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Hydrodynamics of rising air bubbles in mixture of proteins with non-ionic surfactants to declare their interaction at the air-water interface

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Abstract. Evaluation of the behavior of adsorbed layers of the protein-surfactant mixture at air-water interfaces has recently received great attention due to their many applications in food and pharmaceutical industries. This research study employs rising bubble method to investigate the qualitative study of surface activities of two kinds of proteins, i.e., Beta-Lactoglobulin (BLG) and Beta-Casein (BCS), non-ionic surfactant of C_{10}DMPO, and the mixtures of them at different concentrations at the air-water interface. The similarity between measured local velocity profiles results from the fact that all the mentioned materials are surface-active, can create the Marangoni effect, and develop a dynamic adsorption layer. Given the insignificant interaction between the protein and surfactant molecules, stable complex structures cannot be formed in the protein-C_{10}DMPO mixture. The mixture velocity profile is more similar to that of the surfactant resulting from the replacement of protein molecules or complexes with free surfactant at the bubble interface. It is found that the mixture of non-ionic surfactant and BCS has minor synergetic effect, while for its mixture with BLG, a negative synergy resulting from the shape of protein is observed.

1. Introduction

Proteins and surfactant mixtures have gained extensive interest in recent works because of their use in different industries such as food processing, pharmaceuticals, etc. [1–3]. The interfacial characteristics of these mixtures play an important role in the creation and stabilization of foams [4] as well as their emulsion. In other words, changes in interfacial tension, rheological performance of the interface, and dynamic of adsorption can be significantly different in comparison to those of the individual components [5–8]. Of note, the interaction among proteins existing at liquid bulk volume or interfaces depends on the structure of folded polypeptide chains [2]. While absorption of the protein-surfactant mixture has received great attention, even the basic aspects of adsorbed protein at air/water interface remain to be explored for academia and industry.

The adsorption of surfactants and proteins at the interface reduces the interfacial tension, whereas surfactants with a low molecular weight cause the phenomenon of foam/emulsion creation due to rapid adsorption at the interface. Those with higher molecular weights make a foam stable in an extended time span due to the generation of interfacial networks with elastically and electrically charged properties [9,10]. Various techniques including equilibrium and dynamic measurements of surface tension were utilized to evaluate the layers of adsorbed proteins in mixtures with

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surfactants [1,11,12]. The interfacial behavior of the mixture of proteins and surfactants has been discussed extensively in the literature [12–18].

Krågel et al. [19] investigated BLG/Tween 20 adsorption layer at the air/water interface and noticed that within the short adsorption time, interface contains a significant amount of BLG. Proteins are natural amino-acid-made polymers with different chain sizes; therefore, when the concentration of proteins is low, smaller molecules with lower chain size have a higher chance to be absorbed quickly. Upon increasing the concentration of the surfactant and the time duration of adsorption at a ratio of 5:1, the surface would be completely occupied by surfactant molecules. However, it appears that non-ionic surfactants have a weak interaction with proteins such as BLG and BSC [20].

Miller et al. [21] experimentally studied the adsorption phenomenon of HSA-C_{10}DMPO mixture. They observed an induction time of ∼200 s for HSA adsorption at lower concentrations. Only after a competitive adsorption of HSA, C_{10}DMPO begins to adsorb. The mentioned authors reported that at a higher concentration of C_{10}DMPO, adsorption of HSA remains almost absent, while only the adsorption of protein occurs at a lower concentration of C_{10}DMPO and in an equilibrium state.

Kotsmar et al. [22] investigated the adsorption behavior of three mixtures (BLG-C_{10}DMPO, BSC-C_{10}DMPO, and BSC-C_{12}DMPO) at the air/water interface. They found that the adsorption of mixtures was of competitive nature and performed a gradual replacement of the protein molecules at the interface upon increasing the surfactant concentration. In addition, the above authors reported that the more rigid structure of BLG forces positioning proteins on the surface led to a thinner but optically denser adsorption layer than that of the random coil-structured milk protein BCS. C_{12}DMPO molecules can be replaced more effectively with proteins on the adsorption layer rather than C_{10}DMPO.

Mainly, the complexes between non-ionic surfactants and proteins are formed during hydrophobic interactions. Also, the polarizable head of the used surfactants could cause weak interactions with the ionic Amino Acid (AA) side chains of proteins. Nonetheless, this interaction is assumed to be having a rather minor effect [23–27].

