

## Optimization of the Surface Activity of Biosurfactant–Surfactant Mixtures

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### Synopsis

The impact that rhamnolipid (RL) and sophorolipid (SL) biosurfactants has on solution surface activity when used in conjunction with the commercially important zwitterionic surfactant cocamidopropyl betaine (CAPB) is highlighted for the first time through surface tension and surface rheology measurements on binary and ternary mixtures of these surfactants. It was observed that in both the binary (CAPB/RL) and the ternary (CAPB/RL/SL) mixtures, RL tends to dominate at the air–water interface and primarily control both surface tension and surface elasticity behavior. Significant reduction of surface tension and enhancement of surface elasticity is observed as a result of the competitive adsorption/dominance of the RL at the air–water interface and this leads to performance enhancements in terms of foam stability.

### INTRODUCTION

With personal care industry moving toward higher sustainability, the need for greener alternatives for conventionally derived ingredients is increasing significantly. As a result, the demand for novel biosurfactants in the market is anticipated to increase substantially. This demand is due to the expectation of higher sustainability, such as better biodegradability, and more environmental friendly sourcing (1–5). Although biosurfactants have high potential as synthetic surfactant alternatives, their commercial uptake has been limited; this is primarily due to the higher costs, limited scale-up, and limited understanding of formulation design rules for optimizing performance criteria, such as foaming and cleansing. The number of studies on the surface properties of biosurfactant or biosurfactant mixtures is relatively limited (5–14).

Biosurfactants are surface-active agents primarily derived from micro-organisms, and they comprise a hydrophilic and hydrophobic group. These microbial surface-active agents have superlative emulsifying, dispersing, foaming, wetting, and coating capabilities (5). They can function well at acute temperatures and pH and could be derived from waste products, which can reduce their cost (9–11,14).

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Rhamnolipids (RL) and sophorolipids (SL) are two such promising microbial glycolipid surfactants. RL biosurfactants consist of a carboxylate head group, which is anionic in nature and alkyl tail groups (15,17), whereas the SLs can exist in two forms, lactone, as a result of esterification of carboxylic acid on the disaccharide ring, and acidic form, because of two head groups of acetylated dimeric sugar sophorose and carboxylic acid with only one long fatty acid tail to each form (15,18–19). These biosurfactants have individually been shown to enhance cleansing performance (5).

In a surfactant water solution, the surfactant molecules are attracted to the air/water interface because of their amphiphilic nature. These surfactant monolayers at this interface can form a highly elastic interfacial layer and the surfactant monolayer dilational viscoelastic properties can be quantified using elastic modulus (20).

In personal care applications, good foaming performance of the product is highly desired by most consumers. In addition to surface tension, the foaming property of a surfactant solution can be also related to its surface elasticity (21). During foam coarsening, the key characteristic of foam stability and the mean bubble size continuously increase. This is caused by the transferring of gas from bubbles (22). Although the actual mechanism of this transportation is still not clear, there are several factors which may influence this process such as gas permeability (23) and film thickness (24). In the study by Golemanov et al., high surface modulus of surfactant mixtures has significant effect on foam properties, for instance, the rate and mode of foam film thinning and the rate of bubble Ostwald ripening (25).

There are limited studies on the impact of these biosurfactants individually on surface tension, surface elasticity, and surface rheology (5,7,15). However, the impact of RLs and SLs as binary or ternary mixtures on these surface properties has not been investigated (15,18–19). These surface properties of the biosurfactants are related to their cleansing efficacy and foam stability (3,15,25). Also, their specific surface elasticity is related to foam stability, which provides a more pleasant cleansing experience to the consumer (26). High elasticity results in durable foam, which is much more resistant to instability (26,27).

In this study, we systematically evaluated how the surface tension and surface elasticity of these biosurfactants are impacted with respect to their ratio, concentration, and as a mixture with a traditional zwitterionic surfactant, cocamidopropyl betaine (CAPB). This study provides new insights into formulation design, which can lead to enhanced performance in terms of cleansing, foaming, and emulsification.

## MATERIALS AND METHODS

### MATERIALS

As a fermentation product, RL have various structures. The two commonly seen structures are mono-RLs (R1) and di-RLs (R2). The R2 has an extra rhamnose group compared with R1, as shown in Figure 1 (28). The RLs used for the experiment were provided by Natsurfact Laboratories (Fairfax, VA) and have an R1 to R2 ratio of 2:3 w/w.

