SURFACE PROPERTIES AND AGGREGATION BEHAVIOUR OF HEXADECYLTRIMETHYLAMMONIUM BROMIDE-PALM-BASED CAPRYLIC ACID MIXED SURFACTANT SYSTEMS

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ABSTRACT

Surface properties and aggregation behaviour of mixed surfactant systems with varying molar ratios of hexadecyltrimethylammonium bromide (HTAB) and palm-based caprylic acid (OA) were studied in the present work. The critical micelle concentration (CMC), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}), surface pressure at CMC (π_{CMC}), zeta potential and particle size were determined using instrumentations (e.g., surface tensiometer and particle sizer). CMC of HTAB-OA mixed surfactant systems was about 30% (0.532 mM) to 50% (0.359 mM) lower than HTAB single surfactant system (0.787 mM), indicating better surfactant adsorption efficiency. Results also showed that increasing the molar ratio of OA favoured the formation of micelles at low concentration; thus, lowering both CMC and surface tension. However, Γ_{max} of mixed surfactant systems lowered with OA molar ratio, indicating the mixed surfactant systems tend to form stable ion pairs in bulk solution rather than orientating at the air-water interface. CMC values obtained via surface tension measurement were double confirmed by ultraviolet-visible (UV-VIS) absorbance measurement using dye solubilisation. The particle size of mixed surfactant aggregates (250 ± 50 nm) was 50 times larger than the one found in HTAB surfactant (5.6 ± 0.3 nm). Equimolar mixed surfactant system displayed highest colloids stability and aggregates populations. The results suggested the existence of strong synergism when two oppositely charged surfactants are mixed.

INTRODUCTION

Surfactant is an amphiphilic molecule that can adsorb onto surfaces or interfaces and results in remarkable changes in surface tension when present at low concentration (Ahmad *et al.*, 2007; Bhattarai *et al.*, 2021a; 2021b; Lim *et al.*, 2000; Rub *et al.*, 2021; 2022). Surfactants have various industrial

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applications such as pharmaceuticals, cosmetics, detergents, paints, agrochemicals, automobiles, and oil recovery. For practical applications, mixed surfactant systems are preferred over single surfactant. Mixed surfactant systems attract much interest due to their ability to self-aggregate into various microstructures. The mixing of cationic and anionic surfactants has a strong synergistic effect as this combination possesses the highest degree of charged difference (Khan and Marques, 1999). Thus, a lot of effort has been made to better understand this phenomenon.

The synergism of mixed surfactant systems is due to the strong attractive interactions between oppositely charged surfactants (Bergström and Bramer, 2008). Therefore, mixed surfactant systems

offer better surface activity and display complex phase behaviour. Mixed surfactant systems form aggregates at lower concentrations compared to individual surfactants, giving lower critical micelle concentration (CMC) values (Jiang *et al*., 2014; Tsuchiya *et al*., 2007). In general, headgroups of cationic and anionic surfactants in mixed surfactant systems are attracted strongly to each other and closely packed, giving a low minimum area per molecule (A_{min}) with excess surface concentration (Γ_{max}) (Li *et al*., 2008; Mihelj and Tomašić, 2014). This indicates that mixed surfactant systems have higher surfactant adsorption efficiency and effectiveness.

In aqueous, amphiphilic surfactants self-aggregate into complicated aggregates. Self-aggregation of surfactants can be understood as a mechanism for the hydrophobic tail of surfactant to minimise contact with water, while the hydrophilic headgroup presents the balancing force to prevent surfactant from being expelled completely as the separated phase. Different kinds of aggregates like mixed micelles, vesicles and microemulsion are formed from mixed surfactant systems. The most popular microstructure is a vesicle that can act as a vehicle to carry active ingredients in the pharmaceutical industry (Bramer, *et al*., 2007). The potential application of surfactant vesicles in the pharmaceutical industry as drugs, gene delivery systems and even microreactor attracts the attention of researchers worldwide (Caillet *et al*., 2000; Mauryaa *et al*, 2020; Wani *et al*., 2019a; 2020). Studies showed mixed surfactant systems formed vesicles spontaneously in dilute aqueous solutions (Kaler *et al*., 1989; 1992).

