Faculty of Resource Science and Technology

Critical Micelle Concentration of Mixed Anionic and Zwitterionic Surfactant System in Different Media

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LIST OF ABBREVIATIONS

CMC	Critical micelle concentration
SDS	Sodium dodecyl sulphate
ZW3-12	3-(N,N-Dimethylmyristyl-ammonio) propanesulfonate
O	Oxygen
S	Sulphur
P	Phosphorus
N	Nitrogen
CH_2	Hydrocarbon
CF_2	Carbon fluorine
DTAB	Dodecyl trimethyl ammonium bromide
mM	miliMolarity
°C	Degree celsius
g/mol	Gram per mole
Brij-35	Polyoxyethylene lauryl ether
Bp	Boiling point
nm	nanometer
UV	Ultraviolet
M	Molarity
A	ampere
MW	Molecular weight
g	gram
ml	Mililitre
mm	Milimiter
rpm	Revolution per minute
v/w	Volume per weight
PAH	Polycyclic aromatic hydrocarbon
pH	measurement for acidity and alkalinity

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CRITICAL MICELLE CONCENTRATION OF MIXED ANIONIC AND ZWITTERIONIC SURFACTANT SYSTEM IN DIFFERENT MEDIA

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ABSTRACT

Critical Micelle Concentration (CMC) is parameter that commonly used to evaluate and predict the aggregation behavior of surfactant when some particular physiochemical changes occur in solution system. In this experiment, the CMC of the surfactant system of single (ZW3-12 and SDS) in aqueous (phosphate buffer) medium and mixed (SDS+ ZW3-12) surfactant system in different media (aqueous and soil) was determined by using the spectrophotometer method through UV-Vis spectrum of pyrene monomer in specific range of wavelength (263-335 nm) and the data was compared to investigate the significant changes on aggregation behaviour between of both surfactants. Pyrene was added on the surfactant solution to enhance the solubility of surfactant for forming micelle on the aqueous solution. Result show that the CMC the single SDS is high than ZW3-12 surfactant with ZW3-12 give early aggregation while in mixed surfactant system, the CMC was increased with increasing of mole fraction of SDS and the graph pattern of CMC in soil medium show higher measurement than aqueous medium. Based on the data, concluded that the CMC in the certain surfactants are depend on several factor such as their chemical nature in the solution and surfactant, ionic strength and interfacial activity that contribute to alter or promote the interaction forces between surfactant molecule that related to with hydrophilic and hydrophobic section.

Keywords: Critical micelle concentration (CMC), pyrene, mixed SDS-TDAPS surfactant, soil, aqueous.

ABSTRAK

Kepekatan misel genting (CMC) adalah merupakan parameter yang selalu digunakan untuk mengenalpasti sifat pengumpalan surfaktan apabila berlakuanya perubahan dalam physiokimia pada sesetengah sistem larutan surfaktan. Di dalam experiment ini, CMC bagi tunggal ZW3-12 dan SDS surfaktan di dalam akues (phosphate buffer) dan campuran SDS-ZW3-12 system di berlainan medium (akues dan tanah) telah dikenalpasti dengan menggunakan kaedah spektophotometer melalui spectrum UV monomer pyrene pada jarak gelombang lingkungan 263-335 nm dan data yang diperolehi dibandingkan bagi mengenalpasti perubahan ketara diantara dua surfaktan. Pyrene telah dicampurkan pada larutan surfaktan bagi meransangkan kadar pengumpalan surfaktan dalam larutan akues. Keputusan kajian telah menunjukkan nilai CMC bagi SDS ialah 8.0 mM dan ZW3-12 ialah 0.4 mM manakala di dalam larutan campuran SDS-ZW3-12 nilai CMC meningkat dengan peningkatan pecahan mole SDS dan pola graf CMC di dalam medium tanah menunjukkan peningkatan jika dibandingkan dengan medium akues. Berdasarkan dengan data yang diperolehi, secara kesimpulannya perubahan nilai CMC bagi surfaktan adalah bergantung dengan beberapa faktor seperti sifat kimia larutan dan surfaktan, kekuatan ionik dan aktiviti permukaan yang menyebabkan perubahan pola ikatan molekul antara molekul surfaktan dimana dikaitkan dengan bahagian hidrophobik dan hidrophilik.

