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PHYSICO-CHEMICAL PROPERTIES OF MIXED ANIONIC/CATIONIC SURFACTANT SOLUTION: MIXTURES OF SODIUM LAURATE METHYL ESTER α-SULPHONATE AND TETRADECYLTRIMETHYLAMMONIUM BROMIDE

WONG, S P*; LIM, W H; CHENG, S F* and CHUAH, C H***

ABSTRACT

Interface activity between liquid and air (liquid/air) of palm-based anionic surfactant sodium laurate methyl ester α-sulphonate (C_{12}MES), cationic surfactant tetradecyltrimethylammonium bromide (TTAB) and their mixtures at various mixing ratio was investigated using surface tensiometer. Variation of surface tension with concentration was used to determine the critical micelle concentration (CMC) of the individual surfactants as well as their mixtures at different mixing ratios. It was observed that the CMC for the mixed surfactants were 10 times lower than its individual counterpart. This showed that the surfactant mixtures were more effective and had higher surface activity than their single components. The surface tension at CMC for surfactant mixtures were around 25 mN m^{-1}, where as for single surfactants, the value was above 28 mN m^{-1}. Foaming properties (such as foaming power and foaming stability), wetting and emulsification performance of the mixed surfactant systems was also evaluated at different water hardness in this work. Mixed surfactants especially at equimolar mixing ratio were found to exhibit superior performance as compared to their individual parent surfactants.

Keywords: surface activity, mixed surfactants, foaming, wetting, emulsification.

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INTRODUCTION

Surfactants are amphiphilic compound consisting of two moieties namely hydrophilic head and hydrophobic tail. Their unique behaviour to preferentially self-assemble at the interface is an important property in cleaning and detergent industries (Saiyad *et al.*, 1998; Aishah *et al.*, 2007). Generally, performance of a cleaner or detergent is very much linked to the interfacial activity of a surfactant which includes liquid/air, liquid/solid and liquid/liquid interfacial activities. It is also known that interfacial activity is greatly influenced by the attractive and repulsive forces between the surfactant molecules. In the case of single ionic surfactants, hydrophilic group usually contribute repulsive forces to the system while hydrophobic region of the surfactants will contribute attractive forces.

To achieve better performance for detergent and cleaning product, mixed surfactants are commonly used to lower electrostatic repulsive forces between the surfactant heads. One of the best combinations

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* Chemistry Department, Faculty of Science,
University of Malaya,
50603 Kuala Lumpur, Malaysia.
** Malaysian Palm Oil Board,
P. O. Box 10620, 50720 Kuala Lumpur,
Malaysia.
E-mail: limwen@mpob.gov.my

to reduce such repulsive forces is by mixing anionic and cationic surfactants. The oppositely charged surfactants can act as counterions to each other and thus screen the repulsive forces (Sohrabi *et al.*, 2008; Tondre and Caillet, 2001; Li and Liu, 1994).

Foam plays a very crucial role in many detergents and personal care products. The volume of foam produced is often used as an indicator for product quality (Broze, 1999). Arrangement of surfactant molecules at liquid/air interface have direct influence on volume of foam produced and its stability. Besides that, ability to adsorb onto a solid surface is also an important property in detergent and personal care products. It can assist in removing unwanted substance or alter the wetting characteristic of a surface (Myers, 1988). In this study, we have chosen immersional wetting method to determine the interactions between surfactants and solid.

Many detergent and cleaning products occur in emulsions which involve mixing of at least two immiscible liquid. This heterogeneous dispersed system has an extremely large liquid/liquid interfacial area and is thermodynamically unfavoured. By adding surfactants into the system, their molecules will readily adsorb at the two immiscible liquids interface and thus stabilize the system. Emulsion stability is very important as it hinders the system from separating into two distinct phases (Broze, 1999).

In this present work, surface properties of palm-based anionic surfactant sodium dodecyl methyl ester sulphonate (C_{12}MES) and cationic surfactant tetradecyltrimethylammonium bromide (TTAB) mixtures were investigated. This includes determination of critical micelle concentration (CMC) and surface tension at CMC. The anionic/cationic mixed surfactants were also tested for its foaming, wetting and emulsification abilities.

