Study of Mixed Micelles and Interaction Parameters for Polymeric Nonionic and Normal Surfactants

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Surface tension (ST) measurements were carried out on various binary mixtures of the “normal” surfactants, such as nonionic surfactant, hexaethylene glycol mono-n-dodecyl ether (C12EO6), and cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), and polymeric copolymer, Pluronic F127, F127(PPO)-g-PVP, and F127(PEO)-g-PVP. In all cases mixed micellar aggregates were formed and critical micellar concentrations of binary mixtures containing different mole fractions of the surfactants were measured using surface tension measurement. In the region where mixed micelles are formed, the interaction of two “normal” surfactants and three “polymeric” nonionic surfactants showed synergistic behavior and the results were analyzed using an interaction parameter, β, which characterize the interaction in the mixed micelle and introduced by a regular solution theory. The regular solution theory can be applied to describe the interaction between TTAB and C12EO6, and graft polymeric surfactants systems. The results discussed in this paper showed regular solution theory has broader extent of application.

Keywords:

1. INTRODUCTION

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers, commercially known as Pluronic, belong to a group of commonly used water-soluble surface-active compounds.¹ ² “Polymeric” non-ionic surfactants such as Pluronic F127 (Poloxamer 407), can form micelles in aqueous solution when the concentration is higher than its critical micelle concentration (cmc).³–⁵ This entropy driven process is extremely temperature-dependent. The temperature-dependence is due to the difference in the solvation of ethylene oxide (EO) and propylene oxide (PO) blocks. Structural studies showed that at concentrations above cmc or at temperatures above critical micelle temperature (cmt), these non-ionic surfactants formed micelles with a core containing the hydrophobic PO blocks and a shell making up of the hydrated EO blocks.

A combination of the “polymeric” nonionic surfactants and normal ionic or nonionic surfactants are employed in a lot of applications to achieve different emulsification, colloidal stabilization, or suspension effects. Hence, the study of the interactions between polymeric surfactants and normal surfactants in aqueous solution played an increasingly important role in various technological fields. The behavior of mixed surfactants systems has been studied by numerous research groups.⁶–¹⁰ The interaction between F127 and anionic surfactants, sodium dodecyl sulfate (SDS), is mostly widely studied due to the strong interaction between them. In such binary surfactants systems, F127 plays a different role at different concentrations. At concentration below the cmc, F127 behaves like non-associated nonionic polymeric monomers in the solution; but above cmc F127 formed micelles in the solution. At concentration below cmc of F127, SDS forms micelles that are bounded to F127 monomer. This behavior will continue until the normal surfactant concentration reached a critical aggregation concentration normally known as C_{onset} or T. After that, the SDS micelles

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bind to F127 monomers. The study of cationic surfactant, tetradecyltrimethylammonium bromide (TTAB), and nonionic surfactant, hexaethylene glycol mono-n-dodecyl ether(C12EO6), with F127 is less common as compared to the study of the interaction between SDS and F127. The mode of interaction of both normal surfactants, TTAB, and C12EO6 with F127 is found to be same as that of SDS with F127.11,12 The interactions also showed synergistic effect.

The synergistic interactions between the surfactants in binary mixed surfactant systems resulted in the successful practical applications. The synergism of these interactions can be forecasted by some theories. There are two common models used to describe the interactions and they are classified as the ideal and non-ideal models. In the case of ideal mixing of the surfactants, the phase separation model can be used to calculate the cmc of the mixture, CMCmix, from the individual cmc, CMC1, and CMC2, and the respective mole fractions of surfactants (α). Based on the theoretical work by Clint,13 CMCmix can be calculated using a fundamental equation:

\[
\frac{1}{CMC_{mix}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2}
\]

where CMC1 and CMC2 are the CMC of the pure surfactant 1 and 2.

In the non-ideal model, a very useful formula to calculate the extent of synergistic interaction is provided by Rubingh.14 A non-ideality parameter (β) is required in the regular solution theory (RST) description of a binary system. This interaction parameter is related to the activity coefficients of the surfactants.

\[
f_1 = \exp[\beta(1 - X_1)^2]
\]

\[
f_2 = \exp(\beta X_1^2)
\]

where \(f_1\) and \(f_2\) are activity coefficients of the surfactant 1 and 2. \(X_1\) is mole fraction of surfactant 1 in mixed micelle and can be calculated by the following equation.

\[
\frac{X_1^2 \ln(\frac{\alpha_1}{CMC_1})}{(1 - X_1)^2 \ln(\frac{1 - X_1}{CMC_1}) + \frac{X_1^2 \ln(\frac{1 - X_1}{CMC_1})}{(1 - X_1)^2 \ln(\frac{\alpha_2}{CMC_2})}} = 1
\]

Hence, the interaction parameter is given as

\[
\beta = \frac{\ln(\frac{\alpha_1}{CMC_1})}{(1 - X_1)}
\]