Kata kunci: Kepekatan misel genting (CMC),pyrene, Larutan campuran surfaktan SDS-ZW3-12, tanah, akues.

Chapter 1

INTRODUCTION

Surfactant are amphiphilic molecules that commonly exist as active ingredient found in hygiene and cosmetic products that are widely used in daily life (Umur and Pekdemir, 2004). Shampoo, detergent and soap are an example of surfactants that commonly found in market for household and industrial purposes. Briefly, surfactant are most versatile of chemical found in modern formulation which involve their function in most chemical process such as emulsification, detergency, wetting and spreading, solubilizing, foaming, lubricity and biocidal (Hergreaves, 2003). The important characteristic of surfactant is its dual affinity ability property due to presence of two special parts in their molecule (Salager, 2002). These two parts are usually described as hydrophobic tail that mostly contain hydrocarbon chain and the other hand referred as hydrophilic head which content of heteroatom polar group O, S, P or N included in functional group such as alcohol, thiol, ester and etc (Salager, 2002). In another way, the term surfactant designates a substance which exhibits some superficial or interfacial activity (Salager, 2002).

As a consequent, increase of the surfactant application recently causes continuous improvement and development on the various products and the mode of breakdown of such products in the environment for prevention of pollution (Porter, 1999). The important application of surfactant is adsorption at the air–water interface which results to surface tension reduction (Gad *et al.*, 1999).

This statement also agreed by Urum and Pekdemir (2004) work where surfactant is an active-surface agent that has the ability to concentrate at the air-water interface and commonly used to separate oily material from a particular media.

However, in recent surfactant technology usually mixed surfactants system are more preferable rather than single surfactant system for formulation in most daily products. Basically, the performances of mixed surfactants are more efficient compared with the single surfactant. When two surfactants that have different properties are mixed together in certain media, there are several physicochemical properties of the mixture system are changed due to net interaction between the amphipiles and yield enhanced interfacial properties which it referred as synergism (Khan and Marques, 2000). In brief, the mixed surfactant systems have brought many improvements to interfacial properties compared to the single surfactant systems (Fan *et al.*, 2006).

There are lot of study that have been conducted on investigated the interfacial properties on the mixture surfactant system when it applied on various media and the measured critical micelle concentration (CMC) value are used to evaluate the synergism. A fundamental property of surfactant is their ability to form micelle in solution because of their hydrophilic and hydrophobic parts in molecule where this phenomenon gives the surfactants an excellent detergency and solubilization properties (Muherei and Junin, 2009).

Serious environmental cases such as oil spill at sea, the large amount of hydrocarbon compound cover the sea surface and coastal area may affect the ecosystem of the marine life.

By understanding the behavior of surfactant properties, washing the contaminated soil containing hydrocarbon using surfactant can reduce and remove the small percentage of the hydrocarbon in the soil (Urum and Pekdemir, 2004). Hence, surfactant CMC has preferably been used as parameter as the surfactants are able to mobilize or solubilize hydrophobic contaminant in contaminated soil (Muherei and Junin, 2009).

In this research, CMC values of mixed surfactant system of ZW3-12 and SDS are determined and observed in different mediums; which are aqueous and soil solutions. The idea is to evaluate the CMC by adsorption of surfactant on different media in certain concentration using spectrophotometer would help to improve fundamental concept for the application in environmental remediation and improved mixed surfactant system through utilization measurement of CMC. Zwitterionic surfactants are considered been less studied than other surfactant due to several factors such as high production cost and has limited usage in the industrial use and the behaviour of the zwitterionic in the mixed system is still has been not well defined . Consequence of this limitation would inspire for accomplishment to this study which would help for understanding the synergism of mixed surfactant system on application of solid-liquid interfacial. In this study, the CMC value of each surfactant was experimented and the result of single and mixed surfactant systems in different media was compared and the aggregation behaviour was observed through interpretation CMC data by referring to literature.

The objectives of this research are:

1. To measure the CMC of single anionic (SDS) and zwitterionic (ZW3-12) surfactant.
2. To measure the CMC of mixed surfactant systems (SDS+ZW3-12) in different media (soil and aqueous).
3. To compare the CMC between single surfactant and mixed surfactant in aqueous.
4. To compare the CMC of mixture surfactant system in different media.