EXPERIMENT

Materials

TTAB (99%) was purchased from Aldrich and C_{12}MES were obtained from SME pilot plant of Advanced Oleochemical Technology Division (AOTD), Malaysian Palm Oil Board (MPOB). Calcium chloride ($CaCl_2.2H_2O$, 99%) was purchased from Merck and magnesium sulphate ($MgSO_4.7H_2O$, 99%) from BDH Chemicals. All chemicals were used without further purification. Test fabrics that were used in wetting test were AS-9 (soiled cotton) and cotton. Both fabrics were cut into 2 cm × 2 cm by dimension.

Preparation of Surfactant Solutions

The single surfactant stock solutions were prepared with concentration ranging from 1 mM to 40 mM. Mixed surfactants were prepared by mixing stock solutions of respective surfactant according to the desired C_{12}MES: TTAB molar ratios, *i.e.* 5:95, 20:80, 40:60, 60:40, 80:20 and 95:5.

Preparation of Hard Water

A stock solution of hard water (5000 ppm $CaCO_3$) was prepared by dissolving 4.41 g of $CaCl_2.2H_2O$ and 4.93 g of $MgSO_4.7H_2O$ in 1000 ml of deionized water. Appropriate volume of the stock solution was used to prepare water of other hardness (50 ppm and 350 ppm).

Surface Tension Measurement

CMC of the surfactant solution was determined by surface tension measurement using a du Nouy ring tensiometer (KSV Sigma 70, Helsinki) at 25.0 ± 0.1°C. Mixed surfactant concentration was varied by adding a stock surfactant solution of known concentration to a known volume of water in a vessel using a Hamilton microsyringe. The change in surface tension values were plotted as a function of surfactant concentration.

Foaming Test

Foaming test was conducted by stroking the surfactant solution (0.1% w/v concentration) for 30 times using a standard plunger and measuring cylinder. The height of foam produced was measured immediately (foaming power) and after 5 min (foaming stability). The foaming properties were further tested at different water hardness conditions.

Wetting Test

Wetting performance of the surfactant solutions were tested on 2 cm × 2 cm test fabric (AS-9 and cotton) which was conditioned for at least 24 hr. The test fabric was carefully placed on the surfactant samples surfaces. Time was recorded as the test fabric touched the surface of the solutions and became completely immersed. The test fabrics were also tested in different water hardness conditions.

Emulsification Test

Emulsification test was carried out by mixing an equal volume of surfactant solutions with oil.

The mixtures were vortexed for 1 min and the time needed for the emulsion to achieve 10% phase separation was recorded. The test was further examined in different water hardness conditions.

RESULTS AND DISCUSSION

Critical Micelles Concentration (CMC)

Figure 1 shows the surface tension measurement of selected C_{12}MES/TTAB mixtures. CMC of the mixed systems were obtained at the interception between the descending slope and horizontal constant line in the surface tension plots, (γ), against concentration, (M). There were no minimum surface tension values observed in the surface tension versus concentration curve for all the mixed systems. This indicated the absence of surface-active impurities in the systems (Frese *et al.*, 2003; Murphy and Taggart, 2002).

CMC of pure TTAB, C_{12}MES and their mixtures were compared in *Figure 2*. The graphs showed that the CMC for mixed surfactants were at least 10 times lower than both single surfactants. Likewise, surface tensions at CMC for the mixed systems were also lower than the individual surfactants where the surface tension at CMC for mixed surfactants were around 25 mN m^{-1}, while single surfactants was above 28 mN m^{-1}. This showed that the surfactant

