

Importance of 1:3 Molecular Ratio on the Interfacial Properties of Mixed Surfactant Systems

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Introduction

Surfactants are used in a wide variety of industrial applications. Extensive research has been done on mixed surfactant systems, since they can show superior performance as compared to single surfactant systems alone.¹ It was shown earlier²⁻⁴ that in mixed surfactant systems the stoichiometric association between the surfactant molecules can strikingly alter the properties of the system. Mixed monolayers of stearic acid–stearyl alcohol exhibit a minimum area per molecule at the 1:3 molecular ratio, resulting in a minimum rate of evaporation. Foams of decanoic acid–decanol showed a minimum drainage rate at the 1:3 ratio. It was proposed² that these striking changes in the properties of mixed surfactant systems at the 1:3 molecular ratio are due to two-dimensional hexagonal packing of molecules resulting in a close packing and greater stability of mixed films at interfaces.

Another important factor in mixed systems involving interfacial films is chain length compatibility. As surface-active molecules as well as other hydrocarbon molecules are aligned at interfaces, the properties of the interface are impacted to a large extent upon the matching or mismatching of the alkyl chain lengths. The effects of chain length compatibility are particularly important to interfacial properties and technologies such as, surface tension, surface viscosity, micellar stability, foamability, lubrication, contact angle, bubble size, environmental remediation, corrosion, enhanced oil recovery, water solubilization in microemulsions, and microemulsion stability.⁵⁻⁷

The present study attempts to explore the influence of molecular association between anionic and cationic surfactant mixtures at low concentrations on surface properties, such as surface tension, surface viscosity, foamability, foam stability, single film stability, and rate of evaporation. The combination of anionic surfactant, sodium dodecyl sulfate (SDS), and cationic surfactant, cetylpyridinium chloride (CPC), leads to strong ion–ion interactions, thereby significantly influencing the interfacial properties.

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Experimental Section

Materials. Sodium dodecyl sulfate and cetylpyridinium chloride (both 99+% purity) were supplied by Sigma Chemical Co., St. Louis, MO. Submicellar solution properties are very sensitive to impurities present in the water as well as in the surfactants. Hence, precaution was taken to use freshly deionized, distilled water throughout the experimental work. The surfactants were first dissolved separately in water, and consequently the two solutions were mixed in the appropriate volume ratio. All experiments were performed at 22 °C.

Methods. Surface tensions were measured by the Wilhelmy plate method from freshly prepared solutions using a Krüss K10 tensiometer. The platinum plate was always cleaned and heated to a red/orange color with a Bunsen burner before use. Because of the low surfactant concentration, 15 min was allowed for the solution to equilibrate before taking a measurement.

The deep-channel surface viscometer^{8,9} was used to measure the surface viscosity of each solution. Two concentric cylinders form the deep channel of the viscometer. The walls of this channel are stationary, while the floor moves at a constant angular velocity. To measure the center-line velocity of the air/water interface, a small Teflon particle was placed on the surface, and the time for that particle to make one revolution was recorded from visual observation. Using this value, the surface viscosity can be determined using the following equation:⁹

$$\epsilon = \frac{\eta y_0}{\pi} \left[\frac{8 V_b}{\pi V e^{2D}} - 1 \right] \quad (1)$$

where ϵ is the surface viscosity, η the bulk viscosity of the solution, y_0 the channel width, V_b the plate rotational speed, V the center-line velocity of the air/water interface, and D the ratio of depth to width of the liquid channel.

Evaporation studies were carried out by adding 15 mL of the solution to identical Petri dishes and leaving it for 40 h in a closed area to minimize the effect of dust. Weights were measured before and after to determine the percentage weight loss.

A graduated glass cylinder (100 mL) volume was used for the foam stability and foamability measurements. Twenty milliliters solution was poured into the calibrated cylinder. The solution was given 10 uniform shakes in 10 s. The volume of the foam generated was noted as a measure of foamability of the mixed surfactant solutions. The time required for the collapse of the foam to half of its initial height was taken as a measure for the foam stability. The experiments were repeated at least five times.

Single film stability measurements were carried out as described in detail by Patel et al.¹⁰ Platinum wire was used to make loops of 7 mm in diameter at the end of platinum wires that were attached to corks. Each experiment was initiated by placing 10 mL of the surfactant mixture in the vial. The vials were then carefully lowered into a water bath of 22 °C, and the time required for the films to rupture was recorded using a stopwatch. Experiments were repeated at least five times.