Chapter 2

LITERATURE REVIEWS

2.1 Surfactant

Surfactant is organic compound that have special ability to concentrate at the air-water interface (Urum and Pekdemir, 2004). It is a molecules that always used in many application as well this material prefer to be described as a molecule that have ability to reduce surface tension of water by disrupting the hydrogen bonding between water molecules which it will cause to increase the tendency of water molecule to contact and wet a surface. They are molecules that have both hydrophobic and hydrophilic section that impart partial affinity toward both polar and non polar surfaces (Biresaw and Mittal, 2008). Basically the hydrophilic section is composed of ionic functional group while other section for hydrophobic commonly consists of non polar characteristic of group such as long hydrocarbon (CH_2) unit or carbon fluorine (CF_2) units (Biresaw and Mittal, 2008). The dual affinity characteristic of surfactants toward the non polar and polar make it commonly essential in many application of chemical mechanism included emulsification, wetting, foaming, dispersion, adsorption and micellization (Farn, 2006).

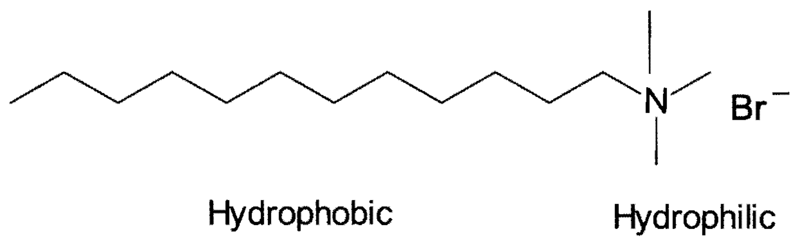


Figure 1: Basic chemical structure of surfactant with two domain section (hydrophilic and hydrophobic).

The surfactants can be classified into several types based on charge constituent on their hydrophilic section for dissociated with water. In the industrial application, the ionic surfactant are classified according to their charge they carry when it dissolve in water at their neutral pH (Urum and Pekdemir, 2004). This hydrophilic section have possibilities to carry positive or negative charge, both positive and negative charge in same molecule or contain no charge on the head portion. Consequence of these variety in surfactant hydrophilic give molecule of surfactants classified into an anionic, cationic, nonionic and amphoteric (zwitterionic) where all of these surfactants are frequently used in the daily life (Farn, 2006).

2.1.1 Types of Surfactants

a. Cationic surfactant

Cationic surfactant is a surfactant that had positive charge present on the hydrophilic section when dissolved in aqueous media from neutral salt form (Biresaw and Mittal, 2008). The cationic surfactant often used in many applications because of their peculiar properties and mostly exist as bactericide which used to clean and sterilize surgery hardware and food bottle or container and also used to formulate heavy duty desinfectants for domestic and hospital use (Salager, 2002). However, cationic surfactants were not good detergent and cannot be mixed in the formulations which contain anionic surfactant (Salager, 2002). The mixture cationic and anionic surfactant were give tendency to form precipitate or liquid crystal phase which have a negative impact on the detergency performance and remediation of oil contamination (Fuangswasdi *et al.*, 2006).

For the commercial purpose, this type of surfactant basically has nitrogen groups that commonly exist on its hydrophilic section (Farn, 2006). However, some others group such as sulfonium and phosphonium groups also available to exist on the positive section which are not commonly used for commercial but also included in this type of surfactant (Farn, 2006). The manufacturing of cationic surfactant can be made via two processes which it included amine preparation and quaterization (Farn, 2006).

Example of cationic surfactants is Dodecyl trimethyl ammonium bromide (DTAB). In overview of its physical properties, the DTAB have molecular weight 308.34 g/mol with the chemical formula is $C_{15}H_{34}NBr$ and have melting point of 246 °C (Thermo Fisher Scientific Ltd, 2010).

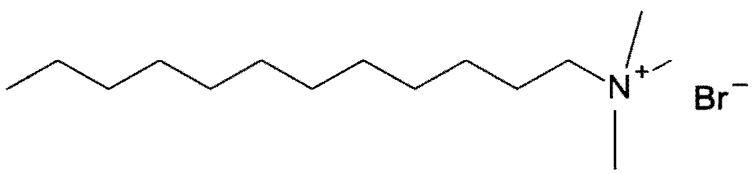


Figure 2: Chemical structure of dodecyl trimethyl ammonium bromide (DTAB).

b. Anionic Surfactant

In anionic surfactants, negative charge is on their heads and mostly this group repelled from most surface. This type of surfactant are most widely used compared with others due it ability to dissociate in water and in an amphiphilic anion and cation (Salager, 2002).