Wüstneck et al. [28] studied the surface tension isotherms of the mixture of BLG and BSC with anionic SDS and cationic CTAB surfactants and determined the formation of surface-active complexes. The surface tension isotherms for the SDS-protein mixtures illustrate the marked plateaus region. This surface saturation is indicated by proteins at specific concentrations. These concentrations are lower than the saturation concentration (at the CMC in phosphate buffer) of SDS. The above authors assumed the complexes of surface-active SDS protein controlling the behavior of mixture surface in the plateau. Moreover, Wüstneck et al. [28] found that in the case of rare quantities of ionic mixtures in which the concentration of surfactant was 100 times less than the protein concentration, the results pointed to a minor growth in surface tension.

Krågel et al. [3] focused on the adsorption behavior of BLG/SDS at the water/air and water/hexane interfaces and hence, analyzed the interfacial structure of adsorbed layers. They realized that after the formation of complexes at higher SDS concentrations, the loss of surfactant would be insignificant. In addition, with the adsorption of protein molecules at the interface between air and water, the adsorbed molecules spread and unfold on the interface, which can be correlated with slight variations in interfacial pressure. Their result recommends that the adsorption is basically a competition between SDS and BLG/SDS complexes in the interface region (water/air interface).

As is shown in Figure 1(a) and (b), the interaction between proteins and surfactants results in the creation of complexes via electrostatic and hydrophobic interactions between protein and surfactants. For ionic surfactants, at the first stage, the adsorption of molecules leads to the formation of complexes to be charged neutral and more hydrophobic; consequently, this process produces higher surface-active complexes. At the next stage, increasing surfactant concentration results in the interaction of protein and surfactant complexes with more surfactant molecules mainly through hydrophobic interaction, leading again to a more hydrophilic and, therefore, less surface-active complex than the original protein. In case of non-ionic surfactants, the hydrophobic interactions result in the creation of a complex which is more hydrophilic and, therefore, less surface active than the original protein.

Kostmar et al. [29] investigated the interfacial behavior of different mixtures of protein/surfactant by two methods of sequential adsorption or simultaneous

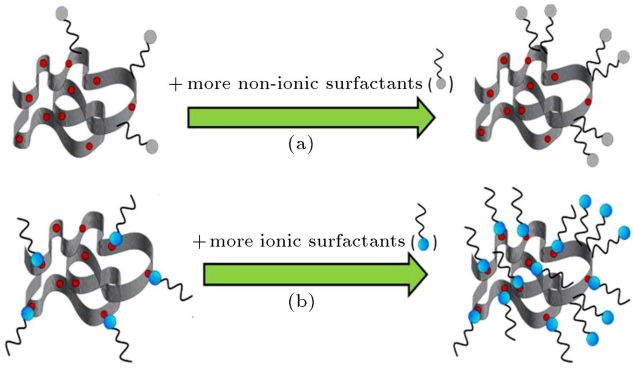

Figure 1. Scheme of protein-surfactant interactions and forming complexes at different surfactant concentrations: (a) Non-ionic surfactants and (b) ionic surfactants.

adsorption. They reported that the mixed adsorption layers formed by both methods would be the same in equilibrium properties, but different in the dynamics. They found that depending on whether the surfactant is ionic or non-ionic, surfactant molecules co-adsorb at the interface and modify the protein. At slight quantities, ionic surfactants can strongly attach the protein to the interface. At higher quantities, it must be noted that when the number of surfactants (ionic or non-ionic) increases, a hydrophobic interaction will set in the resulting hydrophilization of the complex gradually. At the same time, upon increasing the number of free surfactants, a stronger competition at the interface will occur. Finally, both effects result in a progressive reduction in protein attachment on the interface [29].

