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Modified Capillary Cell for Foam Film Studies Allowing Exchange of the Film-Forming Liquid

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Many of the macroscopic properties of foams and emulsions are controlled by the mesoscopic properties of the thin films separating the bubbles or droplets. The properties of these films depend on contributions (1) from the adsorbed surface layers and (2) from the liquid that separates these adsorbed layers. To separate in the experimental studies the effects of these two contributions, we developed a new modified version of the capillary cell for foam film studies (originally developed by Scheludko and Exerowa (Scheludko, A.; Exerowa, D. *Kolloid Z.* **1959**, *165*, 148−151), which allows exchange of the film-forming liquid between the air−water surfaces. This modified cell allows one to distinguish between the role of the adsorbed species (e.g., proteins, particles, or long-chain synthetic polymers) and the species present in the film interior (e.g., particles, electrolytes, or surfactants). The film properties that can be studied in this way include film stability, rate of film thinning, and surface forces stabilizing the film. These properties are of significant interest in understanding and controlling the stability of dispersed systems. The experimental procedure and the capabilities of the modified cell are demonstrated in several examples.

1. Introduction

Many foam and emulsion properties (e.g., rheological behavior, stability to coalescence, and Ostwald ripening) are controlled by the properties of the foam and emulsion films, formed in the zone of contact between neighboring bubbles and drops. Several well-established techniques for studying the properties of these films are described in the literature.[1−9] The most widely used methods are the optical observation of microscopic films in the so-called "capillary cell"[1] and "porous-plate cell".[2,3] Some modifications of the porous-plate method are referred to in the literature as the "surface force balance".[4−7] Several versions of these methods were developed over the years,[8,9] and numerous studies performed with these techniques yielded important information about the type of surface forces and the factors governing the film stability and other film properties.[7]

The stability of foam and emulsion films is often explained by considering the properties of the adsorption layers, formed on the surfaces of the film surfaces. However, it is obvious that even for the most common electrostatic stabilization of thin films there is an important contribution from the liquid core separating the adsorbed layers: adsorption layers determine the surface charge density, and the content of the film interior determines the Debye screening length. Another example of an important contribution of the film interior is the well-known stratification phenomenon (stepwise thinning of the foam and emulsion films), which is observed when surfactant micelles form ordered structures inside the films, thus giving rise to oscillatory forces between film surfaces.[10−15]

There are numerous examples of more complex contributions of the content of the liquid in the thin films to the overall film behavior. For protein-stabilized foams and emulsions, it is suggested that protein multilayers are formed at sufficiently high protein concentrations.[16−21] Several studies[16−19] have shown that the first layer of protein molecules, which are in direct contact with the nonpolar phase (oil or air), is irreversibly adsorbed and remains attached to the interface upon exchange of the bulk liquid with electrolyte solution without protein. In contrast, the subsequent layers of protein molecules are reversibly adsorbed and detach from the surface when the latter is rinsed with electrolyte solutions. The process of multilayer formation could be relatively slow[16,19] and occurs at the background of slow rearrangements of the adsorbed molecules.[20] Experimental studies showed that the

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film stability (and the stability of the overall emulsion or foam) could be affected by both the multilayer formation and the structural changes in the adsorption layers.[18,20,21] With the current experimental methods, the investigation of these processes is not straightforward because the various effects interfere with each other and cannot be separated unambiguously.

Methodological problems of similar type appear when studying particle-stabilized films because it is not obvious whether the stability comes from adsorbed particles only or from particles trapped in the film interior as well.[22−24] For example, in a recent study of the interfacial and foam properties of glycated proteins, Wierenga et al.[25] observed a significant increase in foam stability with the degree of protein glycation, whereas no significant changes in the interfacial properties (e.g., surface pressure or surface elasticity) were observed. Therefore, it was hypothesized[25] that small oligomeric (aggregated) proteins, present inside the film-forming liquid, stabilize the foam films against rupture without measurable effects on interfacial properties. With the existing experimental methods, it is impossible to check this hypothesis directly.

In summary, in most systems both the surface adsorption layers and the liquid content of the film interior play an important combined role in the film properties so that any technique that enables one to study these contributions separately would contribute significantly to the understanding of the more complex systems, which are currently of significant interest. With this aim in view, we propose here an experimental method in which the contents of the film interior can be modified without destroying preformed layers of irreversibly adsorbed protein molecules and/or solid particles.

