

## Mixture of Anionic Extended Surfactant and Cationic Surfactant: Precipitation and Critical Micelle Concentration

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**Abstract.** This research study the precipitation and the critical micelle concentration(CMC) of three sulfated-based anionic extended surfactants and one pyridinium-based cationic surfactant mixtures to improve efficiency of surfactant-based groundwater remediation. Cetylpyridinium Chloride was used as cationic surfactant and Alkyl propoxylated sulfate surfactant with difference in number of propylene oxide(PO) group (4 and 8) and/or number of carbon chain length (C14-15 and C16-17). For the precipitation studies, Mixed surfactants greatly help reducing precipitation regions when compare with conventional surfactant. For the CMC of the propoxylated sulfate extended surfactants,  $C_{14,15}(PO)_4SO_4Na$ ,  $C_{16,17}(PO)_4SO_4Na$  and  $C_{14,15}(PO)_8SO_4Na$ , are 0.038, 0.019, 0.015 mM, respectively while the CMC of mixed system are 0.0013, 0.0010, 0.0011 mM, respectively. Moreover, the results show that CMC values of mixed system are lower when compared with conventional surfactant/CPC or even with each extended surfactant itself.

**Keywords:** precipitation, critical micelle concentration(CMC), extended surfactant, mixed surfactant, propylene oxide(PO).

### 1. Introduction

Non-aqueous phase liquids (NAPLs) are one of the major environmental concerns. These compounds are hydrocarbons which have limited water solubility and present as immiscible phase when contact with water. To overcome with these problems, surfactant-based remediation techniques have been widely used as alternative technologies. Mixtures of anionic and cationic surfactants have been considered as one of a efficient way of remediation technique. There are the great advantages of using the mixed anionic and cationic surfactants, for examples, they can reduce interfacial tension (IFT), reach the lower CMC than the individual anionic or cationic surfactants [1] and also produce microstructure [2]. Although the mixed anionic and cationic surfactants can induce high efficiency in solubilization, they still have some limitations to consider. Generally, mixture of anionic and cationic surfactant system can not be presented in the same formulation due to the crystalline precipitation [2]. The tendency to form precipitates or liquid crystalline phases is the main drawback of anionic and cationic surfactant mixture system which affects to surfactant

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usage in many applications such as detergency performance and subsurface remediation of oil contamination [3-5].

The extended surfactants have been recently developed to enhance the solubilization of organic solutes because the dominant characteristic of these surfactants are the presence of one or more intermediate-polarity groups between the hydrophilic head and the hydrophobic tail.

Therefore, in this research, the synergism of sulfated-based anionic extended surfactants and pyridinium-based cationic surfactants mixtures will be studied and compared to the previous systems.

## 2. Objectives

- To evaluate the precipitation phase boundary of mixtures of sulfated-based anionic extended surfactant ( $C_{14,15}(PO)_4SO_4Na$ ,  $C_{16,17}(PO)_4SO_4Na$  and  $C_{14,15}(PO)_8SO_4Na$ ) and pyridinium-based cationic surfactant (Cetylpyridinium Chloride), to define appropriate concentration regimes in which to conduct the adsorption studies.
- 2. To investigate the critical micelle concentration of individual surfactant system and mixed surfactant system (anionic extended surfactants and cationic pyridinium surfactant) by measuring surface tension versus surfactant concentration.

## 3. Materials and Methodology

### 3.1. Materials

Surfactants used in this research are anionic sulfated extended surfactants and pyridinium-based cationic surfactant.

- Anionic extended surfactants: Anionic extended surfactants used in this research are alkyl branched propoxylated sulfates of Alfoterra<sup>®</sup> series which vary in carbon chain length of either 14 and 15 or 16 and 17, and different moles of propylene oxide (PO) group (3, 4 and 8 moles). These surfactants were donated from Sasol North America Inc. (LA, USA).
- Cationic surfactant: Cetylpyridinium Chloride (CPC, 98% purity), selected as cationic surfactant with a C16 alkyl chain length, was purchased from Fluka Chemical Company Ltd. (Buchs, Germany). The properties of studied surfactants are shown in Table 1.

