Aggregation Behaviour of Mixed Nonionic-Nonionic Surfactant Solution System

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LIST OF ABBREVIATIONS

1. Critical Micelles Concentration (CMC)
2. Sodium Dodecyl Sulphate (SDS)
3. Dodecyl Trimethyl Ammonium Bromide (DTAB)
4. Polyoxyethylene Lauryl Ether (Brij 35)
5. Polyoxyethylene (POE)
6. Alkylphenol Hydroxypropylene (Triton X-100)
7. Cetyl Trimethyl Ammonium Bromide (CTAB)
8. Polycyclic Aromatic Hydrocarbons (PAHs)
9. Hydrophile-lipophile balance (HLB)
10. MeOH: Methanol
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Equation 1: \( \frac{1}{\text{cmc}_{1+2}} = \text{mol fraction 1/ cmc1 + 1-mol fraction 2/cmcm} \)
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ABSTRACT

The aggregation behavior in mixed system of nonionic-nonionic surfactant solution was studied in this research. The solubility of pyrene in Triton X-100 and Brij 35 at different concentration was evaluated and the critical micelle concentration (cmc) value was then determined from the enhancement of pyrene solubility in these nonionic surfactant solutions. UV spectrometer was used to check the cmc of Triton X-100 and Brij 35 and their mixture. The cmc from single and mixed nonionic surfactant system were compared. From this study, the cmc value of Triton X-100 is $2 \times 10^{-4}$ M and for Brij 35, the cmc is $8 \times 10^{-5}$ M. Mixed system of these two nonionic surfactants solutions gave a cmc value of $2 \times 10^{-5}$ M, which is lower than cmc Triton X-100. The effect of organic solvent (methanol) to the cmc of single and mixed nonionic surfactant solutions was also determined. Addition of 4% of methanol volume from total surfactant solution volume decreased the cmc of Triton X-100 to $1.5 \times 10^{-4}$ M, Brij 35 to $6 \times 10^{-5}$ M and for mixed surfactants solution system, decreased to $1.8 \times 10^{-5}$ M. Increasing more methanol volume (20% methanol added from total surfactant solution) to the solution further decreasing each cmc value and the decreasing in cmc is more obvious. The cmc for Triton X-100 after added 20% methanol is $0.5 \times 10^{-4}$ M, Brij 35 is $5 \times 10^{-5}$ M and mixed surfactant solution system is $1.5 \times 10^{-5}$ M. From this research, we can conclude that mixed surfactant solution system has lower cmc and addition of methanol lowered the cmc value for each single and thus decreased cmc of mixed nonionic surfactant solution system.

Keywords: Mixed Nonionic Surfactants, Pyrene, Critical Micelle Concentration (CMC), Methanol

ABSTRAK

Sifat pengumpulan dalam sistem campuran antara surfaktan bukan ionik dengan surfaktan bukan ionik telah dijalankan dalam kajian ini. Kelarutan pyrene di dalam Triton X-100 dan Brij 35 pada kepekatan yang berlainan telah dinilai dan nilai kepekatatan misel genting (cmc) dapat diperolehi daripada keupayaan pyrene melarut di dalam larutan Triton X-100 dan Brij 35. Spektrometer UV telah digunakan untuk menentukan cmc bagi larutan Triton X-100 dan Brij 35 dari campuran kedua-dua larutan surfaktan tersebut. Cmc antara setiap larutan dan larutan campuran dibandingkan. Daripada kajian ini, cmc bagi larutan Triton X-100 ialah $2 \times 10^{-4}$ M, bagi larutan Brij 35, cmc ialah $8 \times 10^{-5}$ M. Campuran kedua-dua larutan ini memberikan nilai cmc $2 \times 10^{-5}$ M, yang menunjukkan kesan penurunan cmc bagi Triton X-100. Kesetaraan presapan organik terhadap cmc setiap satu larutan dan larutan campuran turut ditentukan. Penambahan 4% isipadu metanol daripada jumlah isipadu larutan surfaktan menurunkan nilai cmc Triton X-100 kepada $1.5 \times 10^{-4}$ M, Brij 35 kepada $6 \times 10^{-5}$ M dan larutan campuran kepada $1.8 \times 10^{-5}$ M. Peningkatan penambahan isipadu metanol (20% metanol daripada jumlah isipadu larutan surfaktan) kepada larutan seterusnya menunjukkan penurunan cmc yang lebih ketara. Cmc bagi Triton X-100 selepas ditambah 20% metanol ialah $0.5 \times 10^{-4}$ M, Brij 35 ialah $5 \times 10^{-5}$ M dan sistem campuran larutan surfaktan ialah $1.5 \times 10^{-5}$ M. Daripada kajian yang telah dijalankan, dapat disimpulkan bahawa sistem campuran larutan surfaktan mempunyai cmc yang lebih rendah berbanding setiap satu larutan dan penambahan metanol merendahkan cmc bagi setiap satu larutan dan seterusnya menurunkan cmc bagi sistem campuran larutan.