Even though mixed surfactant systems possess good surface properties and complex aggregation behaviour, some studies showed mixing of cationic and anionic surfactants tend to form precipitates, especially at an equimolar ratio of cationic and anionic surfactants (Horbaschek *et al*., 2000; Kaler *et al*., 1992). This may affect their subsequent applications. The studies indicated that characteristics of mixed surfactant systems are affected by two major factors, electrostatic interactions of hydrophilic headgroup and hydrophobic interactions between hydrocarbon chains (Kaler *et al*., 1989; Marques *et al*., 2003; Wani *et al*., 2019b). In other words, surfactants self-aggregate to achieve a better balance of double-layer electrostatic interactions and packing properties, resulting in complex phase behaviour. These two factors are influenced by temperature, molar ratios, the structure of surfactant, chain length, co-solvent, ionic strength, *etc*. (Sohrabi *et al*., 2008).

In previous studies, the solubility of mixed surfactant systems was closely related to headgroup chemistry (Tomašić *et al*., 1991) and the packing of hydrocarbon chains (Silva *et al.,* 2007). The mixing ratio of surfactants was found to govern self-aggregation behaviour (Kume *et al*., 2008; Zhao

et al., 2009). Generally, the tendency of micelles formation increased with surfactant concentration and ionic strength (Hao and Hoffmann, 2004). When ethanol was added to mixed surfactant systems, a significant increase in the synergism effect was observed (Aslanzadeh and Yousefi, 2014; Huang *et al*., 1999). Therefore, a desired mixed surfactant system can be modified with the nature of the compounds to give different attractive interactions, molecular size and phase behaviour.

Understanding the physico-chemical properties of mixed surfactant systems is theoretically and practically important as single surfactants are rarely used in industrial applications. In the present work, we focus on the study of mixed surfactant systems with varying molar ratios of hexadecyltrimethylammonium bromide (HTAB) and palm-based caprylic acid (OA). OA is a natural-existing surfactant, and it exhibits better biodegradability compared to synthetic surfactants. OA is known to have low solubility in water. Interestingly, HTAB-OA mixed surfactant systems showed good surface activity, and OA solubility increased in the mixed surfactant system. CMC and surface pressure at CMC (π_{CMC}) of mixed surfactant systems were determined, Γ_{max} and A_{min} were calculated using Rubingh's theory from surface tension data. CMC was found to be closely related to dye solubility. The effect of different molar ratios HTAB and OA on zeta potential and particle size were also studied.

MATERIALS AND METHODS

Materials

The cationic surfactant, HTAB, purity of 99%, was purchased from Sigma-Aldrich, Switzerland. Anionic surfactant, OA derived from palm oil, purity of 99%, was obtained from Wilmar PGEO Edible Oils Sdn. Bhd., Malaysia. ORASOL dye was obtained from Ciba Specialty Chemicals Inc., Switzerland. All chemicals were used without any treatment. Distilled water having 1.6 μS cm^{-1} was used throughout the experiments.

Methods

Sample preparation. A stock solution of HTAB with a concentration above CMC was prepared. Mixed surfactants were prepared by adding the desired amount of OA into the HTAB solution according to molar ratios 5:1, 5:3 and 1:1. The mixed surfactant systems were kept for 24 hr in a water bath at 30°C and prepared in distilled water.

Surface tension measurement. CMC for HTAB and mixed surfactant systems were determined by

surface tension measurement using the du Nouy ring tensiometer (KSV Sigma 70, Helsinki). Surface tension measurements were tested at 25 ± 0.1°C. The concentration of the surfactant was varied by diluting stock surfactant with water using a Hamilton microsyringe. The measured surface tension values were plotted against surfactant concentration. Before every measurement, the ring was flamed clean.

In general, interfacial properties of surfactants at the air-water interface were studied by measuring the surface excess concentration Γ_{max}, mol m^{-2} (Rosen, 1989; Tadros, 2005; Wong $et\ al.$, 2012). The Γ_{max} value is known as surfactant adsorption effectiveness. The concentration of surfactant is usually higher in the surface monolayer compared to the bulk system. Γ_{max} can be calculated from Gibbs isotherm following Equation (1) below:

$$\Gamma_{max} = -\left(\frac{1}{2.3\ nRT}\right)\left(\frac{d\gamma}{d\ln C}\right) \qquad (1)$$

where C is the concentration of surfactant, γ is surface tension, R is gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. n prefactor is the number of solute species at the interface whose concentration at the interface changes with the value C.

From Γ_{max} values, we can calculate the minimum area per molecule (A_{min}) at the air-water interface from Equation (2) below:

$$A_{min} = \frac{10^{18}}{\Gamma_{max}N_A} \qquad (2)$$

where N_A is Avagadro's number and Γ_{max} and A_{min} are expressed in mol m^{-2} and nm^2, respectively.

