STUDIES ON AGGREGATION BEHAVIOR IN MIXED SYSTEM OF SINGLE-CHAINED ANIONIC SURFACTANT WITH SINGLE-CHAINED NONIONIC SURFACTANT IN AQUEOUS SOLUTION

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SINGLE-CHAINED ANIONIC SURFACTANT WITH SINGLE-CHAINED NONIONIC
SURFACTANT IN AQUEOUS SOLUTION

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DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

________________________________________
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ABSTRACT
The investigation of mixed surfactants system, mixture of anionic with nonionic surfactants and single surfactants systems, mixture of anionic or nonionic surfactant was investigated using UV/VIS Spectrophotometer to determine the critical micelle concentration, cmc. Mixed surfactants systems studied were mixture of SDS-Triton X-100 and SDS-Brij 35 surfactant solution. While single surfactant systems were SDS, Triton X-100 and Brij 35 surfactant solutions. The determination of cmc that gave aggregations of pyrene between surfactants was characterized. Above cmc, pyrene concentration increased linearly with total surfactant concentration for both mixed and single surfactants system. Mixed surfactant system gave higher cmc than pure surfactant system. The cmc for pure surfactants system gave the following order SDS > Triton X-100 > Brij 35.

Keywords: Critical micelle concentration, Single surfactant system, Mixed surfactant system, Pyrene solubilization

ABSTRAK
Kajian tentang system surfaktan gabungan, gabungan di antara surfaktan anionik dan nonionik dan system surfaktan tunggal, gabungan di antara surfaktan anionic dan nonionic dijalankan dengan menggunakan Spektrofotometer UV/VIS untuk mengenalpasti kepekatan “micelle” kritikal,cmc. Sistem surfaktan gabungan yang dikaji ialah gabungan di antara SDS-Triton X-100 dan SDS-Brij 35, sementara untuk system surfaktan tunggal pula SDS, Triton X-100 dan Brij 35. Apabila melebihi nilai cmc, kepekatan pirena meningkat secara linear dengan kepekatan surfaktan keseluruhan untuk kedua-dua sistem gabungan dan tunggal. Sistem surfaktan gabungan memberikan nilai cmc yang lebih tinggi berbanding system surfaktan tunggal. Nilai cmc surfaktan tunggal meningkat mengikut turutan SDS > Triton X-100 > Brij 35.

Kata Kunci: Kepekatan “micelle” kritikal, Sistem surfaktan tunggal, Sistem surfaktan gabungan, Pemelarutan pirena
CHAPTER 1

INTRODUCTION

Nowadays, mixtures of ionic surfactant and nonionic surfactant are commonly used in many practical surfactant applications. This is because these mixtures surfactants are interesting as they often exhibit highly nonideal behavior (Shiloach and Blankschtein, 1998). These compounds are often classified according to their charge, where those of the anionic and non-ionic classes show the highest volumes of production (Lara-Martí’n et al., 1998). The anionic surfactant is widely applied in laundry detergent formulations (Hill et al., 1993) and example of ionic surfactant solution for this purpose is sodium-n-dodecylbenzenesulfonate, \( \text{C}_{12}\text{H}_{30}\text{O}_3\text{SNa} \). Nonionic surfactant are often used to maximize water hardness tolerance (Hill et al., 1993) and the example of nonionic surfactant solution for this application is dodecylhexa(ethyleneoxide), \( \text{C}_{12}\text{E}_6 \). This is why the mixtures of ionic surfactant and nonionic surfactant are interesting. However it is the nonideal behavior of each mixtures can also be influenced by other structural characteristics of the two surfactants, such as differences in the sizes of the surfactants heads or the lengths of the surfactants tails (Shiloach and Blankschtein, 1998).

Mixed surfactants solution which means the mixture of ionic surfactant with nonionic surfactant widely used are in technical applications in industrial such as detergents, cosmetics, pharmaceuticals and enhanced oil recovery (Nagrajan, 1984).
While the example of application in biochemical domains are precipitation of bacterial cells by polycations (Kawabata et al., 1986), immobilization of enzymes in polyelectrolyte complexes (Margolin et al., 1985) and purification of proteins (Jones, 1992).

The applications of mixed surfactants are vaster than single surfactant because mixed surfactants found to yield better performance than a single surfactant (Fan et al., 2006). Besides that, the addition of nonionic surfactant to ionic surfactant can reduce the electrostatic repulsions between the charged surfactant heads and greatly make easy mixed micelle formations (Shiloach and Blankschtein, 1998).