The regular solution theory can describe the interaction system of F127 and ionic surfactant well. The interaction parameters β between F127 and anionic surfactant, SDS, cationic surfactant, TTAB, and nonionic surfactant, C12EO6, are all negative which means that the interactions between these surfactants are synergistic. The interactions of SDS with polymeric nonionic surfactants at concentrations below and above cmc have been discussed by our earlier work.16

Poly(vinyl pyrrolidone) (PVP) is a well-known water-soluble, biocompatible, and relatively amphiphilic polymer. The highly polar amide confers hydrophilic and polar attracting properties to the polymer while the apolar methylene group in the backbone and the methine group in the ring contribute to its hydrophobic properties. It has been largely used in the pharmaceutical field.15–19

In this work, the interaction of the polymeric non-ionic surfactant F127, F127(PEO)-g-PVP, and F127(PO)-g-PVP with three normal surfactants: cationic TTAB and nonionic C12EO6, F127(PO)-g-PVP is most of PVP grafted on PPO block of F127 and F127(PEO)-g-PVP is most of PVP grafted on PEO block of F127. The procedure of synthesizing graft copolymers F127(PEO)-g-PVP and F127(PO)-g-PVP and characterization were described in our earlier work.16

2. EXPERIMENTAL DETAILS

2.1. Materials

Pluronic F127 (Poloxamer 407) poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer was obtained from Sigma-Aldrich and used as received. Pluronic F127 has a molecular weight of 12600 and 70 wt% PEO and can be represented as EO70 PO67 EO70. Cationic surfactant, n-tetradecyl trimethylammonium bromide, TTAB, are obtained from Lancaster and used without any further purification. Nonionic surfactant, hexaethylene glycol mono-n-dodecyl ether, C12EO6, was obtained from Fluka and used as received. Deionized water is used to prepare the various solutions.

2.2. Sample Preparation

Two concentrations of polymeric nonionic surfactants, Pluronic F127, and its graft copolymers were dissolved in water under gentle stirring –5 wt% which is above the cmc of polymeric surfactants in room temperature and 0.01 wt% which is below the cmc of those surfactants. The solutions were allowed to equilibrate for more than 24 hours. Normal surfactants were added into the solution at different concentrations.

The fixed molar ratio of polymeric nonionic surfactants, Pluronic F127, and its graft copolymers to normal surfactants TTAB and C12EO6 were added into the deionized water at different concentrations. The solutions were again equilibrated for more than 24 hours.

3. METHODS

3.1. Surface Tension (ST)

The surface tension measurement was carried out using First Ten Angstroms system with automatic gain control camera. The surface tension was automatically computed using the Bashforth-Adams technique. The cmc values of block and graft copolymers in the aqueous solution at room temperature were obtained using surface tension

measurements. The cmc of mixture of polymeric surfactants and SDS can also be obtained using ST.

4. RESULTS AND DISCUSSION

4.1. Low Polymeric Surfactant Concentration, 0.01 wt%

All the solutions in this section have been prepared with the fixed concentration of polymeric nonionic surfactants, F127 and its graft copolymers, and the different concentration of normal surfactants, TTAB, and C12EO6. The concentration of polymeric surfactants is below their cmcs.

The typical surface tension behavior due to the interaction between cationic surfactant, TTAB, and “polymeric” nonionic surfactant in monomer state are shown in Figure 1.

Figure 1 shows the effect of an increase in TTAB concentration at a fixed concentration of polymeric surfactant on the surface tension. The curves exhibit variations in surface tension when the TTAB concentration increases from 0.01 to 0.1 mM. This is because there is a weak influence of TTAB on the surface tension. The surface tension of pure water is 72.8 mN/m. The surface tension of the mixture systems is lower than water because of the strong influence of “polymeric” surfactants. The surface tension decreases with increasing TTAB concentration. This corresponds to an increase in surface activity due to the addition of monomeric TTAB at the air/water interface. This decrease stopped when the TTAB concentration reaches C\text{con} which is 0.18, 0.15, and 0.15 for F127, F127(PPO)-g-PVP, and F127(PEO)-g-PVP, respectively. Then the surface tension increases following the binding of TTAB aggregates to “polymeric” surfactants monomers. This results in a loss in the surface activity of polymeric surfactant monomers which are bounded to TTAB and hence left the air/water interface. Finally, the surface tension starts to decrease again after F127 is saturated with TTAB. This second drop is more substantial than the previous one.

The behavior of the interaction of nonionic surfactant, C12EO6, with nonionic “polymeric” surfactant is similar to that in TTAB and polymeric nonionic surfactant binary system as shown in Figure 2. At first, a small amount of C12EO6 was added into the system, and the surface tension decreased due to more C12EO6 going to the air/water interface. As C12EO6 concentration reached C\text{con} which is near the critical micelle concentration of C12EO6, C12EO6 began to bind to polymeric surfactant resulting in an increase in surface tension. The polymeric surfactants left the air/water interface in a form of complex with C12EO6 and this behavior increased the surface tension. As more C12EO6 was added, the surface tension increased due to more “polymeric” non-ionic surfactants leaving the surface as a result of the binding process. When C12EO6 concentration reached about 10 mM, which is denoted as C\text{sat}, the surface tension did not increase more because the “polymeric” surfactants were saturated with normal surfactant C12EO6.