The basic idea of exchanging the subphase below adsorbed layers has been explored in the literature in relation to adsorption studies. Several research groups have presented interesting and nontrivial results about the changes in the properties of adsorption layers, composed of low-molecular-weight (LMW) surfactants or protein molecules, after exchange of the adjacent bulk liquid.[26−30] The liquid exchange was used to study several important phenomena, including the desorption of LMW surfactants,[26,27] the displacement of proteins by other proteins or by LMW surfactants,[28,29] and the subsequent adsorption of proteins and polysaccharides.[30] These liquid-exchange experiments are typically performed in a Langmuir trough or in a drop-shape analysis setup, modified to allow an exchange of the bulk liquid below the preformed adsorption layer.

As an extension of these liquid-exchange studies, we propose in this letter a modification of the well-known capillary cell that is used for foam and emulsion film studies. The cell is modified to allow the exchange of liquid between the adsorbed interfaces of a liquid film. This modification complements the liquid-exchange methods developed for single interfaces because the effects of the changes in the surface layer (upon exchange of the bulk phase) on the properties of the foam films can be directly observed and analyzed. Moreover, the effects of the nonadsorbed material on the film properties and stability can be directly studied by this new technique and separated clearly from the effects of the adsorbed species. The capabilities of the modified cell and the related experimental procedures are demonstrated in several examples.

2. Experimental Setup and Procedures

The experimental cell proposed in the current study is a modification of the original capillary cell developed by Scheludko and Exerowa.[1] The basic elements in the original cell are the film holder (short-vertical capillary) in which the foam film is formed and the side capillary that is attached to this holder. The side capillary is filled with liquid from which the film will be formed. The amount of liquid in the film holder is controlled by a pressure control system connected to the side capillary. By removing/adding liquid from/to the holder through the side capillary, one can form a foam or emulsion film and control its radius. Thinning of the formed film is observed by optical microscopy in reflected light. Usually, the film holder is placed in a closed container to avoid the evaporation of liquid from the film, which would otherwise strongly affect the film thinning pattern and film stability.

To enable the exchange of the liquid in the film's interior, we modified the original cell by connecting a second side capillary to the film holder, as shown in Figure 1. In our procedure, one of the side capillaries is filled with the liquid used for subsequent exchange of the film interior, whereas the second capillary is used to collect the liquid displaced from the film holder in the course of the experiment (Figure 2). For clarity, we call the liquid used to make the original foam film (whose interior will be subsequently replaced by another liquid) the first liquid or liquid 1. Accordingly, the liquid used to replace the interior of the original film (formed from liquid 1) is termed the second liquid or liquid 2.

For clarity of presentation, we call the modified capillary cell shown in Figures 1 and 2 the double-capillary cell, thus denoting the presence of two side capillaries attached to the central film holder.

The typical experimental procedure consists of the following steps:

In step 1, the film holder and one of the side capillaries (indicated as side capillary A in Figure 2) are filled with liquid 2. At that moment, for the initial check of the system, one can make a foam film from liquid 2 and study the film properties, such as the rate of thinning, equilibrium thickness, and stability (Figure 2A). For these studies, optical microscopy with observation in reflected light can be used, as done with the original capillary cell.

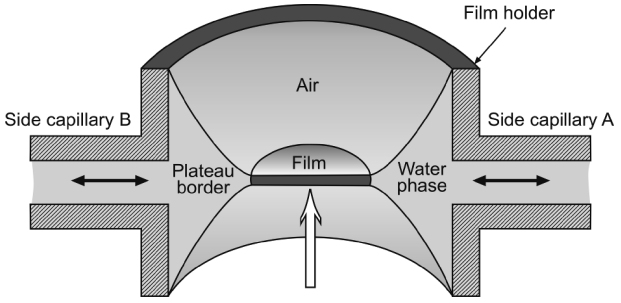

Figure 1. Schematic presentation of the modified capillary cell. This cell is called the double-capillary cell to denote the presence of two side capillaries, which are used to exchange the film-forming liquid inside the central film holder. (See Figure 2 for the procedure.)