UV-VIS measurements. A suitable range concentration of surfactants below and above CMC were prepared in distilled water. Highly concentrated dye in ethanol was transferred into a small vial and ethanol was evaporated. Then, a constant volume of different concentration surfactants was added into the vial containing the excess amount of dye and vortex. After being equilibrated for 24 hr, the surfactant was centrifuged to separate the undissolved dye. The supernatant containing surfactant and dissolved dye were measured using a double-beam UV-VIS spectrophotometer (Varian Cary® 50, USA).

Particle size measurement. The size of surfactant aggregates was determined using the dynamic light scattering (DLS) technique (Malvern Zetasizer Nano S, Malvern, Worcestershire, United Kingdom). The sample was loaded into cuvettes and measured at 25.0 ± 0.5°C after 5 min of thermal equilibration. The light-scattering cells were rinsed with acetone prior to use to ensure it was dust-free. Measurement was performed at λ = 638.2 nm, in back-scattering mode, at cell position 4.65 and attenuator 11. A digital correlator analysed the fluctuations of scattered light intensity. Data obtained were analysed using the CONTIN method.

Zeta potential measurement. Laser-Doppler accessory of DLS equipment was used for zeta potential measurement (Tadros, 2005). The sample was loaded into a U-shape cuvette with gold electrodes and measured at 25.0 ± 0.5°C. Zeta potential was related to electrophoretic mobility, μ and calculated from Equation (3) below:

$$\xi = \mu\left(\frac{4\pi\eta}{\varepsilon'}\right) \qquad (3)$$

where η is the viscosity of the solution and ε' is the static dielectric constant.

RESULTS AND DISCUSSION

Determination of Critical Micelle Concentration (CMC) of Mixed Surfactant Systems

The surface tension of surfactant decreases significantly with increasing concentration of surfactant until a particular concentration known as CMC (Tadros, 2005). When CMC is achieved, surfactant molecules self-aggregate into larger units known as micelles. The most common technique used for the determination of CMC is the break-in surface tension or electrical conductivity *vs.* concentration curve. In the surface tension against concentration plot, the intersection point of two trend lines is generally used to obtain the CMC of a surfactant solution. CMC in aqueous solution can be greatly affected by surfactant concentrations, temperature, pH, chain length of surfactants, mixtures of surfactants, headgroup chemistry of surfactants and their intermolecular interactions (Kume *et al.*, 2008; Marques *et al.*, 2003).

The surface tension of different molar ratios HTAB:OA mixed surfactant systems is shown in *Figure 1*. When the concentration of surfactants increases, surface tension decreases rapidly until a breakpoint where it remains almost constant. This level-off point surfactant concentration corresponded to CMC. CMC of HTAB was 0.787 mmol dm^{-3}, comparable to previous studies (Murphy and Taggart, 2002; Wong *et al.*, 2012; Zhang *et al.*, 2015). *Table 1* shows the CMC of different molar ratios of HTAB:OA mixed surfactant systems.

The surface activity of mixed surfactant systems increased with the increasing molar ratio of OA. All HTAB:OA mixed surfactant systems showed approximately 30% to 50% lower CMC compared to conventional single-tailed surfactant HTAB. The equimolar ratio of HTAB:OA exhibited the lowest CMC of 0.359 mmol dm^{-3}. This implied mixed surfactant systems formed micelle easier than HTAB.

This was supported by previous studies that indicated the effective aggregating ability of mixed surfactants (Jurasin *et al.*, 2013; Wong *et al.*, 2012; Zhao *et al.*, 2009). A recent study also showed binary surfactant system achieved lower CMC than the ideal CMC estimated from the Clint equation and deviated negatively from ideal behaviour (Azum *et al.*, 2016). Increasing the concentration of OA generated a driving force for aggregation to occur and therefore lowered the CMC of the system. This special phase behaviour could be explained by synergistic interactions of mixed surfactant systems. Synergism is more favourable for surfactant mixtures with a higher degree of charge difference (Khan and Marques, 1999). When OA was added, electrostatic interaction within the system was disturbed. The addition of anionic OA reduced electrostatic repulsion force between the cationic

headgroup of HTAB in micelles, easing micelle formation. This phenomenon could be described as OA lowered surface charge density of micelles by entering the polar area of micelles (Huang *et al.*, 1999). However, the reduction of charge density at the micellar surface was caused by a higher degree of counterion dissociation in mixed surfactant systems as OA was present in micelle (Aslanzadeh and Yousefi, 2014). The hydrophilicity of the surfactant system decreased with increasing OA; the reduction of hydrodynamic radius enables a more energetically favourable aggregation (Perinelli *et al.*, 2016). Subsequently, fewer surfactant molecules were required to orient at the air-water interface, and hence CMC was lowered.