The example of mixed surfactants solution is addition of nonionic surfactant pentaethylene glycol mono-n-dodecylether, C_{12}E_5 to nonionic surfactants, sodiumbis(2-ethylhexyl)sulfosuccinate, AOT and sodiumbis(4-phenylbutyl)sulfosuccinate, SBPBS which leads to the formation of mixtures of micelles and vesicles and other intermediate aggregates (Fan et al., 2006).

In this project research, the unique characteristics are intensively studied or investigated more details on why, how or what make the surfactants so special. The research scope is ionic surfactant which was anionic surfactant solution, nonionic surfactant solution and lastly, mixed surfactant solution which was mixed system of anionic surfactant with nonionic surfactant in aqueous solution. The end of the research, when the mixture of the surfactants added together variety of physical properties and aggregate morphology are expected (Kwon and Kim, 2001).
Statement of problem

By only using single surfactant which is ionic or nonionic surfactant, we can apply their application as much as mixed surfactant's application. However it is the mixed surfactant solution of ionic surfactant with nonionic surfactant are found to yield better performance than a single surfactant (Fan et al., 2006). Therefore nowadays, the applications of mixed surfactants are the most used such as in technical applications (Fan et al., 2006), industrial processes (Nagrajan, 1984) and biochemical domains (Kawabata et al., 1986).

Due to the important of surfactant either single or mixed surfactants, the study on the cmc of the surfactants especially found locally are essential to be studied. Specifically, the research is on the aggregation behavior in mixed system of anionic surfactant with nonionic surfactant in aqueous solution. Therefore distilled water is used as solvent for all of the surfactant solutions.

Objective

There are several objectives of these studies, which are:

a. To determine the critical micelle concentration, cmc at a given solution composition of single anionic surfactant solution and nonionic surfactant solution.

b. To determine the critical micelle concentration, cmc at a given solution composition of mixed surfactant system, anionic with nonionic surfactant solution.
CHAPTER 2

LITERATURE REVIEW

Some basic study of surfactants has been carried out for many years; such work has recently
been boosted by the possibility of using surfactants in our daily life. Therefore it is useful to
understand fundamentally how the molecular structures or properties of surfactants in a
surfactant mixture affect the properties of the solutions.

2.1 Surfactant

A surfactant is generally defined as a material that can greatly reduce the surface tension of
water when used in very low concentrations. Because water and oil cannot dissolve in each
other, therefore surfactant has to be added to the mixture of oil and water to keep it from
separating into layers and keep the mixture as an emulsion for better handling.

In the study of surfactant, the interfacial phenomena are usually discussed, which are
dominated by the properties of soluble amphiphilic molecules also called amphiphiles
(Laughlin, 1996). The most interesting part of the amphipiles is it contains a hydrophobic part
and a hydrophilic part where from the point of view of classification is the polar hydrophilic
group. The surfactant is characterized as anionic if on ionization in water the surface-active
portion containing the hydrophobic chain has a negative charge. An example is the alkyl
sodium sulfonate, R-SO$_3$Na which splits into R-SO$_3$Na$^+$ (Miller and Neogi, 1985).
Amphiphilic molecules are present in everyday life and they are essential in many industrial processes. Examples of applications are such as detergents, cosmetics, pharmaceuticals and, enhanced oil recovery and so on (Fan et al., 2006). The other examples of amphipilic molecules application are as flotation agents in the mining industry (Laughlin, 1996) and to recover crude oil from underground petroleum fields (Shah and Schechter, 1977; Johansen and Berg, 1979).
2.2 Anionic Surfactant

Anionic surfactants are amphipatic compounds consisting of hydrophobic parts such as alkyl chains of various lengths, alkylbenzyle ethers, alkylbenzenes, and also consisting a hydrophilic part such as carboxyl, sulfate, sulfonate, or phosphates (Mungray and Kumar, 2008). The common example application of anionic surfactant is in laundry detergent formulations where it is used to maximize solubilization (Shiloach and Blankschtein, 1998). Anionic surfactants are also applied in consumer products like cleaning and dishwashing agents, and personal care products (Mungray and Kumar, 2008).