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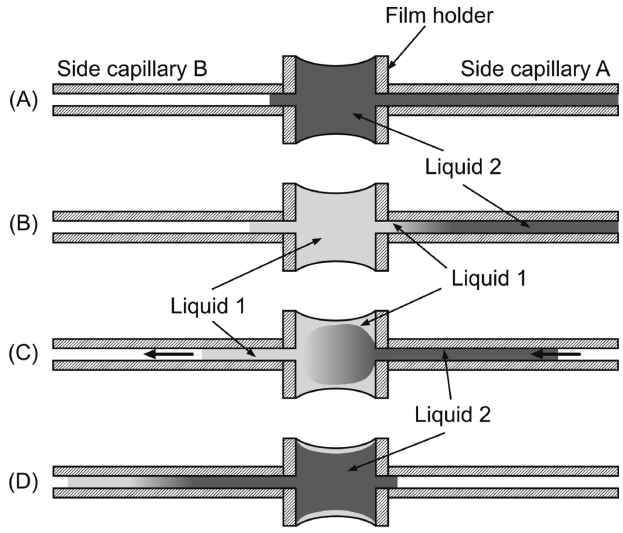

Figure 2. Illustration of the exchange of the liquid in the double-capillary cell. (A) Step 1: filling of the film holder and one of the side capillaries (denoted as capillary A) with liquid 2. (B) Step 2: rinsing of the film holder with liquid 1 (using an external pipet), where a small amount of liquid 1 is sucked into side capillary A. (C, D) Step 3: exchange of liquid 1 in the film holder with liquid 2 while maintaining the adsorption layers formed during step 2.

In our particular experiments, we used a film holder of 2.6 mm internal diameter and 3 mm height. The two attached side capillaries had an internal diameter of 0.8 mm and a length of 25 cm. The optical observations of the foam films were performed with a Jenavert microscope (Carl Zeiss, Jena) in reflected monochromatic light (546 nm).

In step 2, the film holder is abundantly rinsed with liquid 1 (using an external pipet) to remove all residues from liquid 2 in the holder. In addition, a small amount of liquid 1 is sucked into the side capillary (A) that is filled with liquid 2. In this way, a buffer zone is generated with a length of several millimeters to separate the liquid in the film holder from liquid 2 (Figure 2B). The diffusion of the dissolved molecules through the buffer zone is relatively slow so that the holder content is not affected during this period of the experiment by the content of liquid 2. With a typical molecular diffusion coefficient of $\sim 10^{-9}$ m^2/s, one can estimate that about 30 min is needed for molecular diffusion along a 2 mm buffer zone. After liquid 1 is placed in the film holder, a thin liquid film is made from liquid 1, and its properties are studied as described above.

In step 3, after the completion of the investigation of the film formed from liquid 1, we exchange liquid 1 in the film holder with liquid 2 between the adsorption layers formed during step 2 (from the species dissolved or dispersed in liquid 1). To do this, we first gently close the foam film (make it thicker) by adding a small amount of liquid from side capillary A to the film holder. Then liquid 2 is gradually pumped into the holder through capillary A while simultaneously removing liquid from the film holder via capillary B (Figure 2C,D). In this way, we replace bulk liquid 1 with bulk liquid 2 between the two adsorbed layers formed from the surfactant species present in liquid 1 during step 2. In our particular setup, the liquid volume in the side capillaries is around 400 μL, which is approximately 10 times the volume of the liquid contained in the film holder (40 μL). It is possible to attach much larger liquid reservoirs to the side capillaries, thus allowing for more extensive exchange of the liquids during this stage.

The described exchange procedure is rather flexible. If necessary, the liquids can be exchanged more slowly or in small steps so that adsorption and desorption processes can reach equilibrium. Such procedures could be relevant when studying the effect of desorption kinetics of surfactants and/or polymers from the adsorbed surface layers.

Another important version of the procedure is to exchange liquids 1 and 2 after the formation of the foam film without changing its diameter. This procedure is much more difficult and delicate because the volumes of the removed and the introduced liquids should be perfectly balanced (to maintain the film radius as almost constant). Still, it might be of significant interest because this procedure mimics some processes of practical interest (e.g., rinsing of protein emulsions with liquids of different pH and/or electrolyte concentration). In this version of the exchange procedure, the aim is not to change the conditions within the plane-parallel foam film directly but rather to change the solvent conditions in the meniscus (plateau borders). We successfully tested this procedure and showed that it could be realized in the setup described above, especially after proper automation of the liquid exchange system (results not shown).

3. Results from Illustrative Experiments

To demonstrate the capabilities of the modified capillary cell, we performed three different sets of experiments, which are briefly described below.