The movement of bubbles in a liquid is significantly influenced by the adsorption of surface-active agents at the interface of bubbles. This hydrodynamic of a single rising bubble in the surfactant solution has been considered as a significant evaluation for the creation of the adsorption layer in solutions containing surfactants in dynamic environments [30,31]. Since aggregation and adsorption of proteins take place at the interface of bubbles, it is useful to measure the velocity of rising bubbles in solutions containing protein and surfactants because it gives beneficial insights into their effect on the creation of layers of adsorption. Overall, the adsorbed layer limits the motion pattern of a bubble interface and, hence, a 50% reduction of maximum may occur in the rising velocity of a bubble [32–36]. As a bubble forms at the end of a capillary surrounded by a solution containing surfactant, a layer of the adsorbed surfactant is created on the whole surface of the bubble. The adsorption coverage at lower surfactant concentrations is lower than that in equilibrium conditions; however, the coverage occurs in a uniform pattern. Following the separation of the bubble, surfactants begin to adsorb non-uniformly across the surface of the bubble which is referred to as the Dynamic structure of the Adsorption Layer (DAL) [37]. DAL formation can be traced by measuring the rising velocity of an air bubble in the surfactant solution. In general, the motion of the bubble can be divided into three to four steps based on the surfactant concentration: (1) acceleration, (2) maximum velocity, (3) deceleration, and (4) terminal velocity. At maximum velocity, the DAL formation process is going to begin. In the deceleration step, the surface tension and shear forces come to an equilibrium. Finally, in the terminal velocity step, the equilibrium is established and DAL is completely developed [38,39]. This will minimize the amount of coverage in the upper part of the mobile bubble; however, in the lower part, the coverage amount exceeds the equilibrium. This concentration gradient will cause a difference in surface tension, leading to the reduction of the fluidity feature of the bubble (Marangoni effect). Hence, the hydrodynamic drag applied from the liquid to the bubble surface is increased due to the slowness of the bubble, causing a decrease in the bubble velocity. In conventional surfactant solutions, the required time for forming the DAL on the rising bubble surface is influenced by total surfactant concentration and type of surfactant [40–43]. It is reported that the adsorption of protein over the bubble surface can considerably reduce the bubble rise velocity [13,44,45]. To the best of our knowledge, there are few studies reported on the motion of bubbles in mixtures containing protein and surfactant. Hence, the objective of this paper is to further investigate the bubble motion and the dynamic behavior of adsorption layers in the solution of surfactant and protein. The present work investigates the behavior of rising air bubbles in aqueous solutions of BLG and BCS as proteins and C_{10}DMPO as a non-ionic surfactant, as well as the mixtures of these proteins and surfactant. The local velocity of air bubbles in solutions with different concentrations of surfactant and proteins, or their mixtures, was measured with respect to the distance from the capillary tip. The observed profiles were evaluated qualitatively for pure surfactant and protein solutions as well as their mixtures.

2. Materials and experimental procedure

In order to perform the experiments, one non-ionic surfactant and two types of proteins were used. The non-ionic surfactant (C_{10}DMPO) with 98% purity and the BLG protein with 90% purity were purchased from Sigma Aldrich. The BCS protein with 98% purity was also supplied by Serva Company. Deionized water was used to prepare the solutions of pure surfactant and proteins as well as the surfactant/protein mixture.

Prior to each experiment, all laboratory equipment cases containing glass sections were cleaned with a commercial laboratory equipment cleaning liquid supplied by Sigma Aldrich, followed by further rinsing with deionized water to ensure avoidance of any chemical residues. The bubble formation glass was also cleaned with a diluted chromic solution followed by rinsing with deionized water.

The experimental setup used for determining the velocity profile of rising bubble is composed of square glass column (with a 4 cm $\times$4 cm cross-section and 50 cm height) with a capillary at the bottom, bubble generator nozzle, syringe pump for providing air for the nozzle, camera for capturing the bubble motion, and light source. The schematic representation of the experimental setup is shown in Figure 2. The aqueous phase was used to fill the glass column. Bubbles with diameters of 10 μm were created at the bottom of the column using the syringe pump and passed to

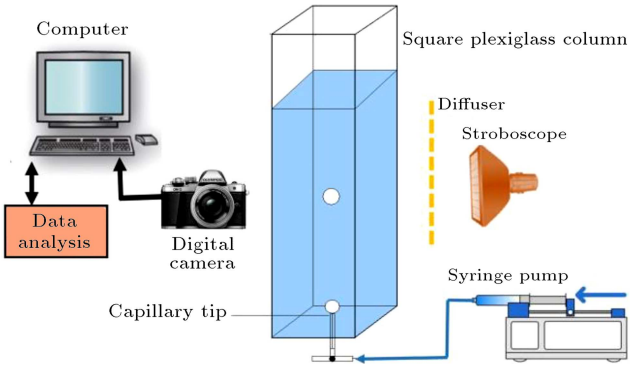

Figure 2. Schematic of the experimental setup.

the aqueous phase through the capillary. The bubble motion was recorded by the camera. The vertical movement of the rising bubble across the glass column was identified by a stroboscope and image processing. The details of the setup and procedure can be found in previous publications [33,37,40,46].