Generally, one of the common ways to discuss the performance of surfactants is surfactant adsorption efficiency. Surfactant adsorption efficiency refers to the surfactant concentration required to produce a given surface tension reduction at experimental conditions. Mixed surfactant systems containing OA displayed lower surface tension; this showed mixed surfactant systems are highly surface-active under experimental conditions. From this experiment, increasing the molar ratio of OA gave a better surfactant adsorption efficiency.
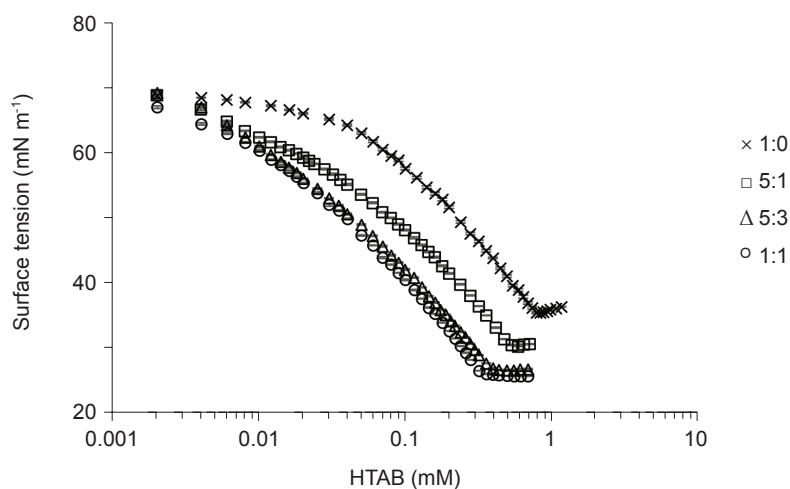

*Figure 1. Surface tension measurements of different ratios (cross - 1:0; open square - 5:1; open triangle - 5:3; open circle - 1:1)
of HTAB:OA mixed surfactant systems at 25.0 ± 0.5°C.*

**TABLE 1. CRITICAL MICELLE CONCENTRATION (CMC), SURFACE EXCESS CONCENTRATION (Γ_{MAX}),
MINIMUM AREA PER MOLECULE (A_{MIN}) AND SURFACE PRESSURE AT CMC (Π_{CMC}) FOR AQUEOUS
HTAB SOLUTION AT DIFFERENT MOLE RATIOS OF OA SYSTEMS AT 25.0 ± 0.1°C**

System (HTAB:OA)	CMC (mmol dm^{-3})		$\Gamma_{max} \times 10^{-6}$ (mol m^{-2})	A_{min} (Å^2)	πCMC (mN m^{-1})
	*ST	*A			
1:0	0.787	0.72	2.26	73.54	35.06
5:1	0.532	0.50	2.20	75.58	40.03
5:3	0.396	0.30	2.16	77.04	43.60
1:1	0.359	0.30	2.12	78.17	44.50

Note: *ST and *A are CMC values obtained from surface tension and absorbance measurements, respectively.

Air/Water Interfacial Properties of Mixed Surfactant Systems

Surfactants lower the surface tension of a solution by forming a monolayer spontaneously at the air-water interface. This is very dependent on the effectiveness of surfactant adsorption, which is another way to discuss the performance of surfactants. Surfactant adsorption effectiveness is defined as the maximum adsorption a surfactant can produce regardless of concentration at given experimental conditions. Γ_{max} and A_{min} were calculated from the Gibbs adsorption equation to determine surfactant adsorption effectiveness. Γ_{max} for all surfactant systems were found to be in the range of 2 to 4×10^{-6} mol m^{-2}, which was similar to single-chain surfactant (Tadros, 2005). Hence, all surfactant systems had a high tendency to adsorb onto the air-water interface. All the HTAB-OA mixed surfactant systems have lower Γ_{max} but higher A_{min} than HTAB.

Single-tailed HTAB system showed the highest Γ_{max} of 2.26×10^{-6} mol m^{-2} and, consequently, the lowest A_{min}, suggesting HTAB is able to form a more closely packed monolayer at the air-water interface. This is because monomeric tails of HTAB are oriented perpendicularly to the air-water interface in a close-packed arrangement. Increasing OA molar ratio in mixed surfactant systems was followed by a slight decrease in Γ_{max} value, from 2.20×10^{-6} mol m^{-2} to 2.16×10^{-6} mol m^{-2} and eventually 2.12×10^{-6} mol m^{-2} for 5:1, 5:3 and 1:1 of HTAB:OA. The calculated A_{min} values were also in agreement with Γ_{max} values for mixed surfactant systems. A_{min} of mixed surfactant systems increased with the OA molar ratio.