1. Changing the Ionic Strength of Micellar Surfactant Solution. Films formed from the anionic surfactant sodium dodecylsulfate (SDS) are known to thin in qualitatively different modes, depending on the SDS concentration and ionic strength of the solution. In the absence of added electrolyte, 50 mM SDS solutions thin down in a stepwise manner. This is known in the literature as the stratification mode of film thinning.[10−15] This phenomenon was extensively studied in the past and was shown to originate in the formation of structured layers of charged micelles inside the thinning films.[10−12] The addition of electrolytes (e.g., 150 mM NaCl) screens the electrostatic repulsion between the surfactant micelles, and the micelle structuring inside the film is suppressed.[13] As a result, the stratification does not occur and the film thins down differently (see below for a description), which is easily observed by microscopy.

These SDS solutions are particularly suitable to illustrate the effect of the exchange of the bulk liquid in the film interior on the mode of film thinning and on the equilibrium film thickness. Note that the bulk-surface adsorption equilibrium is reached very rapidly for SDS solutions (within less than a second),[31] so the exchange of the bulk liquid is accompanied by related changes in the density and structure of the adsorption layers formed from the SDS molecules.

In our experiment, we first placed an aqueous solution of 50 mM SDS and 150 mM NaCl in the double-capillary cell and formed a foam film whose thinning pattern was video recorded (step 1 in the procedure described above). As reported in previous studies,[7] this film thinned down with only one step in thickness, observed at about 40 nm, after which an equilibrium film thickness of 9.5 nm was reached (curve 1 in Figure 3). Note that this step in film thickness is caused by hydrodynamic instability in the thinning film due to van der Walls attraction between the film surfaces (i.e., it is not related to the presence of surfactant micelles in the film).[7,32] Next, the film holder was rinsed with 50 mM SDS solution without electrolyte (step 2 of the experimental procedure). As a result, these films thinned more slowly and in a stepwise manner, with the formation of three consecutive steps, until the final film with an equilibrium thickness of 12 nm was reached (curve 2 in Figure 3). Finally, the liquid between the surfaces was replaced by a solution of 50 mM SDS and 150 mM NaCl (step 3). As expected, the replacement of the bulk liquid with

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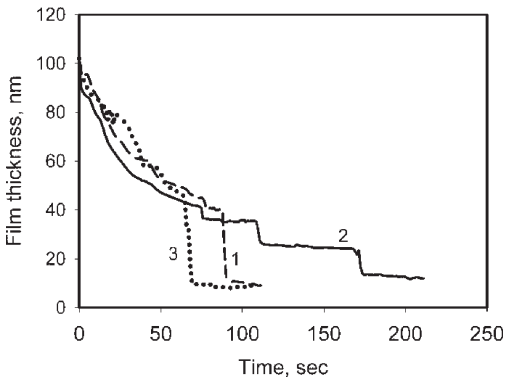

Figure 3. Film thickness as a function of time for (1) 50 mM SDS + 150 mM NaCl, (2) 50 mM SDS, and (3) 50 mM SDS after exchange with 50 mM SDS + 150 mM NaCl, as recorded in the double-capillary cell, by using the procedure shown in Figure 2.

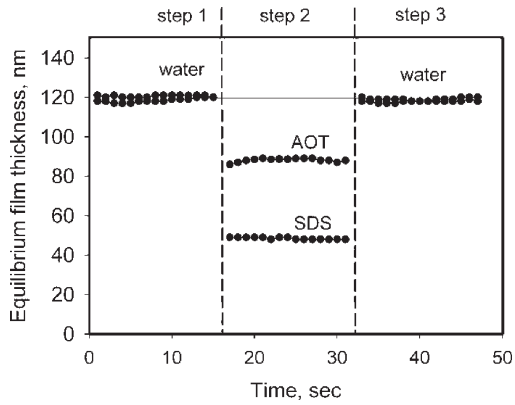

Figure 4. Equilibrium thickness of films formed from (step 1) deionized water, (step 2) surfactant solutions, and (step 3) surfactant solutions, followed by exchange of the bulk liquid in the film holder with pure water. Surfactant solutions are 4.0 mM SDS (◊) and 2.2 mM AOT (□). The film thickness is shown as measured for 10 s after reaching equilibrium.

NaCl-containing solution resulted in the disappearance of the stratification mode of film thinning (curve 3 in Figure 3), as in step 1 of this experiment.