Kata Kunci: Campuran Surfactan Bukan Ionik, Pyrene, Kepekatatan Misel Genting (CMC), Metanol
1.0 INTRODUCTION

Surfactants are a group of chemicals that touch our everyday lives in countless ways (Houston, 2006). Surfactant is acronym to the surface active agent. Surfactants can be present in our daily food, drinks, the products that we used to clean ourselves, cars that we drive and clothes that we wear. The quality of our lives and our health is related to the availability and safe use of surfactants.

The surfactants that usually added in our daily usage normally contain more than one type or single surfactant. These mixtures are frequently used in many practical surfactant applications because the solution behaviors of these surfactants can be complementary and are found to yield better performance than a single surfactant (Fan et. al., 2006). The mixed system almost consistently brings about improved interfacial properties compared to the single surfactant system (Fan et. al., 2000). Various physical properties and aggregate morphology are expected when the mixture of the surfactants are added together (Shiloach and Blankschtein, 1998).

In this research, the cmc of two different nonionic surfactants were determined. Triton X-100 and Brij 35 were used in this experimentation. When these surfactants are mixed together at certain concentration, the mixed surfactants will form aggregates known as micelles. The concentration where the first micelle is formed in a surfactant solution is termed as the critical micelles concentration (cmc). The cmc was studied in this research because the improved performance of mixed surfactants is predicted due to this formation of cmc. The
aggregation behaviors of each of these surfactants were experimented and the result of single and mixed nonionic surfactant solution system was compared.

The objectives of this research are:

1. To determine the cmc of single nonionic surfactants (Triton X-100 and Brij 35).

2. To determine the cmc of mixed nonionic surfactant.

3. To compare the cmc of single and mixed nonionic surfactants.

4. To check the effect of added organic solvent (methanol) to the cmc of single and mixed nonionic surfactants.
2.0 LITERATURE REVIEW

2.1 SURFACTANT

Surfactant is a derivation of surface active agent. A surfactant is composed of two parts. It contains a head which is also known as a hydrophilic part and a tail which is also known as a hydrophobic part. A hydrophilic part tends to attract water while the hydrophobic part tends to distance itself from water. These characteristics of surfactant can be said as a “split personality” because surfactant is made up of two parts which have entirely different tendencies, and thus exhibits a unique reaction when it is added in water.

Surfactant is a substance that when dissolved in water gives a product that able to remove dirt from surfaces like human skin, textiles and other solids. Specific functions of surfactants are removing soil or scouring, wetting and rewetting, softening, retarding dyeing rate, fixing dyes, making emulsions, stabilizing dispersions, coagulation suspended solids, preventing foam formation and deforming liquids (Warren, 1998).

Surfactants also exist in our organ system. Throughout the lung it is in fluid form and is very important to reduce the surface tension which contributes to the stability of the alveoli. This essential fluid is a complex substance that contains phospholipids and a number of apoprotein.