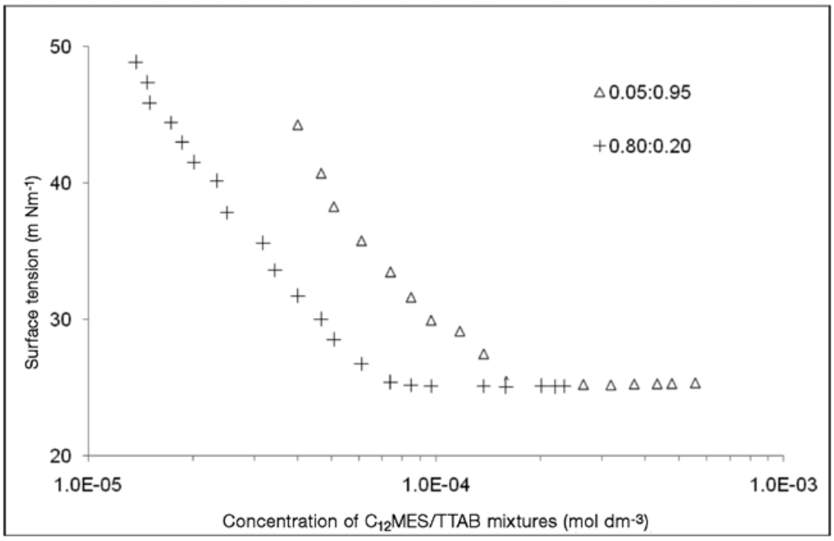

Figure 1. Plots of surface tension against concentration for C_{12}MES and TTAB mixtures at 25 ± 0.1°C.

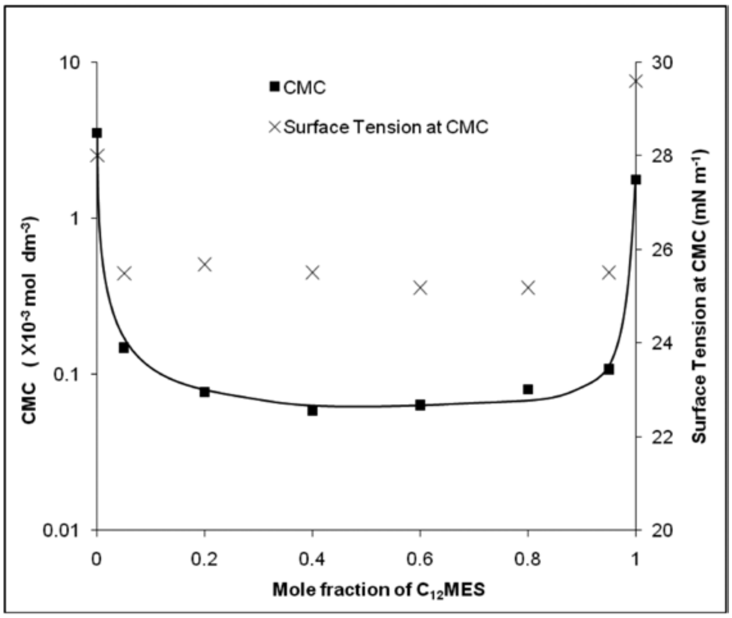

Figure 2. Plots of CMC values and surface tension at CMC for C_{12}MES, TTAB and their mixtures at various mixing ratio at 25 ± 0.1°C.

mixtures were more effective and had higher surface activity than as a single component. This might be due to the oppositely charged surfactant molecule heads were packed more closely and thus allowed more surfactant molecules to be assembled on the liquid/air interface. When more surfactant molecules were packed on the liquid/air interface, the orientation of water molecules at the surface solution was more effectively disturbed and thus reducing the surface tension (Harkot and Janczuk, 2008).

Foaming Test

The results for foaming power and foaming stability at different water hardness are indicated in *Figure 3*. From the graph, we could observe a maximum foaming performance for mixed surfactants near its equimolar at 0 ppm (distilled water) and 50 ppm water hardness. As the charged amphiphiles were more equally paired, the electrostatic repulsion between similarly charged amphiphiles was neutralized. This lead to a closer packing of the surfactant heads and promoted the formation of planar lamellar structure at the surface (Tomasic *et al.*, 1999). Such lamellar structure also contributes to better stability of foams (Anil and Wasan, 1988).