These results convincingly demonstrate that the replacement of the bulk liquid in the film holder was successful and that one can use the described procedure to change the composition of the liquid between the film surfaces.

2. Replacement of an LMW Surfactant Solution by Pure Water. As described by Svitova et al.,[26] the typical LMW surfactants desorb rapidly from the solution surface when the bulk surfactant concentration is lowered by exchange with surfactant-free solution. As an additional, very sensitive test for the completeness of the liquid exchange in our procedure, and as a demonstration of the effect of surfactant desorption on foam film behavior, we exchanged solutions of LMW surfactants with pure water. The surfactant solutions used in these experiments were 4.0 mM SDS and 2.2 mM AOT (anionic surfactant sodium dioctylsulfosuccinate), which are both below the critical micelle concentration.

First we measured the thickness of the thin films made of pure water (step 1, see Figure 4). The small foam films, formed from deionized water, were stable and had equilibrium thicknesses of ~120 nm. This agrees with previous studies,[33] where the stability of foam films, formed without surfactants, was attributed to a negative charge appearing on the water−air interface as a result of the spontaneous adsorption of hydroxyl ions.

Next, side capillary A was filled with pure water, and the film holder was rinsed with surfactant solution (step 2). For both the SDS and AOT solutions, the thin films showed the typical thinning pattern for LMW surfactant-stabilized films. The respective equilibrium film thicknesses were ~50 nm for the SDS solution and ~90 nm for the AOT solution.

Finally, we exchanged the surfactant solution in the film holder with deionized water from capillary A (step 3). The film thinning pattern and the equilibrium film thickness after the exchange were identical to those of pure water (Figure 4). The film properties did not depend on the type of solution that was used in step 2 (SDS or AOT). These results are another convincing demonstration that the exchange procedure of the liquid in the film holder during step 3 is very efficient. It shows also that the result of this exchange is comparable to that in the experiments with single-interface systems (refs 26−30).

3. Replacement of Protein Solution by LMW Surfactant Solution. The LMW surfactants have been shown to be able to replace preadsorbed protein molecules under certain conditions.[34] As a further test of the proposed procedure for more complex systems, we exchanged a protein solution (bovine serum albumin, BSA, 0.01 wt % + 1 mM NaCl) with solutions of LMW surfactants.

First, side capillary A was filled for different experiments with (i) 1 mM NaCl, (ii) 1 mM Tween 20, or (iii) 10 mM SDS (step 1). These solutions were chosen to represent pure electrolyte or different types of surfactants (nonionic − Tween 20 and polyoxyethylene-20-sorbitan monolaurate; anionic − SDS). Then, BSA solution was placed in the film holder and allowed to adsorb for 20 min (step 2). Last, the bulk liquid between the adsorbed layers was replaced by the solution in capillary A (step 3).

The initial films, formed from BSA solutions, exhibited the typical thinning pattern for protein-stabilized films. Thicker regions in the film center (dimples) were formed in the process of film formation. These dimples were rather stable and drained slowly. In about 5 min, a relatively homogeneous film with a thickness of ~30 nm was formed (Figure 5). The film continued to thin gradually until thinner black spots appeared about 13 min after film formation. The final equilibrium thickness of the BSA film, ~18 nm, was reached about 15 min after film formation.

After the exchange of the protein solution with 1 mM NaCl (no surfactant), the behavior of the foam films did not change. This result demonstrates that no significant protein desorption occurred, which is in agreement with the results obtained by other authors[19] with protein systems (by other methods). Furthermore, this result shows that the film properties of this particular system are entirely determined by the adsorbed protein and the electrolyte concentration in the solution.

In contrast, when solutions of LMW surfactants were used in the exchange process, large effects on the film behavior were observed. For both surfactants used (nonionic and anionic), the behavior of the foam films after the liquid exchange was identical to that observed with the original surfactant system (Figure 5). These observations demonstrate that the protein was completely displaced from the interface by the LMW surfactants used in these experiments, which is also a confirmation that the liquid exchange in our setup is comparable to the exchange reported earlier for single-interface systems.[28,34] It must be noted that such