Obviously, the error in measurements is unavoidable and leads to inaccuracy. Therefore, calculation of uncertainty is vital to check the reliability of results. The uncertainty for the bubble diameter is estimated by dividing the accuracy of measurement by the lowest measured value of that variable, which is around 3%.

3. Results and discussion

The rising bubble velocity is achieved by measuring the distance from the tip of the capillary to the upper point of the bubble at specific position intervals divided by the spent time. Then, the Local Velocity Profile (LVP) can be obtained by plotting the measured velocity versus the distance. Results can be explained in two parts: LVPs of single substance solutions and binary solutions.

3.1. LVPs of rising bubble in single substance solutions

There are a number of investigations on rising bubbles in a single substance solution of surfactants, alkanes, or salts in water [13,33–35,37,47] and fewer investigations into the watery solution of protein [13]. Here, one could see LVP measurements for two kinds of protein (BCS and BLG) and the non-ionic surfactant of C_{10}DMPO. For a better understanding of surface activity power, adsorption isotherms of these three substances are shown in Figure 3, as extracted from [2,48].

The local velocity profile of rising air bubbles in deionized water and solution of BCS protein is shown in Figure 4(a) which is measured for the first time. As is shown in Figure 4(a), the velocity profile of deionized water reaches terminal velocity after a sharp acceleration. As is clear in this figure, the bubble starts its motion rapidly in solutions containing BCS and also, the obtained velocity profiles are significantly

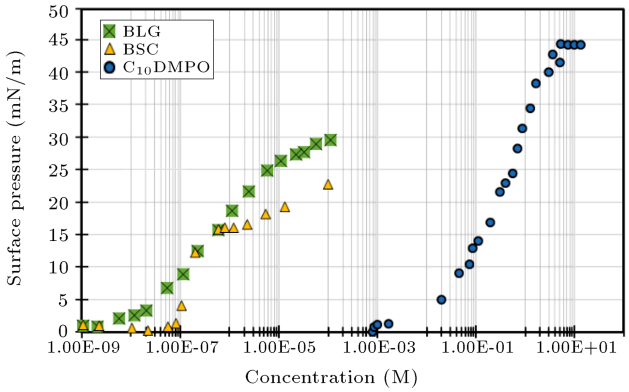

Figure 3. Adsorption isotherm of proteins [2] and surfactant [48].

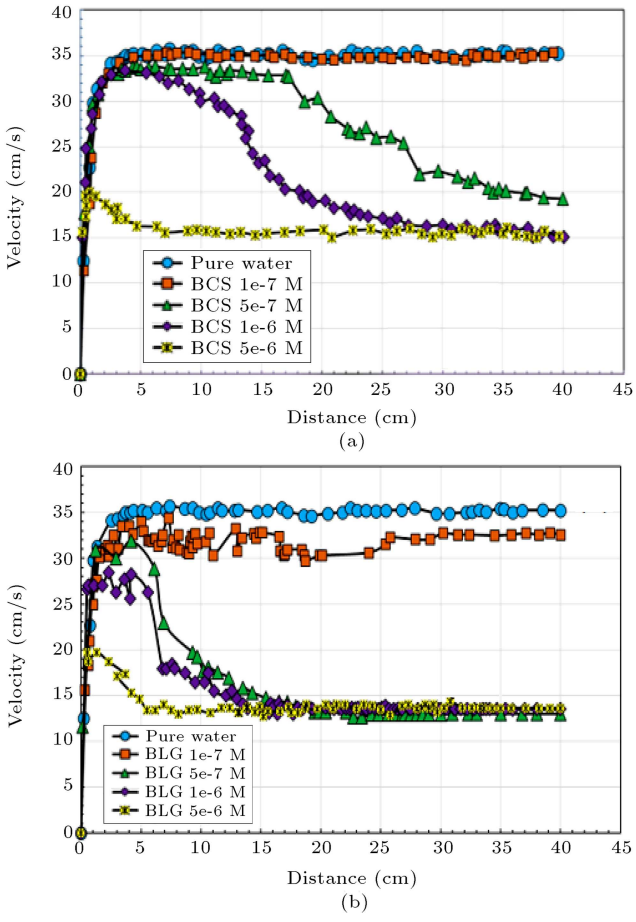

Figure 4. The local velocity profile of rising bubble in (a) BCS solutions and (b) BLG solutions.

influenced by BCS concentration. The velocity profile of the bubble in the solution with the lowest BCS concentration of 1e–7 M is similar to the profile of deionized water in which the terminal velocity is established immediately after the acceleration step. This is due to the fact that at very low BCS concentrations, the amount of adsorbed BCS at the bubble interface is small and the surface tension drag forces on bubbles are not large enough to reduce the bubble velocity.

