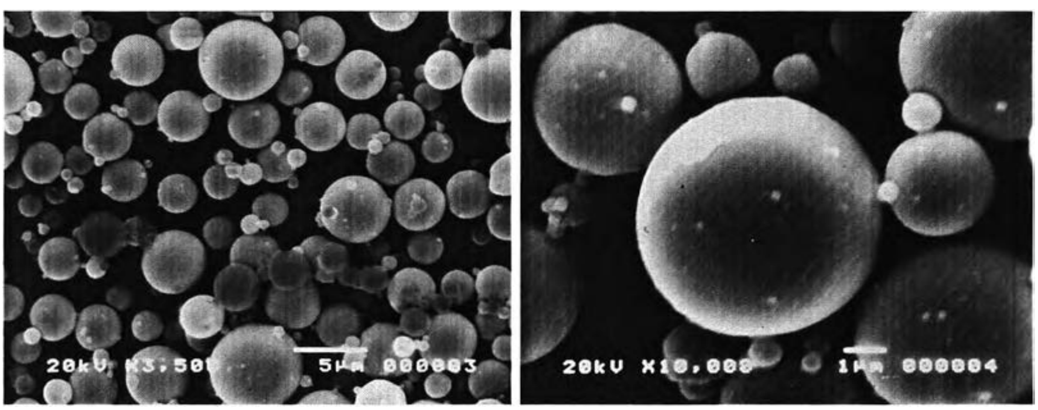


Figure 1.12: Scanning electro microscopy (SEM) photographs of melamine resin microcapsules with Migrin oil [19].

In 2001, Soo Jin Park and coworker prepared urea-formadehyde misrocapsulated lemon oil by *in situ* interfacial polymerization and studied the size distribution of the obtained microcapsules. Factors such as stirring rate and viscosity of the raw materials were being investigated. The sizes of microcapsules were small and the number of microcapsules increased with time. The particle size distribution was narrow (Fig 1.13). The sizes of microcapsules also increased with increasing viscosity of core materials [20].

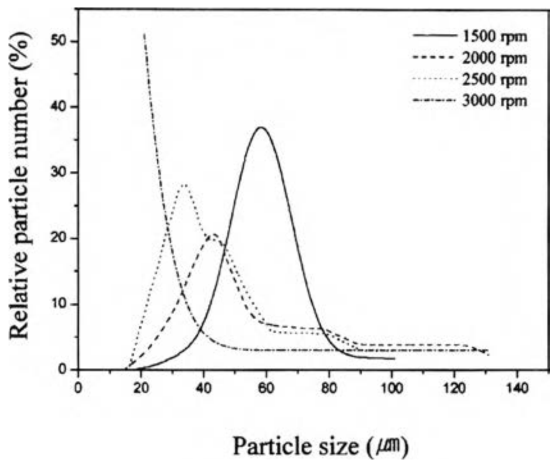


Figure 1.13: The particle size distribution of microcapsules prepared at different stirring rate [20].

In 2005, Nicholas P. and coworker encapsulated three essential oils (oregano, red thyme and cassia oil) into corn zien nanospheres by phase separation technique and studied morphology of particles. The encapsulated sphere exhibited irregularly shaped particles. The essential oil encapsulated particles gave bigger particle size than those made from zien alone [21].

In 2006, with the spray-drying technique, Renata and coworker prepared microcapsules using skimmed milk powder (SMP) and whey protein concentrate (WPC) and encapsulated three essential oils (oregano, citronella and marjoram) into the spheres. Oregano oil-encapsulated SMP particles exhibited well formed spherically shape with smoothed surface but with size of wide distribution size (8 to 224 μm). The surface of WPC capsules exhibited some holes, they also contain deep dents and wrinkles on the surfaces. The oregano oil-encapsulated SMP particles possessed the highest encapsulation efficiency (80.2%), while the majoram-encapsulated WPC particles showed the lowest encapsulation efficiency (54.3%) [22].

In 2008, Fernanda and coworker studied effect of stirring on morphology and size distribution of lemongrass oil encapsulated with polyvinyl alcohol microcapsules (prepared by coacervation technique). The microcapsules obtained were spherical. The particle size of particles obtained at the stirring rate of 900 rpm, was smaller than that obtained at the stirring rate of 500 rpm. The size distribution was strongly affected by the stirring rate. Increased stirring rate led to decreased size distribution. In addition, volume fraction (percentage of the lemongrass oil in the system) also affected the size of particles [23].

The objective of this research

1) To find appropriate method to prepare the citronellal encapsulated spheres.

2) To study compatibility of the obtained suspension with six surfactants, Arquad 2HT-75, Armosoft L, Texapon N 8000, Texapon N 70, EMAL AD-25, ECOLAT NP6 and Tween 80.

3) To investigate the release profile of the fabric softeners made from the fragrance encapsulated spheres on cotton fabric.