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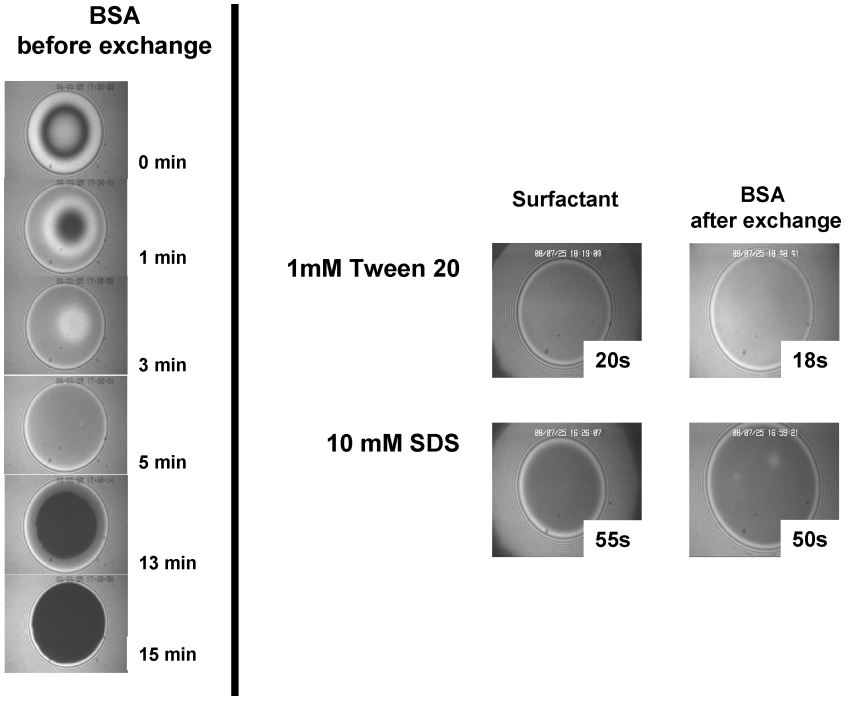

Figure 5. Images of foam films formed from BSA solutions (0.01% + 1 mM NaCl) before and after exchange of the film interior with surfactant solutions in the double-capillary cell. As a reference, images illustrating the evolution of the foam films, directly formed from surfactant solutions, are shown.

displacement depends on the system conditions (time of adsorption, surfactant concentration, etc.)

4. Conclusion and Prospects for Applications

In this letter, we describe a new modification of the known capillary cell, which is suitable for studying thin liquid films before and after exchange of the liquid confined between the adsorbed layers on the two film surfaces. The construction of the modified cell (called a double-capillary cell) and the experimental procedure are described, and the method was demonstrated to work in three experiments.

The main advantage of the new cell modification is that it allows the experimentalist to distinguish between the contributions of the irreversibly adsorbed species on the film surfaces (e.g., proteins, solid particles, or long-chain synthetic polymers) and those of the species dissolved or dispersed in the film interior (electrolyte, micelles, particles or protein aggregates, etc.). As a result, experiments can be performed to determine which processes and mechanisms dominate the properties of thin films. Such experiments could be combined with the determination of the single-interface properties after exchange using other methods.[26−30]

A very promising field of application is that of protein-stabilized films, where the effects of subsequent and/or competitive adsorption of proteins, polysaccharides, and/or LMW surfactants could be studied. Additionally, the effect of protein aggregates (adsorbed or dispersed in the bulk solution) can be analyzed in great detail; for example, by comparing thin films of aggregated protein solutions before and after exchange of the interior liquid for a solution of pure electrolyte, one could clarify whether the observed effects of protein aggregation on film properties are due to changed interfacial properties or the presence of dispersed/adsorbed protein aggregates inside the film.

Similarly, the method could provide valuable information in the area of particle-stabilized foams and emulsions. For example, the effects on film stability of particle adsorption and particle aggregation in the bulk dispersion could be studied separately by replacing the film-forming dispersion (after the formation of the particle adsorption layers) with the respective liquid medium without particles.

Another potential field for the application of this method is that of oily antifoams, where the effects of the antifoam spread on the film surfaces (in the form of oily lenses or a continuous oil layer) could be clearly separated from the effect of the dispersed antifoam globules when using the new technique.[35,36]

Note that the above procedures can also be applied to the study of emulsion films (e.g., oil−water−oil), which is of particular interest for protein-stabilized emulsions. In practice, these emulsions are often obtained in a sequence of several steps involving possible changes in pH and electrolyte concentration, the addition of new species (e.g., polysaccharides), and so forth, which could be mimicked in the proposed cell.

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