SLs are seen in two forms, the lactonic form ( $R1 = R2 = \text{COCH}_3$ ) and the acidic form ( $R1 = R2 = \text{H}$ ), as shown in Figure 2 (11,15). Lactonic form SL (Holiferm, Manchester, UK) is

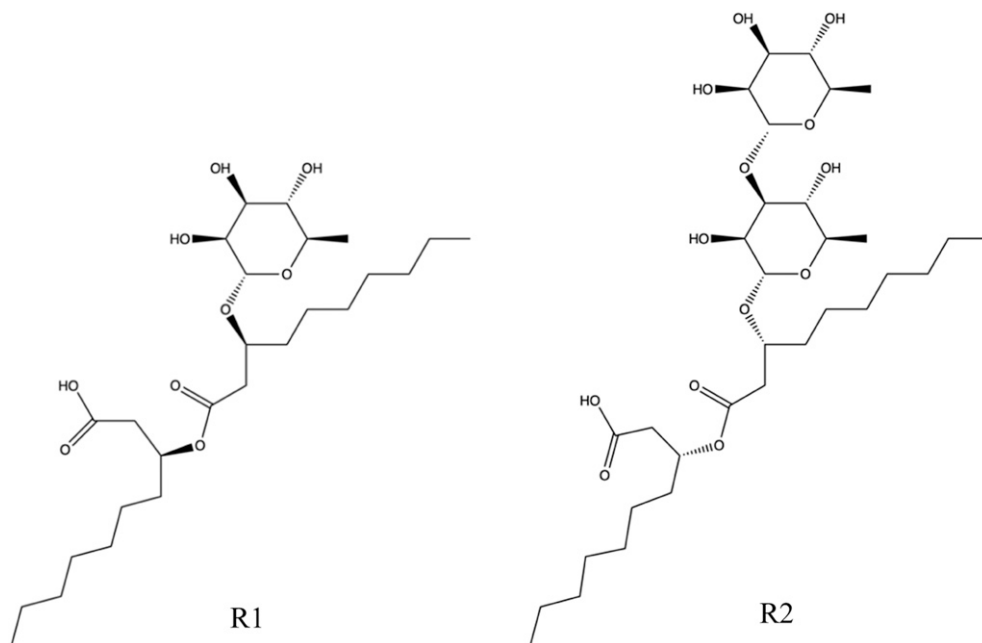


Figure 1. Structure of the two commonly seen RLs R1 and R2.

used in this study as it has better surface tension reduction effect compared with acidic form (3) for optimal cleansing.

CAPB (Lubrizol, Wickliffe, OH) is a zwitterionic surfactant and is commonly used in cosmetic formulations. It is comparatively mild and less irritating as compared with other traditional surfactants (28), and it is used in combination with biosurfactants to aid in surface tension reduction.

Besides the three surfactants, citric acid (Sigma-Aldrich, St. Louis, MS) and sodium hydroxide (Fisher Scientific, Hampton, NH) were used to adjust the sample to the desired pH. Deionized water was added as a solvent. Sodium chloride (Fisher Scientific) concentration of all the concentrated samples has been kept fixed at 2 wt % in all samples.

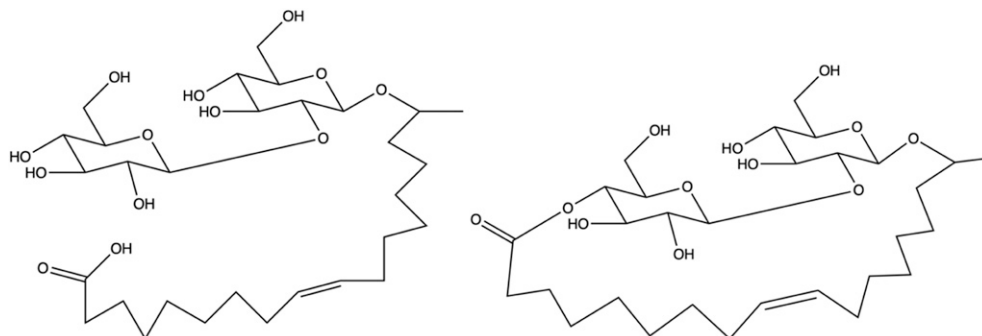


Figure 2. Structure of the two forms of SL. Left: acidic form; right: lactonic form.

## METHODS

The RL mixture samples were prepared such that total surfactant concentration is kept constant at 16 wt %, and the ratio of the different surfactants was varied. The SL mixture samples were prepared at a total surfactant concentration of 10 wt %, with the variation of surfactant ratio in the binary to ternary surfactant system.