Most of anionic surfactant is used in cleansing application because in high concentration it able to form more foaming in solution above their CMC value and this property is important for cleansing application (Farn, 2006). Even though it has good cleaning ability but the implication on the environment considered will give some effects. Anionic surfactants can be classified based on their polar head groups which these group known as are sulphonates, sulphates, phosphate ester and carboxylate (Biresaw and Mittal, 2008).

SDS is one of the examples of anionic surfactant and it was surfactant that used for this study. In laboratory, SDS is common component in cell lysis buffer and routine protein electrophoresis (Thermo Fisher Scientific Ltd, 2010). SDS has molecular weight 288.5 g/mol and CMC value in range 7 to 10 mM within water solution at 20-25 °C (Thermo Fisher Scientific Ltd, 2010).

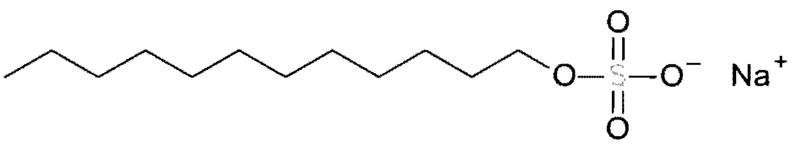


Figure 3: Structure of sodium dodecyl sulphate (SDS)

c. Nonionic Surfactant

The other type of surfactant is nonionic surfactants which have no charge on hydrophilic section therefore it not found in salt forms (Biresaw and Mittal, 2008). The usage of the nonionic surfactant for past few decades has increased about 40 % in total of market production worldwide especially for cosmetic, industrial products and extensively used in soil remediation (Farn, 2006).

Nonionic surfactant generally consists of alcohols, polyglucosides and poly (ethylene oxide) that have attached on hydrocarbon chains (Biresaw and Mittal, 2008). The nonionic surfactants do not ionize in aqueous solution and particularly less sensitive to electrolyses and can be used in hard water with high salinity (Salager, 2002). Consequently, nonionic surfactants are compatible with other types of surfactant and have ability to form complex mixture as well as found in many commercial products (Salager, 2002).

Nonionic surfactants also are good detergent, wetting agent, emulsifier and some of them able to form a good foaming characteristic (Salager, 2002). Nonionic surfactants are often used in environmental remediation and extensively studied because of their lower CMC, higher degree of surface-tension reduction, and have relatively constant properties in presence of salt which resulting in better performance and require low concentration (Muherei and Junin, 2009). Polyoxyethylene lauryl ether (Brij-35) is an example of nonionic surfactant that is commonly used in many application systems such as protein methods. The chemical formula for Brij-35 is $C_{12}H_{25}O$ (Thermo Fisher Scientific Ltd, 2010).

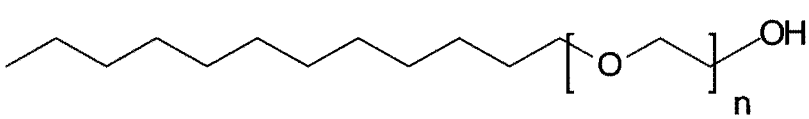


Figure 4: Structure of polyoxyethylene lauryl ether (Brij-35).

d. Zwitterionic Surfactant

Zwitterionic surfactant also known as amphoteric surfactant is a substance that has two charges on it hydrophilic section which is anionic and cationic. Basically this surfactant often been used in pharmaceuticals and cosmetics application. Unlike with other type of surfactant, zwitterionic surfactant has posses lot of unique properties but limited in usage for the industrial purpose because it has high cost of production (Mclachlan and Marangoni, 2005). This surfactant considered mild substance when contact to skin and eyes making them particularly suited for use in personal care and household cleaning products. Besides that, other properties make them very unique than other surfactant are they exhibit low toxicity, display excellent water solubility, has broad isoelectric range, high foam stability and resistant to hard water and degradation by oxidizing or reducing agent (Mclachlan and Marangoni, 2005).