This result further proved the synergistic effect in the HTAB-OA mixed surfactant systems. When the molar ratio of OA increases, OA and HTAB tend to form ion pairs which are stable in bulk solution, reducing the tendency to orient at the air-water interface monolayer. This could be explained in terms of better penetration of the surfactant hydrocarbon molecules chains into the air-water interface (Murphy and Taggart, 2002). Our finding was in parallel with the previous study by Aslanzadeh and Yousefi (2014). A_{min} was found to be higher in the mixed surfactant system, indicating surfactants were closely packed at the air-water interface with an almost perpendicular orientation (Azum et al., 2016). This is, however, in contrast to the previous studies that stated mixed surfactant systems induced effective reduction of A_{min} due to strong interaction between hydrophilic headgroups of cationic and anionic surfactants that are packed densely at the air-water interface (Li et al., 2008; Mihelj and Tomašić, 2014).

Assuming HTAB is arranged perpendicularly to the air-water interface, the effectiveness of adsorption is controlled by the size of the hydrophilic headgroup, especially when the cross-sectional area of the hydrophilic headgroup is larger than that of the hydrophobic chain (Rosen, 1989). More ion pairs formed when the concentration of OA increased. Since cationic and anionic headgroups were held tightly by electrostatic interaction and appeared as a single molecule, the area occupied by the hydrophilic headgroup was larger than a cross-sectional area of the hydrophobic chain. Similarly, as stated earlier, fewer surfactant molecules adsorbed at the surface of saturation, resulting in lower Γ_{max} with higher A_{min}.

π_{CMC} was the reduction of surface tension, closely related to surface tension. Higher π_{CMC} means more reduction of surface tension occurred, so the surfactant was more surface-active. Atoms formed at the outmost layer of the air-water interface play an important role in surface tension. The contribution of the methylene group in surface energy was much greater than the methyl group, resulting in lower π_{CMC}. Even though the area occupied by the methylene group increased more than the methyl group when OA concentration increased, a less compact arrangement of surfactant molecules in a mixed surfactant system leads to a high π_{CMC} value.

From here, we can conclude that the packing and orientation of surfactant molecules at the air-water interface was the main factor affecting the effectiveness of surfactant adsorption. In terms of surfactant adsorption effectiveness, HTAB-OA mixed surfactant systems were less effective as their Γ_{max} is much lower and A_{min} is higher than a single surfactant system.

CMC of Mixed Surfactant Systems from Dye Solubilisation

For several decades, dye solubilisation was used as one of the methods for the determination of CMC (Hartley, 1938). By using UV-VIS spectroscopy, the corresponding absorption peak of dye in the visible light region can be revealed. CMC of surfactants could be obtained by plotting the absorbance of a dye-surfactant solution against surfactant concentration. Similar to surface tension, CMC is the intersection point of two trend lines or the point where absorbance starts to increase. Surfactants with low CMC were generally known to enhance the solubility of hydrophobic compounds, including dye.

CMCs of mixed surfactant systems obtained from absorbance measurement are shown in *Table 1*. The results were in good agreement with CMC obtained from surface tension measurement. CMC of mixed surfactant systems decreased with an increase in OA molar ratio. In the full UV-VIS absorbance spectrum of red dye solubilised in HTAB, the corresponding maximum absorbance (λ_{max}) was 533 nm. All HTAB-OA mixed surfactant

systems had the same red dye solubilisation pattern as HTAB. At concentration below CMC, no solubilisation of red dye occurs and thus, resulting in extremely low absorbance with a plateau trend. When CMC was reached, absorbance increased rapidly with increasing surfactant concentration. This suggested red dye solubilisation took place at the CMC of the surfactant. At CMC, surfactants self-aggregate into micelles, accommodate dye within micelles and dissolve in solution (Tadros, 2005). This clearly indicated that surfactant micelles are responsible for improved dye solubilisation, which had been proven previously (Tehrani-Bagha *et al.*, 2013; Tehrani-Bagha and Holmberg, 2013). Decrement of CMC implied more micelles present at constant concentration, and more dye could be accommodated into micelles. Again, the results showed that increased OA concentration in mixed surfactants system improved dye solubilisation, indicating better surface activity.

Determination of Zeta Potential and Particle Size of Mixed Surfactant Systems

Dynamic light scattering measurements were carried out to determine zeta potential and particle size at different molar ratios of HTAB:OA mixed surfactant systems. Zeta potential is one of the commonly used parameters to evaluate the stability of the colloidal system. It is a measure of electrostatic

interactions in terms of charge repulsion or attraction between particles. Suspension with low zeta potential is known to be unstable as they aggregate or flocculate readily. Suspension with zeta potential values ± 30 mV or higher is considered to have good colloids stability because the particles tend to repel each other from coagulating. So, zeta potential is the energy barrier that prevents particles from approaching each other.