Known masses of each surfactant were added to glass vials, and then known masses of deionized water were added to dissolve the surfactant. The vials were then gently shaken until the surfactant was fully dissolved. Sodium chloride was added to the mixture, and then the mixture was carefully shaken until the salt fully dissolved. After letting the sample sit for 24 h, the concentrated surfactant mixture is then diluted to 10 times of the original concentration to test the surface tension and surface elasticity.

After the dilution, the samples were adjusted to the desired pH value using citric acid or sodium hydroxide. All samples were allowed to equilibrate for 24 h before starting the experiment. The surface tensions of the diluted samples were measured at 20°C using du Noüy ring technique with an Attension Sigma 701 Tensiometer (Nanoscience Instruments, Phoenix, AZ).

The surface elasticity response of the sample is evaluated with the rheometer Discovery HR-3 (TA Instruments, New Castle, DE) using the Double Wall Ring accessory at 20°C. After adding the sample into the cuvette and letting it rest for 30 min, an amplitude oscillation measurement was performed. All the measurements were repeated five times.

The foaming of the samples was tested as follows: 3 ml of the surfactant solutions were added into the same-size glass vials. The samples were allowed to sit until all the bubbles disappeared. Then the samples were taped into a bundle and shaken by hand for equal length of 10 s. The quality of the foam was observed at 0-, 5-, 15-min, 30-, and 45-min intervals.

## RESULTS AND DISCUSSION

## INFLUENCE OF RL ON SURFACE BEHAVIOR IN THE CAPB AND RL BINARY SURFACTANT SYSTEM

CAPB is one of the most commonly used zwitterionic surfactants in the personal care industry, and it is usually used in conjunction with anionic surfactants, such as SLES (29). The combination of zwitterionic surfactant and anionic surfactants give rise to not only an optimized rheological property such as proper viscosity in concentrated solutions but also good surface properties allowing good cleansing and foaming performance when diluted.

All of the binary surfactant mixtures are adjusted to pH 5.5, which is close to the skin pH. The isoelectric point of the micellar CAPB is 6.5, which means in the pH 5.5 solution, the zwitterionic surfactant CAPB takes on more of cationic nature (30). Figure 3 shows the variation of the surface tension as the RL concentration is increased in this binary mixture. The surface tension is seen to reduce dramatically from 32.37 mN/m to 27.61 mN/m on the addition of a small amount of RL. As the concentration of the RL is increased to 8 g/L, the surface tension decreases even further to 24.67 mN/m, close to the surface tension of pure RL, which is 25.87 mN/m. When the composition of the RL is increased, the surface tension of the sample remains close to the surface tension of pure

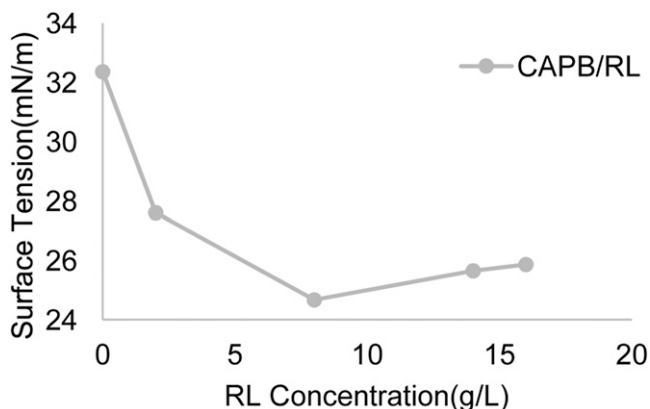


Figure 3. Effect of increasing RL concentration on surface tension.

RL system. This indicates that the RL is more competitive at the air–water interface compared with the CAPB, which leads to the domination of RL at this interface.

The phenomenon observed from the surface tension measurement was further corroborated with the surface elasticity measurements. Figure 4 shows the surface elasticity exhibited within the binary system. This result is in agreement with the surface tension measurements. The pure CAPB shows the lowest surface elasticity compared with the sample with pure RL. The surface elasticity of the 8:8 CAPB:RL mixture sample has a similar value to that of the pure RL sample. This indicates that RL forms a strong elastic structure at the air–water interface and is the dominant species at the air–water interface.