Anionic surfactants are also applied in management of the environmental system especially in solving a pollution problem. For example, contamination of soils and groundwater by toxic and/or hazardous organic pollutants is a widespread environmental problem. To solve this problem, the removal of hydrophobic organic compounds (HOCs) which involving anionic surfactant solution from them has become a major concern (Zhou and Zhu, 2008). As been studied, surfactants can increase the solubilities of hydrophobic organic compounds by partitioning them into the hydrophobic cores of surfactant micelles above the critical micelle concentration, 

\[ \text{cmc} \]

(Kile and Chiou, 1989; Edwards et al., 1991; Jafvert et al., 1994; Pennell et al., 1997).
### 2.3 Nonionic Surfactant

Nonionic surfactants are having neither charged cation nor anion in its hydrophilic part. The hydrophilic part derives its water solubility from highly polar groups such as polyethylene oxide or sugars. Alkylethylene oxides, also called alkylethylene glycols, belong to the group of nonionic surfactants. Two examples of nonionic surfactant are $\text{C}_{10}\text{H}_{21}(\text{OCH}_2\text{CH}_2)_8\text{OH}$ and $\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_6\text{OH}$. Alkylethylene glycols are usually written as $\text{C}_n\text{E}_n\text{E}$, where the index $n_C$ indicates the number of carbon atoms in the alkyl chain and $n_E$ is the number of ethylene oxide units in the hydrophilic head. The short notations for the above molecules are $\text{C}_{10}\text{E}_8$ and $\text{C}_{12}\text{E}_6$, respectively (Butt et al., 2006).

Another class of nonionic surfactants is the alkyl glycosides, also known as alkyl polyglycosides (Rybinski and Hill, 1998). They consist of mono- or oligosucrose, glucose or sorbitol as hydrophilic head group with an alkyl chain as hydrophobic tail (Butt et al., 2006).

The most frequently used nonionic surfactants are prepared by adding ethylene oxide to long chain hydrocarbons with terminal polar groups. This procedure introduces ethoxy groups, which are polar in nature (Schick, 1967) and form hydrogen bonds with water. The solubility of nonionic surfactants in water would be increased. However, the resulting molecules still have amphiphilic character and micelle formation takes place. As the reaction of the addition of the ethoxy groups is a polymerization reaction, these commercially produced surfactants do not exist in pure form (Miller and Neogi, 1985).
Nonionic surfactants tend to show the opposite temperature effect. As the temperature is raised, a point may be reached at which large aggregates precipitate out into a distinct phase. The temperature at which this happens is referred to as the cloud point (Butt et al., 2006). Besides that, due to the length of the ethoxy groups, their conformations are of interest (Roshc, 1967). In fact, calculations show that various entities, for example cmc are affected by it (Nagrajan and Ruckenstein, 1979). The main effect of the length of the polar groups is also on the cloud point. The cmc is by far more sensitive to carbon number than to the number of ethoxy groups (Hall and Pethica, 1967).
2.4 Triton X-100

Triton X-100 is a nonionic detergent which is often used in biochemical applications to solubilize proteins. Triton X-100 has no antimicrobial properties (Wexler, 1963). Triton X-100 does absorb in the ultraviolet region of the spectrum. Therefore, this type of surfactant can interfere with protein quantitation by absorption at $A_{280\text{ nm}}$. The chemical structure of Triton X-100 is shown in Fig. 1.0.

The Triton X series of detergents are produced from octylphenol polymerized with ethylene oxide. The number of ethylene oxide units in the structure is related to the number of 100. Triton X-100 has an average of 9.5 ethylene oxide units per molecule with an average molecular weight of 625. During the reaction, a by-product formed is polyethylene glycol which is a homopolymer of ethylene oxide. To neutralize the product after the vaso catalyzed reaction completed, acid is added. Commercially, preparations of Triton X-100 have been found to contain peroxides, hydrogen peroxide, ($H_2O_2$) equivalents. This may interfere the biological reactions.

By using the spectrophotometric measurement of the concentration of a Triton-ammonium-cobalt-thiocyanate complex, the Triton X-100 can be detected (Crabb and Persinger, 1965). Interfering substances in this assay have been discussed (Goldstein and Blecher, 1975). The spectrophotometric measurement absorbance change at $\lambda = 335$ nm also used to determine the critical micelle concentration, cmc of Triton X-100 when mixed with pyrene. This will result to the range of cmc value of Triton X-100 between 0.2 to 0.3 mM.
Triton X-100 is soluble in all proportion at 25°C in water, benzene, toluene, xylene, ethanol, isopropanol and ethylene dichloride. In water, it gives a clear to slightly hazy solution, from clear to slightly yellow in appearance (Neugebauer and Hjelmeland, 1990). In solution form, the Triton X-100 is stable to autoclaving but at certain concentrations the solution may be cloudy. The cloudy occurrence should clear with stirring upon cooling (Tiller et al., 1984).

Triton X-100 is considered stable for years if stored and sealed at room temperature. Storage under argon or nitrogen at 2-8°C may be preferred for a special applications.