Regardless of its origin, the primary property of surfactants are as surface active agent, and thus where ever it exist, it will act as a surface active agent, depending on charge types of the surfactants.
Surfactants are classified according to the nature of the hydrophilic group. The negatively charged of hydrophilic head is known as anionic surfactant, where this type of surfactant is commonly used in cosmetics and personal care products. An example of anionic surfactant is Sodium Dodecyl Sulphate (SDS). Cationic surfactant is another type of surfactant which its hydrophilic head is positively charged. For example, Dodecyl Trimethyl Ammonium Bromide (DTAB) which is commonly used in textiles and fibers products. Another type of surfactant is nonionic surfactant which has a polar but not fully charged hydrophilic head. Polyoxyethylene Lauryl Ether (Brij-35) is an example of nonionic surfactant which usually used in detergents and cleaners products. Another type of surfactant is zwitterionic surfactant where this type of surfactant has both potential positive and negative groups which it charges depends on pH of the medium. As an example, 3-((N, N-Dimethylctylammonio) propanesulfonate inner salt is commonly used in metal processing (Farn, 2006).

2.2 NONIONIC SURFACTANT

Nonionic surfactant is one type of surfactant that is widely used in many fields of applications. One of special properties of this type of surfactant that differentiate it form other type of surfactant is that this surfactant material is electrically neutral. Other than that, the most important advantages can include a significantly lower sensitivity to the presence of electrolytes in the system, a reduced effect of solution pH and the synthetic flexibility of the ability to design the required degree of solubility into the molecule by the careful control of the size of the hydrophilic group.
The most numerous and important type of nonionic surfactant is polyoxyethylene (POE) (Mayers, 2004). This type of nonionic surfactant has a general formula of RX(CH₂CH₂O)ₙH, where R is normally a typical surfactant hydrophobic group, but may also be a polyether such as polyoxypropylene, and X is O, N or another functionality capable of linking the hydrophobe. The n value must be greater than 5 to impart sufficient water solubility to make the materials useful (Mayers, 2004). The cmc of nonionic surfactant is generally low compared to other ionic surfactants.

### 2.2.1 POLYOXYETHYLENE LAURYL ETHER (BRIJ 35)

Polyoxyethylene lauryl ether or commercially known as Brij-35 is widely used in biochemical and chemical processes for its qualities such as high stability, well-dissolved and easily mixing with other typical surfactants for a mixed use (Cheng, 1994). The chemical formula of Brij-35 is C₁₂H₂₅O(CH₂CH₂O)₂₃H. Brij is found to have cmc value of 5 to 9 uM (DETERGENTS, 2009). Brij-35 can be mixed with other types of surfactants such as Sodium Dodecyl Sulphate (SDS) which is anionic surfactant, Dodecyl Trimethyl Ammonium Bromide (DTAB), a cationic surfactant and is also mixed with bacteria, soil and oil to enhance application and improved properties.
2.2.2 ALKYLPHENOL HYDROXYPOLYETHYLENE (TRITON X-100)

Triton X-100 is a commercial name for Alkylphenol hydroxypolyethylene. The molecular formula of Triton X-100 is C$_{14}$H$_{22}$O (C$_2$H$_4$O) n, n is 9 to 10. This type of nonionic surfactant has a structure as shown in Figure 1:

![Structure of Triton X-100](image)

Figure 1: Structure of Triton X-100 (Source: MP Biomedicals, 2009)

Triton X-100 has a physical property of clear colorless viscous liquid. In figure 1, x indicates the average number of ethylene oxide units in the ether side chain. The principle applications of Triton X-100 are in industrial and household detergent applications and in emulsifying agent. The applications are ranging from heavy-duty industrial products to gentle detergents for fine fabrics. Because of that, Triton X-100 is normally mixed with other types of nonionic surfactant or with other classes of surfactants. The predicted cmc of Triton X-100 is 0.2-0.3 mM (Zhu and Feng, 2003).
2.3 MIXED SURFACTANT OF NONIONIC SURFACTANT

The study of analyzing surfactant composition is very important in mixed surfactant solution. This is because mixed surfactant solution exhibits surface properties significantly better than single surfactant. The used of mixed surfactant system is considered as a method for obtaining the optimal performance for any surfactant application such as coating operations, personal care, and petroleum recovery. Thus, a surfactant mixture with a distribution of lengths, or a mixture of two or more different type of surfactants often is a more desirable for the industry.