Results and Discussion

Experiments were performed using a total concentration of [SDS] + [CPC] = 1 mM. It was found that higher concentrations result in significant precipitation, lower concentrations than 1 mM do not show significant changes in any of the interfacial properties. The critical micelle concentrations (cmc's) of SDS and CPC are reported to be 8.2 and 0.9 mM, respectively.¹¹ This suggests that micelles are only present in the pure CPC solution. However, since

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additives significantly lower the cmc of a pure surfactant solution, dye absorption¹² measurements were carried out to determine up to which composition of SDS/CPC, micelles are present. It was found that up to a ratio of 40/60 SDS/CPC, micelles are present. Mixtures of 50/50 and 60/40 SDS/CPC contain submicellar aggregates difficult to detect due to precipitation. Solutions ranging from 65 to 100% SDS do not show the presence of micelles. This confirms that the cmc is significantly lowered by mixing anionic/cationic surfactants, which explains some of the experimental observations.

A master diagram showing all the experimental results is presented in Figure 1. The surface tension shows two minima at the 1:3 and 3:1 molar ratios of SDS/CPC. This can be attributed to a closest hexagonal arrangement of the SDS and CPC molecules at the air/water interface. Another parameter indicating the close packing of molecules at the air/water interface is surface viscosity. In this figure the 1:3 and 3:1 ratios of SDS/CPC mixtures show significant higher surface viscosities. At compositions of 40/60, 50/50, and 60/40 SDS/CPC, turbidity was developed due to the interaction between the two surfactants resulting in precipitation. Apparently, a hexagonal packing of SDS and CPC molecules together with strong ion-ion interactions results in the highest surface viscosity. This close packing at the interface is supported by the evaporation data. A minimum evaporation rate at the 1:3 and 3:1 ratios of SDS/CPC is observed, indicating a very dense molecular packing at the air/water interface. A proposed two-dimensional hexagonal arrangement of surfactant molecules at the 1:3 and 3:1 molar ratios in mixed surfactant systems is shown in Figure 2. Molecules of one type occupy the corners and those of the other type occupy the center of hexagons. It is important to note that the interfacial properties discussed above show clear minima and maxima at the 3:1 ratio of SDS/CPC. At this ratio no micelles are present in the system, however, there is an adsorbed film at the air/water interface. The molecular packing in this film exhibits a minimum in surface tension, maximum in surface viscosity, and hence a minimum in rate of evaporation. Properties, such as foamability and foam stability, require an additional amount of surfactant monomers (provided by micelles), to stabilize the newly created interface, and therefore no changes in foam properties were found at the 3:1 ratio of SDS/CPC. As can be seen in Figure 1, foam stability was almost negligible as long as mixtures were rich in SDS. No significant foam was produced due to the absence of micelles. Above 60% of CPC, however, foam stability increased and was observed to be highest at 1:3 molar ratio of SDS/CPC (220 min). It is known that foam stability increases with bulk viscosity or surface viscosity.^{13,14} The shielding of ionic charges and a hexagonal packing results in a high surface viscosity and, hence, high film stability. Another important factor influencing foam stability is the micellar structure inside the thin liquid film, which has been investigated by Wasan and co-workers.^{15,16} The stratification of thin liquid films can be explained as a layer-by-layer thinning of ordered structures of micelles inside the film. This structured phenomenon is affected