Results for zeta potential and particle size of different molar ratios HTAB:OA of mixed surfactant systems are shown in *Figure 2-5*. Zeta potential results indicated mixed surfactant systems had greater colloid stability. HTAB cannot form a stable colloid system as it showed low zeta potential. All mixed surfactant systems displayed higher zeta potential than HTAB, but only ratios 5:3 and 1:1 HTAB:OA showed zeta potential higher than 30 mV. The zeta potential of mixed surfactant systems increased with a molar ratio of OA. Therefore, an increase in zeta potential of colloids stability can be attributed to the addition of OA. At a molar ratio 5:1 HTAB:OA, the amount of OA added is still not sufficient to stabilise the colloid system as there are a lot of free HTAB molecules. When more OA was added, more ion pair was formed, and the stability of colloids was enhanced. At the equimolar ratio, zeta potential increased sharply after CMC. This indicates that the aggregates formed were stable. Mixed surfactant systems in the previous study also showed good colloids stability, especially at equimolar ratio (Wu *et al.*, 2014).
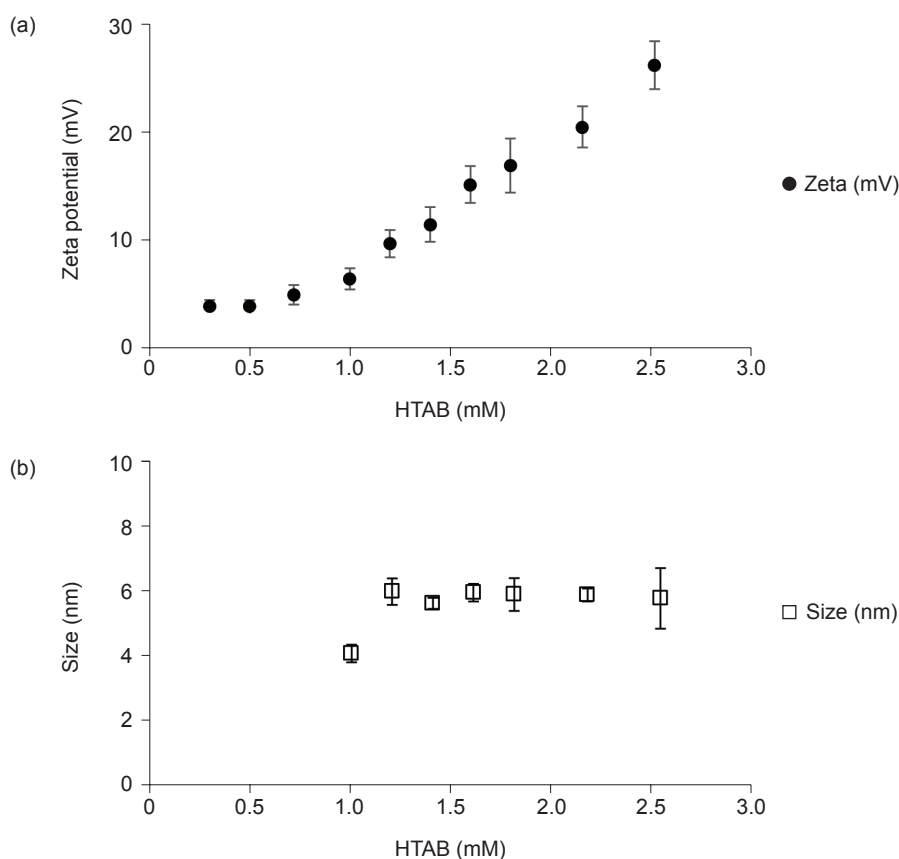

Figure 2. (a) Zeta potential, and (b) particle size measurement of HTAB surfactant solution at 25.0 ± 0.5°C.