#### EFFECT OF SL BINARY AND TERNARY SYSTEM MIXTURE RATIO ON SURFACE BEHAVIOR

In general, using surfactant mixtures in the solution may allow a further reduction in surface tension or enhancement of surface elasticity through potential synergistic interactions between surfactants or through formation of a mixed surfactant layer exhibiting high surface elasticity (31). The synergistic effect was not achieved with the RL and CAPB system as shown in Figures 3 and 4; in this binary system, RL dominates surface

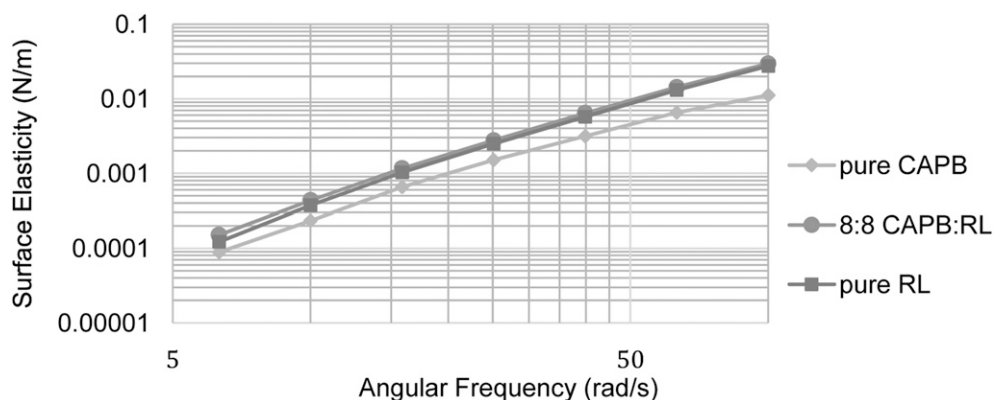


Figure 4. Difference of surface elasticity of pure CAPB, pure RL, and CAPB and RL mixture sample.

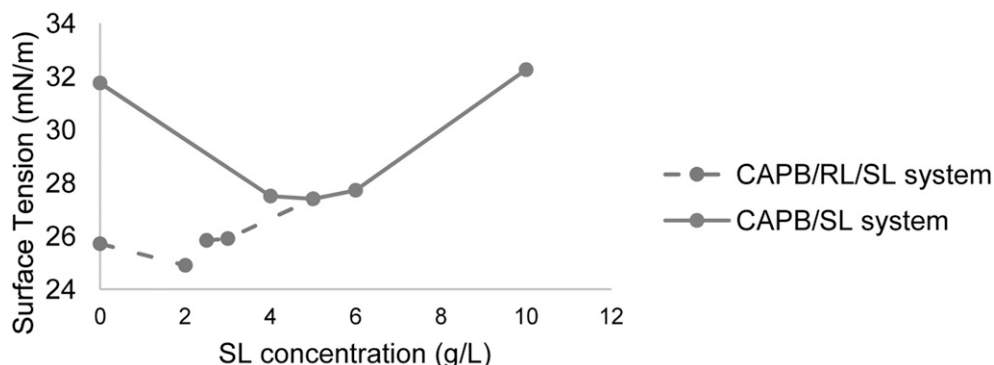


Figure 5. Effect of SL addition in the binary system with CAPB and ternary system with CAPB and RL.

behavior at air–water interface. SL was explored as a potential addition to the system to understand whether it brings about any additional new synergistic effect.

Figure 5 highlights the behavior of SL in both binary and ternary surfactant systems; in the binary system with CAPB, CAPB is incrementally substituted with SL. It is observed that a surface tension value below that of either pure SL or pure CAPB is achieved at equal ratios. This clearly shows an synergistic interaction between CAPB and SL. In the ternary system with the addition of SL to CAPB and RL mixture, there does not seem to be significant impact on the surface tension reduction, with lowest surface tension in the system being 24.9 mN/m, close to pure RL. This indicated that RL seems to dominate at the air–water interface.

Figure 6 highlights the surface elasticity behavior of SL in both binary and ternary systems. The surface elasticity of the ternary system with CAPB/RL/SL is higher than both binary system of CAPB/SL and the pure SL system. This further corroborates that RL is competitive at the interface, being substantiated with both surface tension and surface elasticity measurements. This can result in an elastic layer and tighter packing for high foam stability, ideally desired in a personal cleansing application.