The velocity profiles exhibit dissimilar trends as the BCS concentration increases. In other words, at higher BCS concentrations, after the acceleration section, a steady decrease occurs in the velocity profile before reaching the terminal velocity. According to Figure 4(a), the velocity, position, and length of the maximum velocity region are not different from the concentration of BCS. The increase in BCS concentration decreases the length of the region of maximum velocity and moves the maximum point to lower velocities and smaller distances. However, the value at which the curves level off at terminal velocity is nearly the same at higher BCS concentrations.

The velocity profile of rising air bubbles in deionized water and solution of BLG protein is shown in Figure 4(b). This figure shows that the velocity profile of BLG protein exhibits a trend and behavior identical to that of BCS protein. To make a comparison, at the same concentration, rising bubbles in BLG solutions exhibit faster DAL development and lower maximum and terminal velocity, meaning that BLG is more surface active than BSC. These results are almost in accordance with the isotherm shown in Figure 3, where at the same concentration, surface pressure of BLG is higher than that of BCS. Although it takes much time to obtain isotherms, rising bubble is highly dynamics; therefore, it seems that the kinetic of BLG adsorption at the air/water interface is faster than BCS [48] because of difference in their structures in bulk and at the interface, as shown in Figure 5.

On the other hand, at 5e-6 M, both BLG and BSC cause the same LVPs, indicating that at a higher concentration, the presence of protein at the interface alters the LVP and increases the drag more than that of DAL formation. However, when the concentration is high enough, the DAL becomes fully developed and the minimum terminal velocity of the bubble in BLG solution is lower than that in BCS. In addition, as is shown in the case of BCS, maximum velocity is close to terminal velocity.

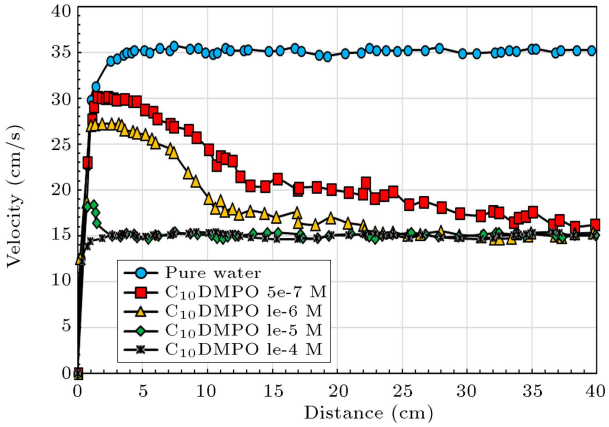

Figure 6. The local velocity profile of rising bubble in C_{10}DMPO solutions.

Moreover, rising bubbles in BLG solution were investigated in [33] and then, the effect of pH was studied.

The local velocity profile of the rising bubble in C_{10}DMPO solution is shown in Figure 6. Overall, the velocity profiles at different surfactant concentrations are similar to those of BLG and BCS proteins. The similarity between velocity profiles can be due to the fact that at specific concentrations, the protein remains in spherical shape and the unfolding process does not occur; hence, the protein and C_{10}DMPO molecules behave similarly.

According to Figure 6, at a concentration of around 5e-7 M, the effect of C_{10}DMPO on LVP is less than BLG, but more than BCS. However, increasing the concentrations is more effective for proteins than C_{10}DMPO. After the concentration of around 1e-4 M, the LVP does not show the decreasing stage and reaches terminal velocity immediately after the acceleration stage. For more information about interfacial properties of C_{10}DMPO, refer to [49–52].