Foaming power and foaming stability results at 50 ppm water hardness were also superior when compared to that in 0 ppm water hardness. The presence of salts in the surfactant solutions could have reduced electrostatic repulsions between the surfactant heads and thus induced micelles formation (Hao *et al.*, 2006). However, at 350 ppm water hardness, foaming power and foaming stability of mixed surfactants near equimolar seemed to deteriorate quite substantially. These phenomena were caused by the precipitation of mixed anionic/cationic surfactants occurred near equimolar which subsequently decreased their efficiency.

Wetting Performance

Testing of detergency ability is always represented by wetting ability of the systems since both processes involved liquid/solid interface activity. *Figure 4* shows the wetting test results on cotton (with and without soiled) in different

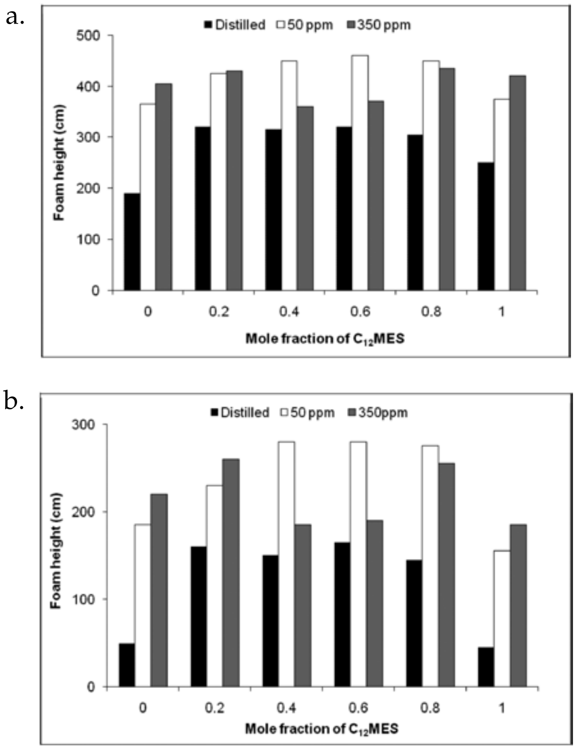

Figure 3. Foam height of C_{12}MES, TTAB and their mixtures at various mixing ratios for (a) foaming power and (b) foaming stability in different water hardness.

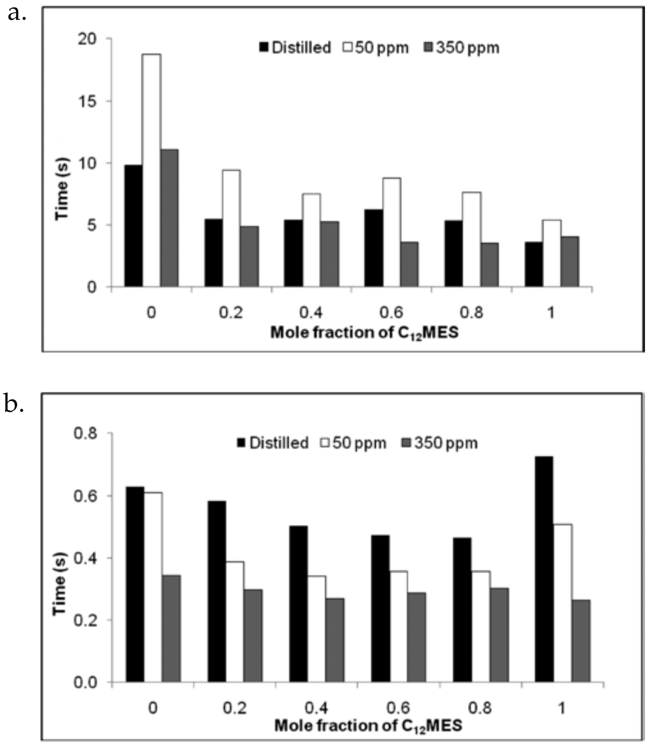

Figure 4. Time taken for a 2 cm × 2 cm test fabric: (a) AS-9 and (b) cotton to totally immersed in the solutions of C_{12}MES, TTAB and their mixtures of various mixing ratio in different water hardness.

water hardness. The graphs showed that the wetting performance of mixed surfactants on soiled cotton (AS-9) was intermediate for both single surfactants. As for cotton (without soiled), mixed surfactants near equimolar showed the best wetting performance. This might be due to the presence of higher number of surfactants on the liquid and air interface which contributed to better surface activity. Besides that, wetting performance improved with increasing water hardness. This could be due to the dehydration of surfactant heads by salts as explained in foaming test section.