Table 1 Surfactant properties

Surfactant	MW	Number of carbon in alkyl chain	Formula
<b>Anionic Extended Surfactants</b>			
Alkyl propoxylated sulfate C14,15-3PO	483	14-15	$C_{14,15}(PO)_3SO_4Na$
Alkyl propoxylated sulfate C14,15-4PO	554	14-15	$C_{14,15}(PO)_4SO_4Na$
Alkyl propoxylated sulfate C16,17-4PO	578	16-17	$C_{16,17}(PO)_4SO_4Na$
Alkyl propoxylated sulfate C14,15-8PO	715.5	14-15	$C_{14,15}(PO)_8SO_4Na$
<b>Cationic Surfactant</b>			
Cetylpyridinium Chloride	358.01	16	$C_{21}H_{38}ClN$

PO: Propylene oxide ( $C_3H_6O$ )

### 3.2. Methodology

#### 3.2.1. Precipitation Study

The stock solutions of mixed surfactant were prepared as series of samples in 15 mL vials with Teflon-lined caps (Fisher Scientific, Denver, CO). The electrolyte concentration was controlled at 1 mM NaCl. NaOH and HCl were used to adjust solution pH at  $7.0 \pm 0.5$ . The samples were precipitate at  $0^\circ \text{C}$  for 2 days to avoid supersaturation effects. Then these samples were kept at room temperature of  $25 \pm 2^\circ \text{C}$  and shaken periodically for one week. The presence of precipitate and undesirable phase in solution were examined by visual inspection with high intensity light.

### 3.2.2 CMC Measurements

The CMC of the individual and mixed surfactant systems were determined using a Wilhelmy plate tensiometer (DCAT 11, Data Physics, Filderstadt, Germany). The experiments were performed at room temperature ( $25 \pm 2^\circ \text{C}$ ) and electrolyte concentration of 1 mM. The surface tension versus the logarithm of the total surfactant concentration were plotted. Then the CMC of each surfactant was indicated by a sharp change in the slope of the plotted point.

## 4. Results and Discussion

### 4.1. Result of the precipitation at 1mM NaCl

Figure 1 presents the precipitation phase boundary of anionic extended surfactants and cationic surfactant at 1 mM of NaCl. The results show that there is extremely reduction in the precipitation regions of mixed system when compared with mixed system of conventional surfactant. In addition, from the precipitation diagram, the lower number of PO group and/or longer carbon chain length takes effect to increase precipitation phase boundary.

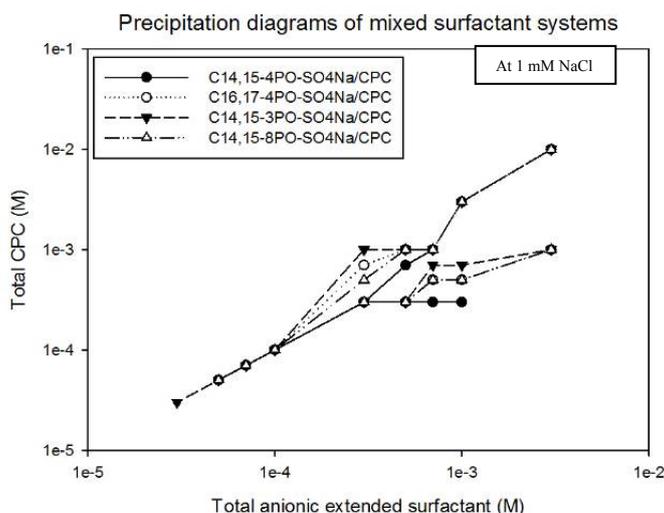


Fig. 1: Precipitation diagrams for mixed surfactant systems at 1 mM NaCl

### 4.2. Results of the CMC study of the individual surfactant and the mixed surfactant at 1 mM NaCl

The CMC of surfactant system is defined as the breakpoint plateau in the graph of surface tension versus logarithm of surfactant concentration as shown in figure 2-5.

In the individual surfactant system, the CMC of CPC is the highest. The CMC of  $\text{C}_{14,15}(\text{PO})_4\text{SO}_4\text{Na}$ ,  $\text{C}_{16,17}(\text{PO})_4\text{SO}_4\text{Na}$  and  $\text{C}_{14,15}(\text{PO})_8\text{SO}_4\text{Na}$  are 0.038, 0.019, 0.015 mM, respectively. The CMC decreases with increasing number of PO group for the surfactant with the same number of carbon of carbon in alkyl chain because of the higher hydrophobicity in surfactant molecule. Moreover, the CMC also decreases with increasing number of carbon in alkyl chain for surfactant with the same number of PO group due to the same reason. The results from Figure 2 indicate that the CMC of  $\text{C}_{16,17}(\text{PO})_4\text{SO}_4\text{Na}$  and  $\text{C}_{14,15}(\text{PO})_8\text{SO}_4\text{Na}$  are not significantly different.

In the mixed surfactant system, the CMC of all individual systems are higher than mixed systems about ten times due to synergism effect. The CMC of  $C_{14,15}(PO)_4SO_4Na/CPC$ ,  $C_{16,17}(PO)_4SO_4Na/CPC$  and  $C_{14,15}(PO)_8SO_4Na/CPC$  are 0.0013, 0.0010, 0.0011 mM, respectively. The results from Figure 2 indicate that the  $C_{14,15}(PO)_4SO_4Na/CPC$ ,  $C_{16,17}(PO)_4SO_4Na/CPC$  and  $C_{14,15}(PO)_8SO_4Na/CPC$  are not significantly different. Figure 3-5 provide the graphical results of mixed system. The values of CMC for both individual surfactant system and mixed surfactant system are summarized in Table 2.