3.2. LVPs of rising bubble in binary solutions

Ulaganthan et al. [13] in 2014 investigated rising bubble hydrodynamics in a mixture of BLG as a protein with

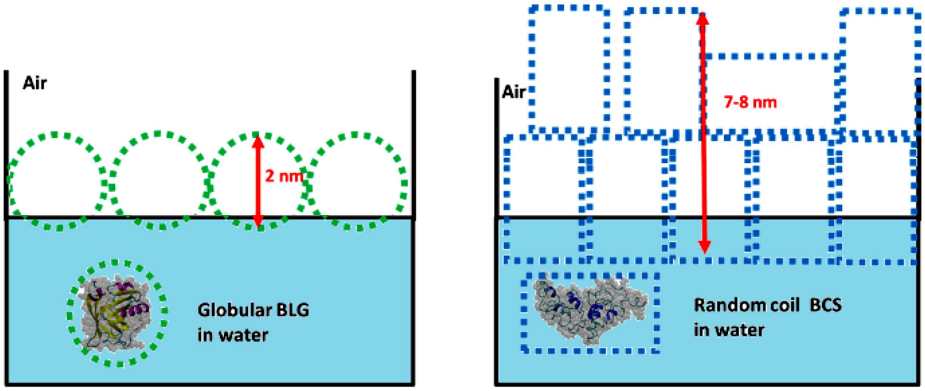

Figure 5. Schematics of proteins structure and thickness of adsorbed layer at air/water interface in equilibrium with help of Ref. [53].

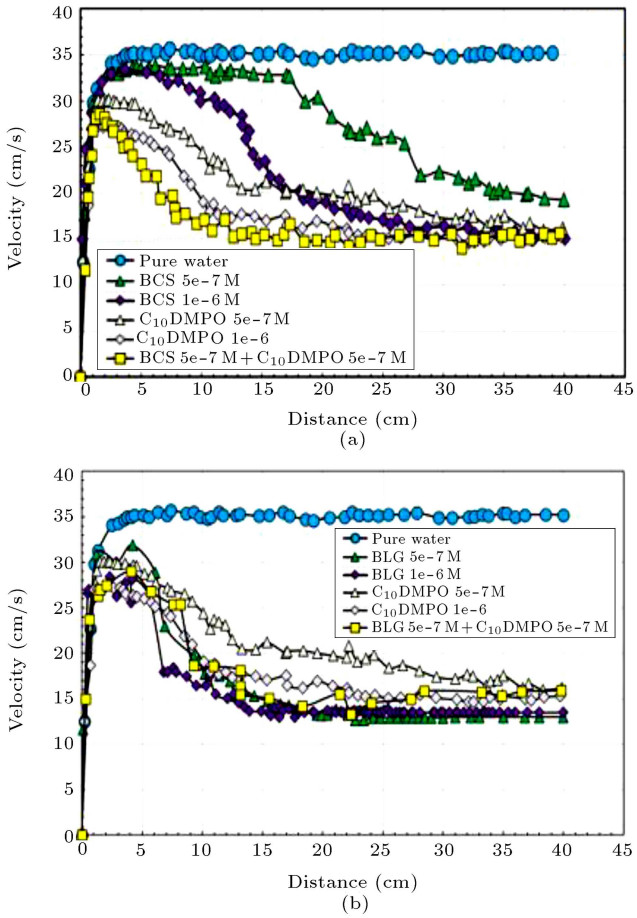

Figure 7. The velocity profile of rising bubble in mixture of (a) BCS with C10DMPO and (b) BLGwith C_{10}DMPO.

SDS, CTAB, and C_{12}DMPO as surfactants for the first time. Here, a mixture of BCS and BLG as proteins with C_{10}DMPO is presented to clear their interactions.

The LVPs of the rising bubble in the mixture of BCS and BLG with non-ionic C_{10}DMPO surfactant are depicted in Figure 7(a) and (b), respectively. According to these figures, the mixture of protein and non-ionic surfactants exhibits a pattern of rising bubble velocity identical to those obtained in solutions of pure proteins or surfactants. In other words, the velocity increases in the acceleration step and upon reaching a maximum point, it follows a steady decrease until levelling off at terminal velocity. According to Figure 7(b), at a mixture of 5e-7 M BCS and 5e-7 M C_{10}DMPO, a complex is formed which is in competition with free surfactants to adsorb at the interface; therefore, the LVP of the mixture is almost the same as 1e-6 M C_{10}DMPO. In other words, the bubble velocity values for pure BCS solution are higher than those for pure C_{10}DMPO surfactant, and the final velocity profile of their mixture is closer to that for the pure C_{10}DMPO surfactant.