Emulsification Test

Emulsification test at different water hardness were indicated in *Figure 5*. A similar trend was observed where maximum stability was achieved near equimolar mixing ratio of the mixed surfactants, while no trend was discovered for studies carried out in different water hardness levels. Time needed for 10% phase separation of the surfactant/oil mixtures in this study was used as an indicator for emulsion stability (Stirton *et al.*, 1965). This is in accordance with our expectation that as the more equally paired amphiphiles were more closely packed and repulsions between surfactant molecules were more effectively screened. Thus, more surfactant molecules were assembled at the water/oil interface.

It was observed from the emulsification experiments that the bottom part for C_{12}MES/TTAB mixtures near equimolar was cloudier than others. This suggests that the emulsions of the mixtures were very stable at that particular mixing. We also discovered that the emulsions of C_{12}MES/oil at 350 ppm water hardness were totally broken after equilibrium. This showed that C_{12}MES emulsions formed were unstable at high salt content and could be due to the imbalance of hydrophilic and lipophilic parts (Myers, 1988; Broze, 1999).

CONCLUSION

Surfactant mixtures especially anionic/cationic possess excellent surface properties than a single surfactant system. CMC values for all the mixtures were very low, indicating strong synergistic interactions amongst the surfactant molecules in a mixed micelle formation. In the foaming, wetting and emulsification tests, maximum performance was achieved near equimolar ratio between the oppositely charged amphiphiles. At this ratio, the surfactants were more equally paired and thus, effectively screened the repulsive forces between the hydrophilic heads. The present study also found that the surface activity of surfactants can be improved by adding salts. However, excessive amount of salts in the systems, especially mixtures of surfactants near equimolar, could induce precipitation which can decrease surface active effectiveness.

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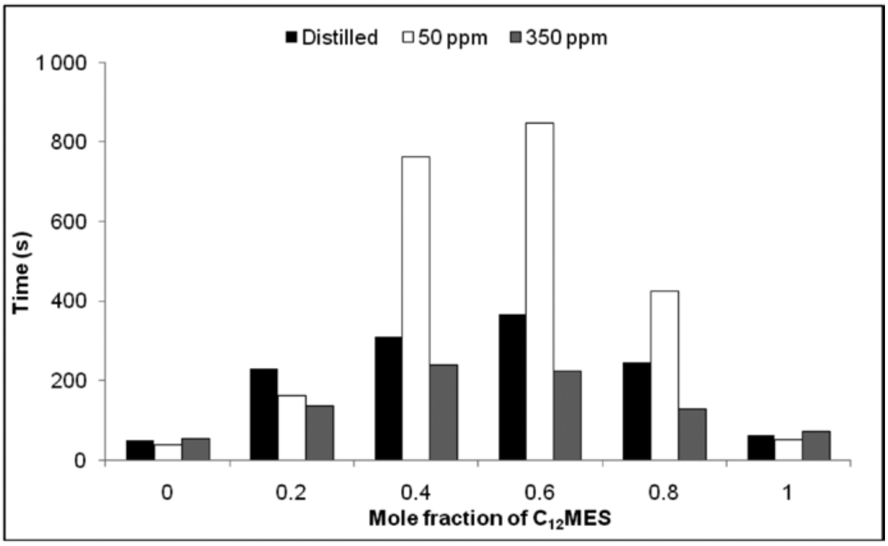

Figure 5. Time taken for 10% phase separation of C_{12}MES, TTAB and their mixtures at various mixing ratios in different water hardness.

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