The nature or behaviors of zwitterionic surfactant are influence by the added electrolyte, pH and temperature to determine which group would dominate the molecule (Salager, 2002). Their nature can be described as the cationic more favour with acidic pH and the anionic with alkaline pH (Salager, 2002).

At the isoelectric point the zwitterionic show tendency to both charge and it will minimize the interfacial activity and maximize the solubility with water (Salager, 2002). Betaine, imadazine-derived amphoacetates, alkylamino propionates and glycinate are those group generally included in amphoteric surfactant (Zoller, 2009). 3-(N, N-dimethylmyristyl-ammonio) propanesulfonate (ZW3-12) is an example of zwitterionic surfactant and the molecule structure is illustrated in figure:

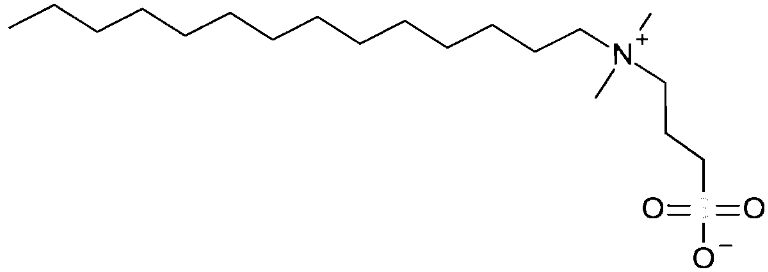


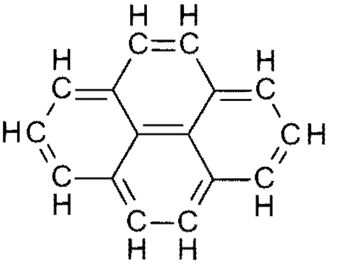
Figure 5: Structure of 3-(N, N-dimethylmyristyl-ammonio) propanesulfonate (ZW3-12).

2.2 Pyrene

Pyrene is a polycyclic aromatic hydrocarbon (PAHs) that consisting 4 fused benzene ring in their molecule. Basically of this chemical exist as colourless crystal-like solid and sometimes in yellowish colour which indicate the present of impurities. Pyrene is formed during the incomplete combustion of organic compound such as coal tar.

For safety precaution, pyrene is considered has slight carcinogenic and toxic properties and very persistent in the environment which they quiet resistance to biodegradation (Thibault *et al.*, 1996). The chemical properties of pyrene were presented on the Table 1.

Table 1: Chemical properties of pyrene

Chemical name	Chemical formula	Chemical structure	Mw (g/mol)	Mp (°C)	Bp (°C)
Pyrene	$C_{16}H_{10}$		202.25[a]	145-148[a]	404[a]

[a] data retrieved on April, 6 from http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/12pyrene.html#Property

Pyrene also absorbs light below the 350 nm in spectrophotometer measurement and mostly excited at 335 nm (Fan *et al.*, 2006). The UV spectrums of pyrene in various wavelengths are shown in the Figure 6.

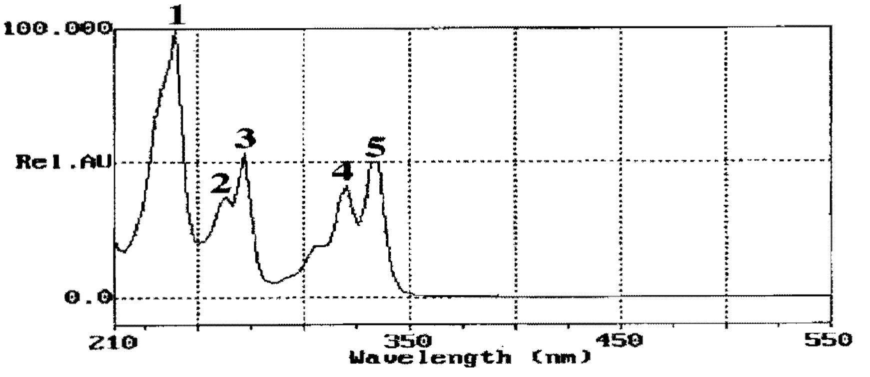


Figure 6: UV- Spectrum for pyrene in wavelength 239nm (1), 263nm (2), 272nm (3), 320nm (4) and 335nm (5). Data was retrieved on April, 6 from http://chrom.tutms.tut.ac.jp/JINNO/PAHSPECTRA/sp12pyrene.gif

In determination of CMC of surfactant system has a great deal with the solubility of the hydrophobic compound in the solution. The research that has been conducted by the Fan et *al.*, (2006), presence of pyrene on the surfactant system can be dramatically enhancing the solubility ability.