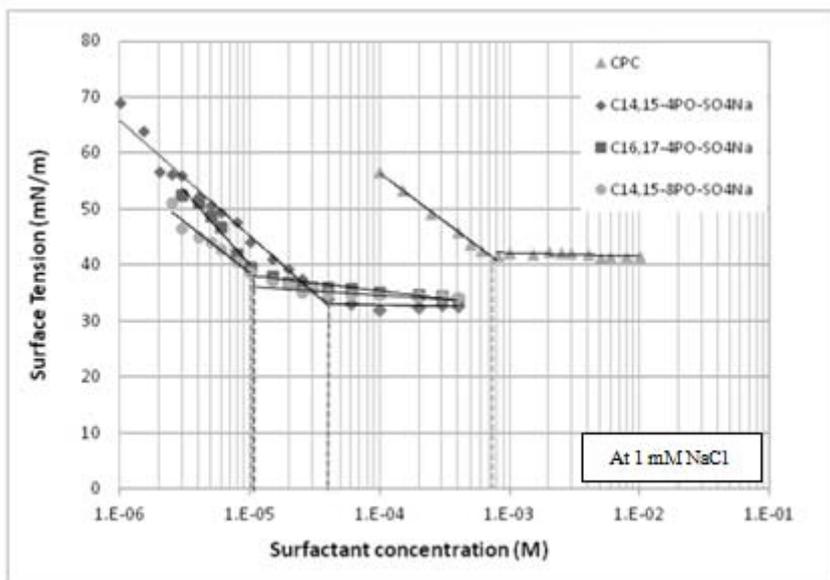


Fig. 2: Surface Tension of individual surfactants

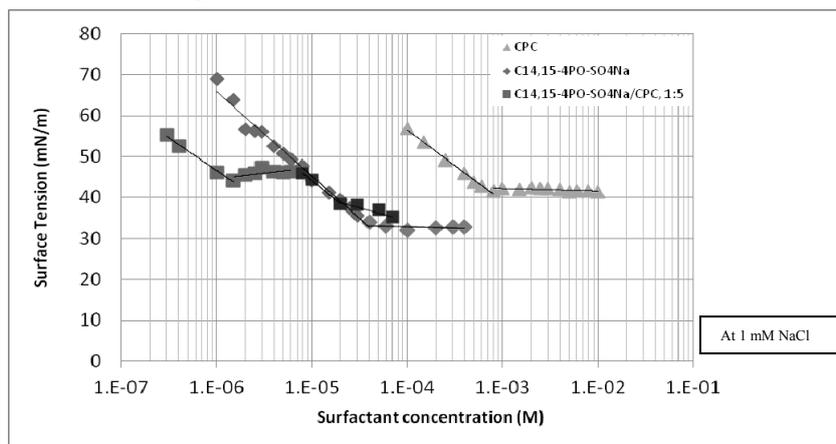


Fig. 3: Surface Tension of CPC,  $C_{14,15}(PO)_4SO_4Na$  and  $C_{14,15}(PO)_4SO_4Na /CPC(1:5$  molar ratio)

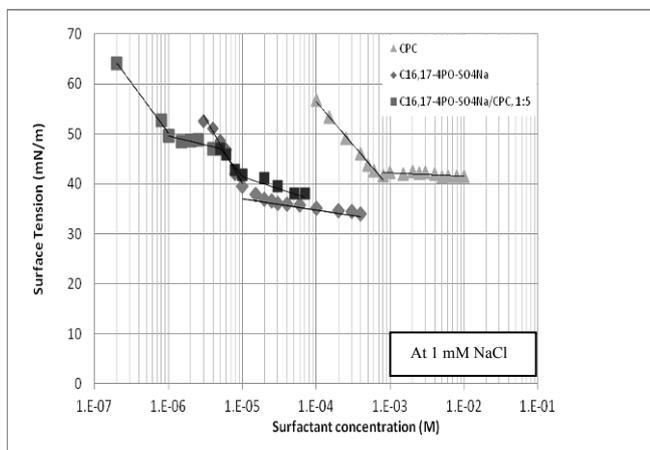


Fig. 4: Surface Tension of CPC,  $C_{16,17}(PO)_4SO_4Na$  and  $C_{16,17}(PO)_4SO_4Na /CPC(1:5$  molar ratio)