Theoretically, cmc of surfactant mixtures and their respective components have been developed by considering the effective mole fraction of each species in a binary mixture at the cmc. However, in some cases where there is a sufficient difference between the chain lengths of two surfactants, this theoretical assumption has a deviation. This is due to the relatively small changes in mole fraction of the smaller chain component due to the preferential aggregation of the more hydrophobic material. It is also affected by the difficulty of addition of the longer chain into micelles of the shorter chain. In some findings, the shorter chain may act as an added electrolyte rather than becoming directly involved in the micellization process. This is true for cases where the chain lengths of two surfactants are largely different (Mayers, 2004).

For nonionic surfactant mixtures, mixed cmc value can be predicted by using an equation 1:

\[
\frac{1}{\text{cmc}_{1+2}} = \text{mol fraction 1} / \text{cmc}_1 + 1 - \text{mol fraction 2} / \text{cmc}_2
\]  

(1)
Equation 1 is only acceptable for the cmc value of nonionic mixtures that composed of small different value in each of their single surfactant. However, when two surfactants with very different cmc’s value are mixed, this equation gives a large deviation from its experimental result (Clint, 1975). Although the properties of single nonionic surfactants can be determined experimentally or by the theory, but the mixtures of this type of surfactants cannot be simply predicted from the knowledge of those single components (Bakshi, 2000). For example, a mixture of nonionic surfactants that have approximately the same polyoxyethylene chain but have different in their hydrophobic chain has a smooth decrease in the cmc of the mixture (Mayers, 2004). Besides, mixed micelles are more compact thus generate a more hydrophobic interior (Bakshi, 2000).

The cmc of nonionic-nonionic mixed surfactant system is influenced by both of these nonionic surfactants but, for ionic-nonionic surfactant system, the cmc value is only influenced by the nonionic surfactant (Kiyoshi and Motoharu, 1990). Research conducted by Zhang and Yin (2005) found that the cmc of mixed surfactant is decreased or lower than their single cmc value. In this research, the mixture of polyoxyethylenated alcohols/ Sodium Dodecyl Sulphate, and polyoxyethylenated alcohols/cetyl trimethyl ammonium bromide were investigated. The polyoxyethylenated alcohols represented the nonionic surfactant, Sodium Dodecyl Sulphate (SDS) represented anionic surfactant and cetyl trimethyl ammonium bromide (CTAB) represented cationic surfactant. These mixtures gave a cmc value of 0.11mM and 0.135mM respectively, where this value is significantly lowered than cmc of SDS (7mM) and CTAB (0.9mM) alone.
Due to the natural existence of surfactants in the organisms and nutrients, the nonionic surfactants are also mixed with bacteria, protein, fat and many types of organisms and nutrients, for it to become more functional to the organ system and useful in many applications such as in detergents, cosmetics, enhanced oil recovery, and pharmaceuticals.

The mixtures of nonionic surfactant with different length or other type of surfactants are frequently used in many practical surfactant applications because the solution behaviors of the mixed surfactants can be complementary and are found to yield better performance than a single surfactant (Fan et al., 2006). The mixed system almost consistently brings about improved interfacial properties compared to the single surfactant system (Fan et al., 2000). Various physical properties and aggregate morphology are expected when the mixture of the surfactants are added together (Shiloach and Blankschtein, 1998).

2.4 PYRENE AND SURFACTANT

Pyrene is a group of Polycyclic Aromatic Hydrocarbon (PAHs). Chemical formula of pyrene is \( \text{C}_{16}\text{H}_{10} \) with molecular weight of 202.25 g/mol, and other physical properties of pyrene are melting point and boiling point of 156°C and 404°C respectively, and this compound is colorless crystal-like solid but can also look yellow. Pyrene consists of four aromatic fused rings, as shown in the Figure 2.
Due to the resistance of pyrene to biological degradation, pyrene has the ability to be very persistent in the environment (Leslie, 2004). This type of PAHs group is slightly soluble in organic solvents and insoluble in water. Therefore, surfactant is needed in order to enhance the solubility of pyrene. Because of that, the use of pyrene as an indicator has been widely adapted by the researchers (Huang and Somasundaram, 1996).