Increasing of solubility will provide the environment for aggregation of surfactant more favourable and promote obvious result on spectrophotometer measurement on micelle formation due to pyrene tend to move toward the mixed surfactant micelle as a polarity attraction. In this research, the CMC of the both mixed surfactants and single surfactants system in different media were determined from the measurement of UV-absorption of pyrene in surfactant. Thus, present of pyrene with water solubility 6×10^{-7} M expected to continuously enhance the water solubility on the surfactant solution which pyrene will be used act as a solubilizer and qualitative indicator of organic matter polarity (Fan *et al.*, 2006).

2.3 Mixed Surfactants System

Research on fundamental physicochemical properties such as CMC value of surfactant is very important in order to predict the behavior of mixed surfactant system in certain medium. Based on Khan and Marques (2000), when the different types of surfactant are mixed together to form a mixture of surfactant system there will appear several physicochemical properties that is interesting to be investigated.

Sodium dodecyl sulphate (SDS) and 3-(N,N-dimethylmyristyl-ammonio) propanesulfonate (ZW3-12) are surfactant have been selected in this work because both of these surfactant are frequently used as a precursor in most industrial application and they readily available while both are extensively studied for the synergism of surfactant system. From past researches, mixed surfactants system has shown the result that this system is able to enhance the interfacial properties in surfactant technologies (Khan and Marques, 2000).

Various physical properties and aggregate morphology are expected when two different type of surfactants are mixed together (Fan *et al.*, 2006). Synergism in mixed micelle formation considered accepted when the CMC of the mixture less than that the individual surfactant among the mixture (Muherei and Junin, 2009).

Mixed surfactants solution are very important in many technical applications such as detergent because mixed surfactant has better performance compared single surfactants (Fan *et al.*, 2006). In mixed surfactant system, the interaction among surfactant molecule expected to be either synergistic or antagonist (Acosta *et al.*, 2006). The formations of micelle by the mixed surfactant in certain medium are influenced by the mole fraction of individual species of surfactant contained in the binary mixture (Mclachlan and Marangoni, 2005).

The process of micellization in mixed surfactant also depends on their hydrophobic chain length and the size of heads group of the attracted molecules. According to Sahari (2009), if small changes of mole fraction on the species chain component, it would change the behavior of micelle formation. In some findings, micelle with compact head group such as SDS consider to have lower polarity which indicates a smaller water penetration in this micelle formation compared to micelle in larger head group such as Brij-35.

The mixture of cationic and anionic surfactants also known as a cataionic system. The formation and their transformation can be described in term of interaction forces and surfactant geometry. The combination of this surfactant tends to form precipitate or liquid crystal phases in their final product (Fuangswasdi *et al.*, 2006).

In high water composition, the surfactant system is precipitate at equilmolar concentration while in a non-equilmolar concentration the system forms a micelle with different size and shape (Khan and Marques, 2000). The increase of the hydrophobic portion on the system will decrease the CMC thus promoting the micellization.

For ionic and nonionic surfactant, this type of mixed surfactant system is extensively investigated especially for anionic and nonionic. Nonionic surfactant is suitable use for many application systems because they has lower cmc value, higher degree of surface-tension reduction and relatively constant properties in presence of salt which this contribute to better performance result and particularly lower concentration requirement (Muherei and Junin, 2009). The mixed of ionic and nonionic surfactants always give an improvement the overall performance compared to single system.

The interaction between surfactant in mixture can produce remarkable interfacial effects due to change in adsorption and charge density off the surface (Muherei and Junin, 2009). In the interaction between the nonionic and anionic surfactant the CMC of mixed surfactant is very low than of CMC in individual ionic (Muherei and Junin, 2009). This happen because with the increase of mole fraction of nonionic surfactant the CMC decrease continuously from the CMC of individual ionic. Kile and Chiou (1989), also suggest that the non-ionic ethoxylate surfactant is good for the removal of organic contaminants from soil because of their high solubilization capacity and biodegradability.

In the mixture of the surfactants either nonionic or ionic with the zwitterionic surfactant are less studied than other type of surfactant.