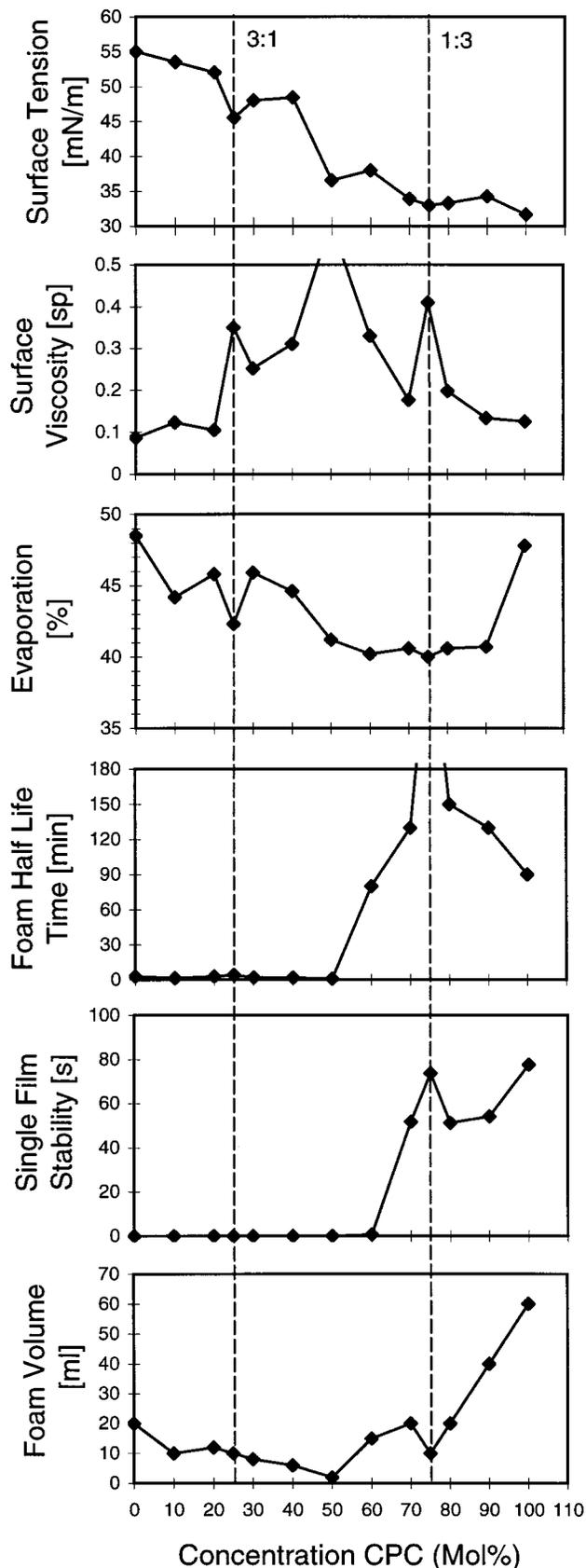


Figure 1. Interfacial properties of SDS/CPC mixtures (1 mM total concentration).

by micellar effective volume fraction, their stability, interaction, and polydispersity. The increased stability of aggregates at the 1:3 molecular ratio of SDS/CPC could be an additional factor accounting for the highest foam

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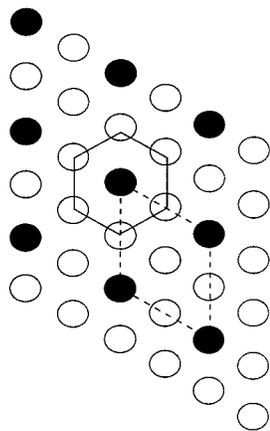


Figure 2. Proposed 2-D hexagonal arrangement of molecules at the 1:3 and 3:1 molecular ratios in mixed surfactant systems.

stability obtained. The foam stability data are supported by the single film stability measurements. At the 1:3 molecular ratio of SDS/CPC, the thin liquid film was the most stable.

The last property studied was foamability. Foamability was minimum at the 1:3 molecular ratio of SDS/CPC. Foamability depends on the surface activity of the surfactant molecules according to¹⁷

$$W = \gamma \Delta A \quad (2)$$

where W is the work done, γ the interfacial tension at the air/water interface, and ΔA the change in interfacial area. Obviously, when the same amount of work is applied, a lower surface tension results in more interfacial area (either by decreasing the bubble size or by increasing foam volume), provided enough surface active molecules are

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available for adsorption at the newly created interface. This study attempts to show that a hexagonal molecular packing as proposed earlier for insoluble surfactants seems to also hold for mixtures of oppositely charged surfactants at low concentrations. Still, the hexagonal packing between surfactant molecules is a proposed mechanism, which needs more in-depth investigation, for example, X-ray diffraction of the monolayer. However, that is beyond the scope of this paper.

Conclusions

The effect of molecular association in mixed anionic/cationic surfactant systems on interfacial properties was investigated, which led to the following conclusions.

1. The addition of SDS to CPC solutions (or vice versa) at low concentrations causes a decrease of the cmc, thereby significantly influencing the interfacial properties.

2. As proposed earlier by Shah,² a compact hexagonal arrangement of insoluble surfactant molecules at the air/water interface for the 1:3 and 3:1 molar ratios seems to also hold for mixtures of water-soluble anionic and cationic surfactants. A two-dimensional hexagonal packing of molecules results in a close packing and greater stability of mixed films at interfaces.

3. At the 1:3 and 3:1 molar ratios of SDS/CPC, minimum surface tension, maximum surface viscosity, maximum foam stability, maximum single film loop stability, minimum rate of evaporation, and minimum foamability were observed.

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