Pyrene absorbs light below 350nm by using UV-spectrometer and other spectrofluorometer (Diaz and Velazquez, 2007). This fluorescence activity is depending on the concentration of pyrene (Leslie, 2005). The excimer of pyrene can be avoided at $10 \times 10^{-5}$ M and at concentrations more than $1.0 \times 10^{-4}$ M, pyrene excimer is detected (Krueger, 2002).

The research on a convenient method for determination of cmc has been done by Basu, et.al (2006). In this research, the cmc of both ionic and nonionic surfactants can be conveniently determined from the measurement of UV-absorption of pyrene in surfactant solution. The result on a number of surfactants has agreed with that realized pyrene fluorescence measurements, as well as the cmc value determined from conductometer, tensiometer and calorimeter methods.
Research regarding pyrene in single and mixed surfactant has also been done (Zhu and Chiou, 2001). In this research, the water solubility enhancements of pyrene by both single and mixed surfactant has been evaluated and compared. The solubility of pyrene in water was greatly enhanced by each of Triton X-100, Triton X-405, Brij 35 and SDS, in which the water solubility enhancements increased with increasing surfactant concentrations. The order of pyrene solubility enhanced by surfactant concentrations below the cmc is Triton X-100 > Brij 35 > Triton X-405 > SDS. While for the mixed of anionic and nonionic surfactant mixtures, the order was found to be SDS-Triton X-405 > SDS- Brij 35 > SDS- Triton X-100. The water solubility of pyrene is synergistically enhanced by mixed surfactant micelles because pyrene tend to moves into mixed micelles than into single micelles because the polarity of the former is lower (Zhu and Feng, 2003)

2.5 EFFECTS OF ADDED ORGANIC MATERIAL (METHANOL)

The interaction of surfactants and alcohols have become of greater importance as a result of the intense interest in microemulsions and their potential application in different field of technology (Myers, 2006).

Organic materials with low water solubility can be solubilized in micelles to produce system with substantial organic content (Myers, 2004). In this system, without the presence of surfactants, the solubility would not occur. The added organic materials will change the size of the aggregates and the curve of its surface. Due to these changes, it is expected that the energetic requirements of interactions among the component parts of the surfactants in the
micelle, especially the head groups at the micelle surface will also change. Besides, the changes in the hydrophobic interaction among the hydrocarbon tails due to the insertion of additive molecules into the core may also occur. The combined effect of the presence of this organic material of solubilized material is usually by producing a slight decrease in the measured cmc of the system. When used in combination with chemical surfactants, alcohols are typically referred to as co-solvents or co-surfactants. The term alcohol flooding refers to the use of very high-concentration alcohol solutions or pure alcohol only (CHAPTER 4, 2009). However, the effect of added organic material is substantially smaller than the effect of electrolyte, but it still gives changes to the cmc of the surfactant.

Organic additives that have considerable water miscibility like the lower alcohols, dioxane, acetone, glycol and tetrahydrofuran is expected not participated into the interior of the micelle when present in small amounts. The effects of these materials are considered as minor. When the number of carbon additive is more than 2 carbon molecules, the inherent surface activity of alcohols can start to become significant. Otherwise, these materials may be considered as a co-solvent when it is at high concentrations. Thus, the effect will become major. The properties of surfactant solution are found to have rapid changes when the alcohol used has 4 carbon molecules or more (Myers, 2006).