![Chemical Structure of Triton X-100](Openwetware.org, 2009)
2.5 Mixed Surfactant

Generally mixed surfactants are mostly used in many practical surfactant applications such as detergent, cosmetics or pharmaceuticals. This is because, mixed surfactants system are found to yield better performance than a single surfactant (Shiloach and Blankschtein, 1998). Mixed surfactants are solutions that contain more than one type of surfactant solution such as mixture of ionic (cationic or anionic) surfactant with nonionic surfactant. In recent years, mixed surfactants system such as mixture of ionic with ionic surfactants, ionic with nonionic surfactants and nonionic with nonionic surfactants have been investigated by different methods (Ruiz and Aguiar, 2000; Junquera et al., 2004; Sulthana et al., 2000). The mixed surfactant or the mixed system almost invariably brings about enhanced interfacial properties compared to the single surfactant (Fan et al., 2006).

In thermodynamic studies of mixed system, mixtures of different surfactants often exhibit synergism in their effects on the properties of a system (Lucassen et al., 1981; Hua and Rosen, 1980; Rosen et al., 1982; Zhu and Rosen, 1984). This synergism can be attributed to nonideal mixing effects in the aggregates which results into critical micellization concentrations, cmc and interfacial tensions that are substantially lower than would be expected on the basis of the properties of the unmixed surfactants alone (Razavizadeh et al., 2004). By understanding the behavior of mixed surfactants system, this situation has generated both theoretical and practical interest in developing industry such as applications in detergency (Reif and Somasundaran, 1999; Scamhorn, 1986; Kurzendorfer et al., 1978).
The study of different types of surfactants which form mixed surfactant or mixed system, various physical properties and aggregates morphology are expected to occur (Kwon and Kim, 2001). The study has been done focusing more on revealing the mechanism of vesicle to micelle transition (Lopez et al., 2001; Heerklotz et al., 1996; Johnsson and Edwards, 2000) and this process has been described by three stage models which are vesicle saturation, formation of mixed micelles and complete vesicle solubilization (Lichtenberg et al., 1983).
2.6 The Critical Micelle Concentration, CMC

One characteristic property of surfactants is that they spontaneously aggregate in water and form well-defined structures such as spherical micelles, cylinders and bilayers (Gelbart et al., 1994). These structures are sometimes called association colloids. The simplest and best understood of these is the micelle. To illustrate this we take one example sodium dodecylsulfate, SDS and observe the changes when more SDS is added to water. At low concentration the anionic dodecylsulfate molecules are dissolved as individual ions. The surface tension decreases strongly with increasing concentration. At a certain critical micellization concentration or cmc, the decreasing tendency stops. The cmc for SDS in water is 8.3 mM. Above the CMC, the surface tension remains almost constant (Butt et al., 2006).

The cmc of the mixed and pure surfactant systems were obtained using surface tension and potentiometric methods. Surface tension was measured using a Kruss tensiometer (Razavizadeh et al., 2004) or Wilhelmy plate tensiometer (Shiloach and Blankschtein, 1998). The results were accurate within ±0.1 mNm⁻¹. This method is based on the fact that below the cmc, the surface tension decreases rapidly with increasing surfactant concentration.

While above the cmc, any changes in the surface tension with increasing surfactant concentration is almost the same. The surface tension of a mixed surfactant solution of a given composition is measured as a function of the total surfactant concentration. The cmc was identified as the break point in a plot of surface tension versus log surfactant concentration (Shiloach and Blankschtein, 1998).
2.7 Pyrene and Surfactants

Solubilization of pyrene by nonionic surfactant such as Triton X-100 and anionic surfactant such as sodium dodecyl sulfate, SDS was investigated by determining the total amount of carbon dissolved (Deo et al., 2003). Fig. 2.0 shows solubilization of pyrene as a function of the SDS concentration.

Pyrene is a commonly used probe molecule for microheterogeneous aqueous solutions, (Winnik and Regismond, 1996) and was employed to investigate the nature of the single and mixed surfactant. The nonpolar pyrene possesses a stronger affinity to nonpolar surfactant such as SDS micelles than to polar surfactant such as Triton X-100 (Deo et al., 2003). The dissolved amount of pyrene in surfactant was determined by UV spectroscopy.

At SDS concentration below 8 mM almost no pyrene’s concentration was detected. But at above 8 mM concentration of SDS, measurable amount of pyrene were dissolved and the changes of pyrene solubility at 8 mM is in accordance with the cmc value of SDS (Mukerjee and Mysels, 1971). Above 8 mM concentration of SDS, the value concentration of pyrene is increasing continuously and is attributed to the pyrene solubilization in the SDS micelles (Deo et al., 2003).
Fig. 2.0: Pyrene dissolution SDS in water measured by UV spectroscopy (Deo et al., 2003).