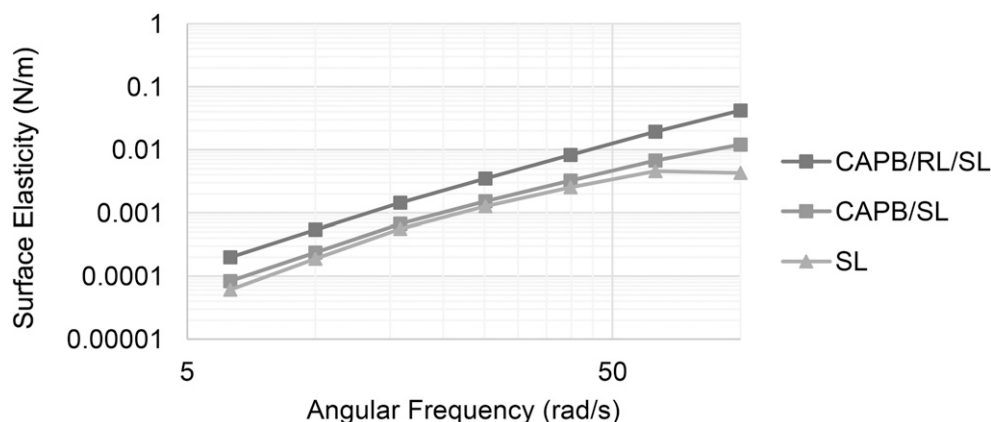


Figure 6. Surface elasticity comparison of the ternary CAPB/RL/SL system with binary CAPB/SL system and pure SL system.

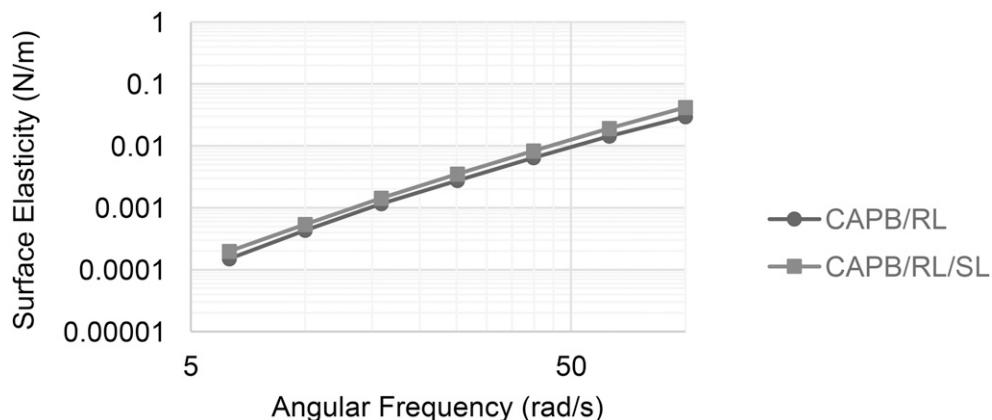


Figure 7. Comparison of the surface elasticity of CAPB/RL/SL and CAPB/RL.

Figure 7 compares the surface elasticity of the ternary CAPB/RL/SL system with the binary CAPB/RL system. Here, it is seen that the surface elasticity of the two samples was approximately the same, which indicates that the RL is the dominant species at the air–water interface. The RL at the air–water interface provides a strong surface layer, which potentially enhances foam stability.

#### FOAMING PROPERTY

To directly evaluate the performance aspects of the surface tension and the surface elasticity optimization with RL, a foaming test was performed.