According to the theory, alcohols are mutually miscible in both water and Non Aqueous Phase Liquid (NAPL) (CHAPTER 4, 2009). Polyaromatic Hydrocarbon is one type of NAPL and because of that, pyrene is considered as NAPL (Glosary, 2009). The partition of alcohol into
the NAPL cause swelling of the NAPL and will reduce the NAPL density. The reduce in NAPL density thus cause changes in micelles properties such as their aggregation size, the hydrophobic core and their surface curve.
3.0 MATERIALS AND METHODOLOGY

The nonionic surfactants used in this research were Alkylphenol hydroxypolyethylene (Triton X-100) and Polyoxyethylene lauryl ether (Brij 35). Pyrene was used as an indicator to determine the cmc of these nonionic surfactants. The solubilisation of pyrene in surfactant provided information of cmc values. Methanol was used as an organic additives added in each nonionic surfactant to determine the effect of organic solvent on the cmc of nonionic surfactants.

3.1 SINGLE NONIONICS

The nonionic surfactants (Triton X-100 and Brij 35) were diluted with distilled water to produce different concentrations of nonionic surfactant solutions which were within the range of cmc value. 0.010g pyrene was weighed and placed into centrifuge tubes. 10ml of distilled water and 5ml of each nonionic surfactant samples were added into the centrifuge tube to solubilize pyrene. The undissolved pyrene was separated after 48 hours, by centrifugation and filtration, according to the method reported by Deo et al., (2002). The pyrene concentration in the supernatant was measured using UV spectrometer at a wavelength of 335 nm. The concentration of pyrene in the supernatant versus surfactant concentration was plotted and the cmc of nonionic surfactant was determined from this graph.
3.2 MIXED NONIONIC SURFACANT

The method used in preparing mixed nonionic surfactant samples was improvised and adapted from method reported by Deo et al., (2002). Each nonionic surfactant was diluted with distilled water to produce 0.20M concentration solution. These two nonionic surfactants were mixed together to form a mixture solution of 0.10M concentration. This mixed solution was diluted with distilled water to produce different concentration solution samples which were in the range of cmc of Triton X-100 and Brij 35. 0.010g of pyrene was placed into centrifuge tubes. 10 ml of distilled water and 5ml of each mixed nonionic surfactant samples were added into these centrifuge tubes. The undissolved pyrene was separated after 48 hours, by centrifugation and filtration. The pyrene concentration in the supernatant was measured using UV spectrometer at wavelength of 335nm. The concentration of pyrene supernatant versus surfactant concentration was plotted and the cmc of mixed nonionic surfactant was determined from this graph.

3.3 THE EFFECT OF ORGANIC SOLVENT ADDITIVE: (METHANOL)

The single and mixed nonionic surfactant samples were prepared as described in part 3.1 and 3.2. 4% and 20% methanol volume of total surfactant solution samples volume were added into each of the samples. Based on the method reported by Deo et al., (2002), the undissolved pyrene was separated after 48 hours, by centrifugation and filtration. The pyrene concentration in the supernatant was measured using UV spectrometer at wavelength of 335 nm. The concentration of pyrene supernatant versus surfactant concentration was plotted and the
changes in cmc value of each single and mixed nonionic surfactant were determined from this graph.
4.0 RESULTS AND DISCUSSION

4.1 CMC OF NONIONIC SURFACTANTS

The cmc for each single nonionic surfactant and mixed nonionic surfactant were determined by plotting the concentration of pyrene supernatant versus the nonionic surfactant solution for various concentrations. The cmc of Triton X-100 was $2 \times 10^{-4}$ M as shown in Figure 3, and this value was within the range of reported values (Zhu and Feng, 2003). For Brij 35, the cmc was $8 \times 10^{-5}$ M as shown in Figure 4. This obtained value was in good agreement with those reported in literature (DETERGENTS, 2009). The cmc of mixed surfactant solution system was lower than cmc of Triton X-100 and Brij 35 at $2 \times 10^{-5}$ M as shown in Figure 5.
Figure 3: Graph of supernatant pyrene concentration versus Triton X-100 at different concentrations shows the cmc of Triton X-100 of $2 \times 10^{-4}$M from the enhancement of pyrene solubility in Triton X-100 at different concentration, determined by UV measurement.