With the addition of C_{10}DMPO surfactant to pure BCS solution, the protein molecules at the bubble interface are gradually replaced by the surfactant molecules causing the behavior of the bubble velocity in the mixture to be more identical to the pure surfactant solution. However, a minor difference in the maximum velocity and DAL development of mixture against 1e-6 M C_{10}DMPO results from the slow adsorption kinetic of the formed complex. The LVPs of pure C_{10}DMPO and BLG solutions with their mixture are depicted in Figure 7(b), thus revealing that the mixture of 5e-7 M BLG and 5e-7 M C_{10}DMPO is generally similar to that of pure solutions at a concentration of 1e-6 M. According to the reports in [22], the surface tension for the mixture of BCS or BLG with C_{10}DMPO is the same and, interestingly, of the same impact on rising bubble hydrodynamics.

For a better comparison, the distance from nozzle in which bubble reaches its terminal velocity is considered as the characteristic distance, which is shown in Figure 8. From this figure, it is clear that the mixture of non-ionic surfactant and BCS has a minor synergetic effect, while for its mixture with BLG, a negative synergy is observed.

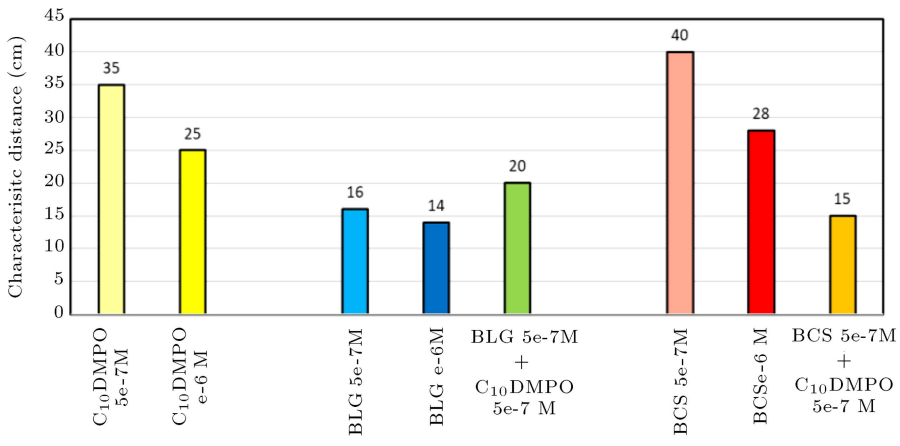

Figure 8. Characteristic distance from the nozzle for single and binary solutions of BLG, BCS, and C_{10}DMPO.

4. Conclusion

Knowledge about dynamic interfacial properties plays a significant role in surface engineering for study of multiphase flows of gas-liquid or liquid-liquid involved in many processes in different industries. However, in some cases of dynamic and unsteady conditions of two-phase flow (e.g., rising bubble columns), investigation methods are not enough to qualify the interface properties.

In the current work, a new laboratory tool named "rising bubble method" was applied for investigating the highly dynamic two-phase condition in order to collect some data on the behavior of the surfactant-protein mixture at the interface. In this research, the rise of air bubbles in pure solutions of BLG or BCS proteins and their mixtures with non-ionic C_{10}DMPO were investigated. Overall, in pure solutions of BLG, BCS, and C_{10}DMPO, the bubble velocity profile exhibited a rapid acceleration stage followed by a steady decrease until levelling off at terminal velocity.

It was concluded that at a mixture of 5e-7 M BCS and 5e-7 M C_{10}DMPO, a complex is formed which is more surface active than 1e-6 M C_{10}DMPO or 1e-6 M BCS. The bubble velocity values for pure BCS solution were higher than those for pure C_{10}DMPO surfactant. Moreover, the final velocity profile of their mixture was close to the pure C_{10}DMPO surfactant. Of note, some small synergetic effect occurred.

The LVPs of pure C_{10}DMPO and BLG solutions with their mixture of 5e-7 M BLG and 5e-7 M C_{10}DMPO revealed that there was no positive synergy and the behavior of the formed complex was similar to that of pure solutions at a concentration of 1e-6 M.

The obtained results of this study can be used as a pioneering method for extraction and separation of surfactant and protein processes in food and pharmaceutical industries or diagnose of diseases caused by adsorption or coagulation of proteins.

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