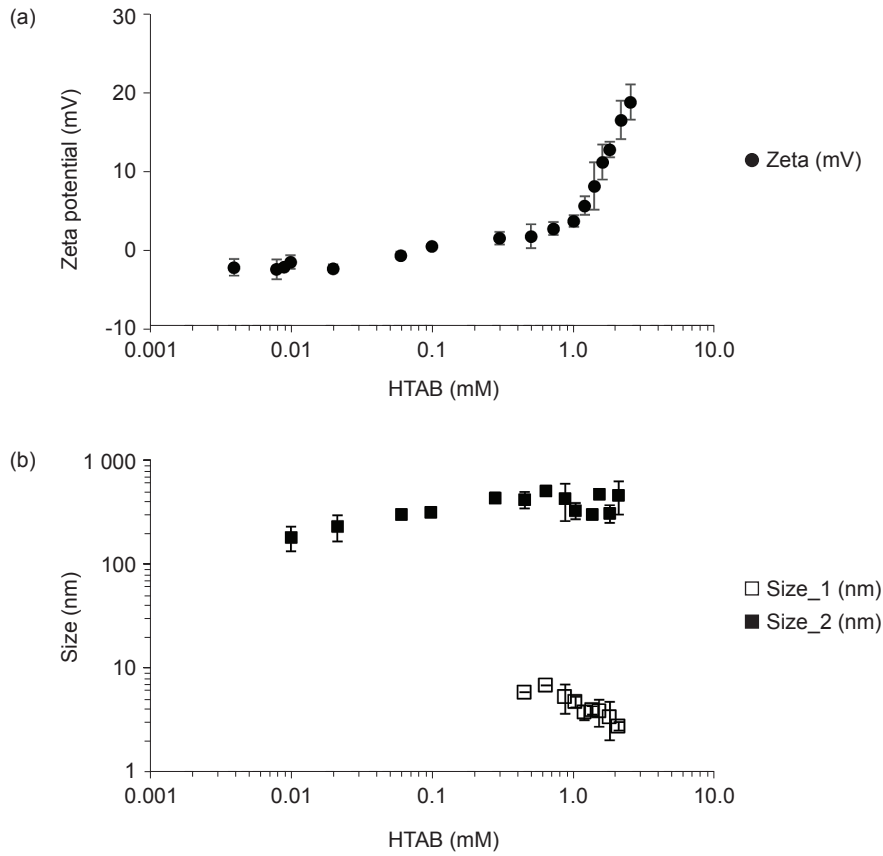*Figure 3. (a) Zeta potential, and (b) particle size measurement of ratio 5:1 of HTAB:OA mixed surfactant systems at 25.0 ± 0.5°C.*

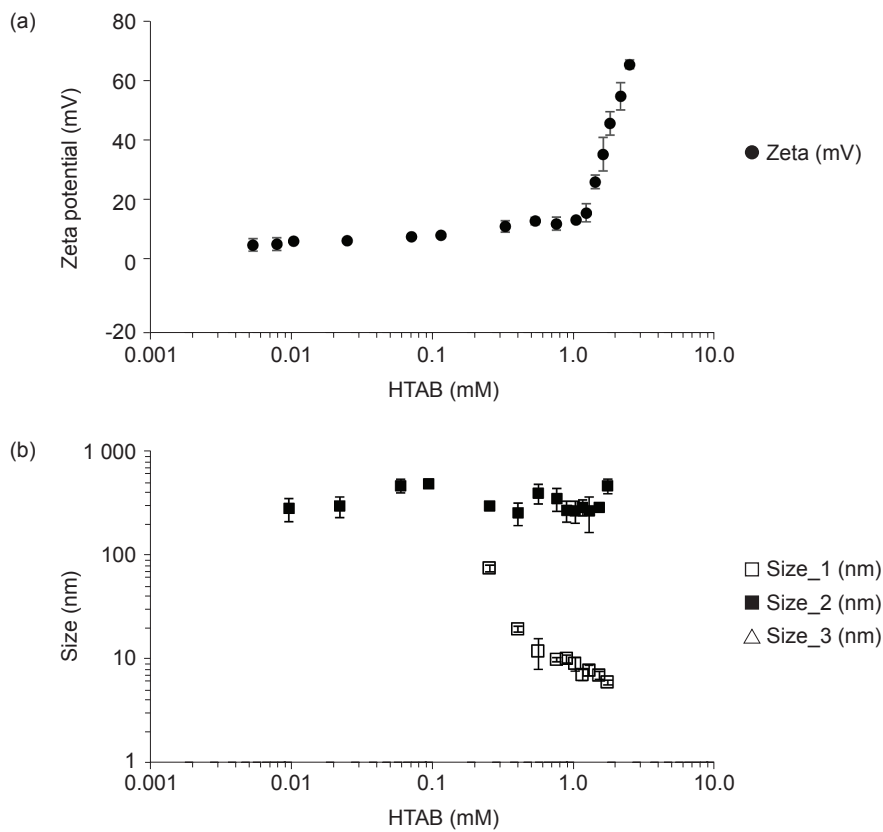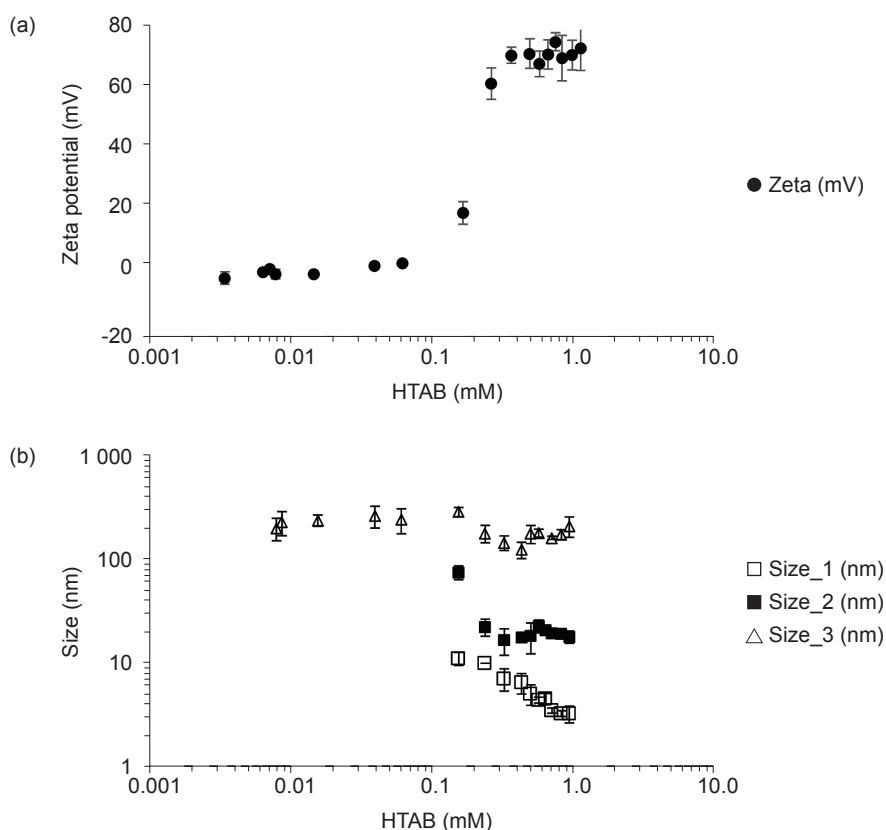*Figure 4. (a) Zeta potential, and (b) particle size measurement of ratio 5:3 of HTAB:OA mixed surfactant systems at 25.0 ± 0.5°C.*