4.2. Moderate Polymeric Surfactant Concentration, 5 wt%

At a fixed polymeric surfactant concentration above cmc of F127 (5 wt%), the effect of increase of TTAB concentration on the surface tension is shown in Figure 3. The surface tension for micellar “polymeric” surfactant systems at the lowest TTAB concentration is measured to be 38 mN/m which is much lower than that of the monomer systems. The decrease prior to a is due to the addition of TTAB to the air/water interface. From a to b, the surface tension increases slightly for the onset of breakdown of “polymeric” surfactants/TTAB mixed micelles. From b to c, the surface tension varies slightly due to a combination of effects. The decrease in surface tension is due to an increase in the concentration of TTAB. The increase in surface tension is due to the replacement of polymeric surfactants by TTAB at the air/water interface. As TTAB concentration increases, polymeric surfactants are drawn
from the air/water interface to form mixed micelles resulting in a depleting of polymeric surfactants. Some of the TTAB molecules will take the place of the polymeric surfactant at the interface. Since TTAB molecules are less effective in surface tension deduction as compared to polymeric surfactants, the surface tension increases. After c, the decrease in surface tension is probably because of the increased surface activity resulting from polymeric surfactant monomers being released into solution and hence the air/water interface. From d to e, the increase in surface tension is due to monomers leaving air/water interface resulting from the binding of TTAB aggregates.

The surface tension behaviors of C12EO6 with micellar “polymeric” non-ionic surfactant are shown in Figure 4. When C12EO6 was first added to micellar “polymeric” surfactants, the surface tension decreased due to an increase in C12EO6 concentration. After that, the surface tension increased from a to b because of the formation of complexes of polymeric surfactant with C12EO6. After b, the decrease in surface tension was probably because of the increased surface activity resulting from polymeric surfactant unimers being released into solution and, hence, the air/water interface. The replacement of polymeric surfactants is caused by the breakdown of the mixed micelles. From c to d, the increase in surface tension was due to unimers leaving air/water interface resulting from the binding C12EO6 aggregates. When the C12EO6 concentration was beyond d, the surface tension decreased. The C12EO6 saturated the polymeric surfactant in the solution. The surface tension decreased is due to more and more C12EO6 aggregated to the air/water interface. At high C12EO6 concentration, the surface tension remains constant due to the formation of C12EO6 micelles in the solution.

4.3. Investigation of the Synergism Between the Various Surfactants.

In this section, we are going to determine if the interaction between the surfactants is synergistic. This is done using regular solution theory as mentioned before. The experimental values of CMCmix of the graft copolymers, F127(PPO)-g-PVP, with TTAB fit well to the curves calculated by using the regular solution theory. The experimental values of CMCmix of the graft copolymers, F127(PEO)-g-PVP, with TTAB fit well to the curves calculated by using the regular solution theory. The typical figure about modeling these binary surfactant systems using RST is shown in Figure 5. The results showed synergistic interactions of polymeric surfactants, F127(PPO)-g-PVP, and F127(PEO)-g-PVP with cationic surfactant, TTAB and nonionic surfactant, C12EO6, shown in Table I.

Table I. Average interaction parameters β of binary surfactant systems.

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<tr>
<th></th>
<th>TTAB</th>
<th>C12EO6</th>
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<tbody>
<tr>
<td>F127</td>
<td>−1.87</td>
<td>−2.37</td>
</tr>
<tr>
<td>F127(PPO)-g-PVP</td>
<td>−2.02</td>
<td>−2.75</td>
</tr>
<tr>
<td>F127(PEO)-g-PVP</td>
<td>−2.46</td>
<td>−2.89</td>
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Phoronic F127 consists of both PEO and PPO. Due to the hydrophilicity of PEO, F127 can interact with anionic surfactants better than with cationic surfactants. As PVP is more hydrophilic than PPO, the graft copolymer should also interact better with anionic surfactant.19 If the polymer is more hydrophobic, it will interact better with cationic surfactant. The graft copolymer can interact better with cationic surfactant, TTAB, because of the presence of PVP. Since the PVP is more hydrophobic than PEO, the graft copolymers will interact with TTAB better in comparison to F127 with TTAB.

From the data above, we can confirm that hydrophobic interaction is one of the most important factors that will affect the interaction between “polymeric” surfactant and “normal” surfactant systems.

5. CONCLUSIONS

The micelle formation of polymeric surfactants is strongly influenced by additives such as surfactants. Cationic surfactant, TTAB, and nonionic surfactant, C12EO6, interact with the polymeric nonionic surfactant F127, F127(PPO)-g-PVP, and F127(PEO)-g-PVP. The surface tension measurement can provide an indirect method of deducing the type of the interaction between “polymeric” nonionic surfactants and “normal” surfactant. By chemically grafting a polymer PVP that is more hydrophobic than PEO, the interaction between the Phoronic and cationic and nonionic surfactants becomes more synergistic.

References and Notes


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