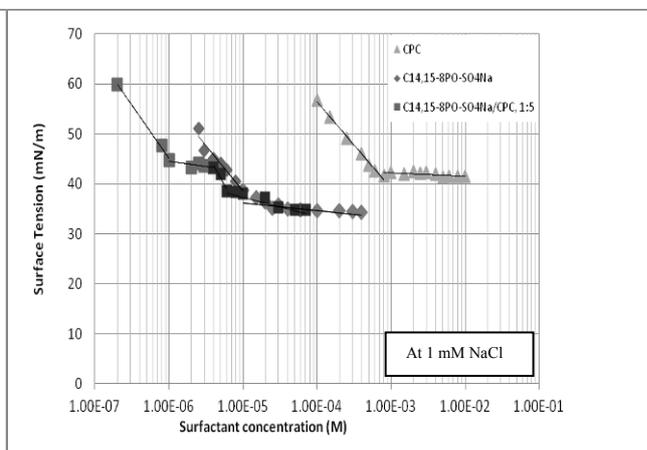


Fig. 5: Surface Tension of CPC,  $C_{14,15}(PO)_8SO_4Na$  and  $C_{14,15}(PO)_8SO_4Na /CPC(1:5$  molar ratio)

Table 2 CMC values and properties of individual surfactant system and mixed surfactant system , temperature 25±2 °C, pH 7.0±0.5 and 1mM NaCl at liquid-air interface

Surfactants	CMC(mM)	Slope	R <sup>2</sup>
<b><i>Individual system</i></b>			
Cetylpyridinium Chloride(CPC)	0.66	-7.51	0.99
Alkyl propoxylated sulfate C14,15-4PO	0.038	-8.93	0.98
Alkyl propoxylated sulfate C16,17-4PO	0.019	-11.32	0.97
Alkyl propoxylated sulfate C14,15-8PO	0.015	-7.88	0.98
<b><i>Mixed system (In 1:5 Molar ratio)</i></b>			
Alkyl propoxylated sulfate C14,15-4PO/CPC	0.0013	-6.87	0.99
Alkyl propoxylated sulfate C16,17-4PO/CPC	0.0010	-8.72	0.99
Alkyl propoxylated sulfate C14,15-8PO/CPC	0.0011	-9.25	0.99

## 5. Conclusions

The extended surfactant can effectively reduce the tendency to precipitate of surfactant when compare with conventional surfactant. The mixed ratio of anionic-cationic surfactants used in adsorption studies is 1:5 since it was ensured to be outside precipitation regions. According to the CMC results, the extended surfactant had very low critical micelle concentration. In addition, the numbers of PO groups and carbon chain length take effect to CMC value that CMC decreases with increasing number of PO and/or longer carbon chain length.

For CMC study of individual surfactant, very low critical micelle concentration of extended surfactants corresponds to theory. In addition, the numbers of PO groups and carbon chain length take effect to CMC value. Increasing PO numbers and/or longer carbon chain length results in lower CMC. Moreover, the results show that higher number of PO group, 4PO and 8PO, take similar effect to longer in carbon chain length 14-15 and 16-17 carbon chain length.

For CMC study of mixed surfactant, CMC of all mixed surfactants are lower than CMC of individual surfactants but CMC of three mixed systems are not significantly different. Nevertheless, Characteristics of surface tension at liquid-air interface versus surfactant concentration graph is not the same as regular graph because surface tension still decrease after it seems to reach plateau. This reason may cause the mixed surfactants in systems are unstable, micelle forms may be convertible depending on time and/or concentration, moreover, the change in slope after reaching CMC of the mixture may be affected by CMC of each individual surfactant system itself.

## 6. Acknowledgement

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## 7. References:

- [1] Mehreteab A (1999) Anionic-Cationic Surfactant Mixtures. In: Broze G (ed) Handbook of Detergents, Part A: Properties. Marcel Dekker, New York, pp 133-136
- [2] Kume G, Gallotti M, and Nunes G (2008) Review on Anionic/Cationic Surfactant Mixtures. J Surfact Deterg 11: 1-11
- [3] Stellner KL, Amante JC, Scamehorn JF, Harwell JH (1988) Precipitation Phenomena in Mixtures of Anionic and Cationic Surfactants in Aqueous Solutions. J Colloid and Interface Sci 123:186-200
- [4] Rodriguez CH, Lowery LH, Scamehorn JF, and Harwell JH (2001). Kinetics of Precipitation of Surfactants. I. Anionic Surfactants with Calcium and with Cationic Surfactants. J Surfact Deterg. 4:1-14
- [5] Rodriguez CH, Scamehorn, JH (2001) Kinetics of Precipitation of Surfactants. II. Anionic Surfactant Mixtures. J Surfactants Deterg. 4:15-26