Figure 5. (a) Zeta potential, and (b) particle size measurement of ratio 1:1 of HTAB:OA mixed surfactant systems at 25.0 ± 0.5°C.

For a single HTAB surfactant system, only a type of population was found, and the particle size remained small, less than 10 nm. The particle size increased with increasing of OA. Besides, an increase in OA leads to the appearance of a second population with larger particle size for 5:1 and 5:3 molar ratios HTAB:OA. Interestingly, a third population was discovered with a further increment of OA to equimolar ratio. The previous studies also discovered a second population when the molar ratio of anionic surfactant increased; wide size distribution also implied the existence of phase transition (Aslanzadeh and Yousefi, 2014; Jurasin *et al.*, 2013). Other than that, the mixed surfactant system was found to have larger aggregates than simple micelles formed by the pure surfactant system (Nabi *et al.*, 2015). We may describe the smallest aggregates as monomer micelles, medium aggregates as unilamellar vesicles and largest aggregates as multilamellar vesicles. This showed that mixed surfactant systems have complex phase behaviour. Herein, we suggested that mixed surfactant systems displayed wider size distribution and colloids stability than HTAB.

CONCLUSION

In this experiment, mixed HTAB-OA surfactant systems exhibited higher surface activity compared to a single surfactant system, HTAB. CMC and surface tension values of the mixed surfactant system decreased with a molar ratio of OA. Interactions within the mixed surfactant systems increased because OA increased the synergism by acting as the driving force for aggregation to occur. In other words, surfactant adsorption efficiency increased with the increasing molar ratio of OA. The mixed surfactant systems with the low CMC enhanced the solubility of hydrophobic dye by accommodating dye molecules into the hydrophobic core of micelles. The mixed surfactant systems exhibited complex phase behaviour with good colloid stability. Among all tested mixed surfactant systems, the equimolar ratio mixed surfactant system was found to have the highest surfactant adsorption efficiency, highest colloids stability and complex phase behaviour (Wani *et al.*, 2019b; Wong *et al.*, 2012). In conclusion, the addition of OA into the HTAB surfactant system was found to increase the synergism effect of the mixed surfactant system.

ACKNOWLEDGEMENT

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