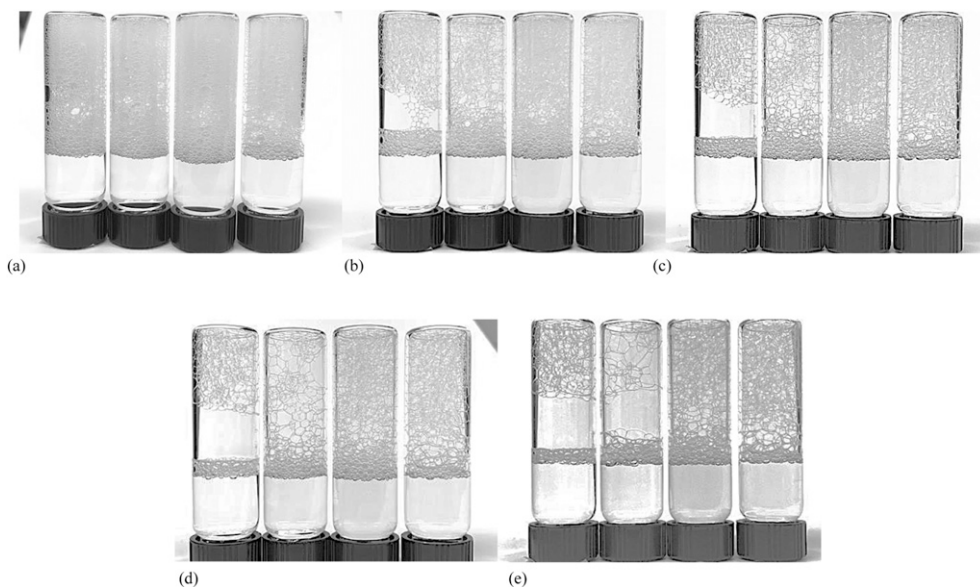


Figure 8. Result of the foaming test. Bottles from left to right: pure CAPB at pH 5.5, pure CAPB at pH 7.0, CAPB/RL at pH 5.5, and CAPB/RL/SL at pH 5.5. Times of photo taken were as following: (A) after shaking; (B) after 5 min; (C) after 15 min; (D) after 30 min; (e) after 45 min.



The result of the foaming test is shown in Figure 8. After shaking for 10 s, the sample with binary 8:8 CAPB/RL and ternary CAPB/RL/SL formed a denser and an even bubble size foam than the pure CAPB sample by themselves. Five minutes later, the bubbles in pure CAPB sample were significantly coarsening and draining, whereas the bubble size and quality of the samples with RL were still intact. After 45 min, the foam formed by the two pure CAPB samples almost disappeared, whereas the foam in the other two samples was coarsening, but there was no large gap which appeared in between.

This strongly complements the results from the surface tension and surface elasticity measurement. With the RL in the surfactant system, the surfactant solution formed a more elastic layer at the air–water interface, which resulted in denser and more stable foam. Compared the performance of CAPB/RL and CAPB/RL/SL sample in this foaming test, the differences were subtle. This result supports the surface tension and surface elasticity experimental results, which also have minimal differences between these two samples.

## CONCLUSION

This study has shown the strong impact of biosurfactants such as RL and SL on the surface properties in binary and ternary mixtures with a commonly used zwitterionic surfactant such as CAPB. Significant surface tension reduction and high surface elasticity was observed in all formulations, both binary and ternary when RL was present. As shown in Figure 9, this indicates the high surface activity of RL. The RL potentially dominates at the interface for both CAPB/RL and for CAPB/RL/SL mixtures, forming tightly packed elastic layers at the air–water interface as shown by the high values of surface elasticity. This results in denser and more stable foam formation. The SL behavior is significantly different. In the binary SL/CAPB mixtures, it seems to exhibit synergistic interactions and forms a mixed layer. This is further corroborated through the surface elasticity measurements. These new insights on binary and ternary mixtures of two biosurfactants, RL and SL, together with CAPB should provide new formulation guidance for personal care products. The study also highlight the importance of surface tension and surface elasticity as two highly complementary techniques to better understand surface structuring in surfactant and biosurfactant mixtures.

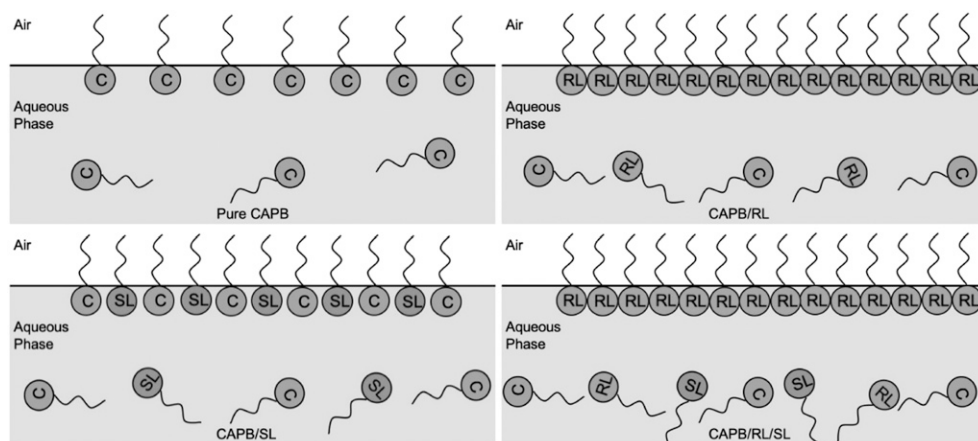


Figure 9. Schematics of surfactant molecule orientation at air–water interface in different surfactant systems.



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