Adsorption of Protein Layers at the Water/Air Interface As Studied by Axisymmetric Drop and Bubble Shape Analysis

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Experimental studies of dynamic and equilibrium surface tensions of aqueous β-casein solutions were performed by using the pendent drop and bubble techniques. A comparison of the results shows good agreement at higher protein concentrations. However, at low protein concentrations a significant difference between the data is observed, caused by the loss of protein molecules from the bulk at the drop surface due to the limited solution reservoir. In bubble experiments the reservoir is larger by more than 2 orders of magnitude so that losses become essential at much lower bulk concentrations. Loss of protein and the diffusional transport in the limited reservoir of a small drop lead to the formation of an adsorption layer with properties quite different from those obtained at a bubble surface.

Introduction

The adsorption and mechanical properties of adsorption layers formed by proteins at liquid interfaces are significant both in fundamental studies and in many practical situations, such as in stabilization of emulsions and foams in food technology,[1,2] coating processes, etc.[3]

The adsorption behavior of protein layers is often investigated by surface/interfacial tension methods.[2] Among others, drop or bubble shape methods are suitable techniques for such investigations, as they require only small amounts of the protein samples.

Two different experiments, axisymmetric drop and bubble shape analysis,[4,5] were performed to determine the adsorption kinetics and adsorption isotherms of β-casein at the water/air interface. The two methods differ mainly in the amount of the protein solution reservoir. This difference, however, can lead to strong deviations between the experimental data, in particular at low protein concentrations.

The same techniques are suitable also for relaxation experiments based on sinusoidal or trapezoidal area deformations.[6,7] Such studies, providing data on the diffusional exchange of matter between surface and bulk or on other relaxation mechanisms in the adsorption layer, and the dilational elasticity, are under way.

Materials and Methods

β-Casein (C6905 Lot 12H9550, molecular weights of 24 000) was purchased from Sigma (Germany) and used without further purification. All measurements were performed at room temperature (22 ± 0.1 °C) and in phosphate buffer solutions prepared by mixing appropriate stock solutions of K_2HPO_4 and KH_2PO_4. The surface tension of the buffer solution at pH 7 was 72.5 mN/m.

The dynamic surface tensions of the protein were measured by using both axisymmetric drop and bubble shape analysis as described elsewhere in detail.[4,5] The solution drops were formed at the tip of a PTFE capillary immersed into a cuvette filled with a water-saturated atmosphere, while the bubbles were formed at the tip of a capillary immersed into a cuvette filled with the aqueous solution. The drop and bubble volumes were ca. 0.03 and 0.04 cm^3, respectively. The accuracy of the experiments in this study was better than ±0.25 mN/m.

Results and Discussion

The adsorption of surfactants or proteins from inside a drop at its surface, or from a large external solution bulk to a bubble/drop surface, is characterized by a number of particular features which can result in a different adsorption behavior, both in equilibrium and under dynamic conditions. First, the conditions which regulate the diffusion of the surfactant or protein to a spherical surface are different: for a drop the diffusion takes place from a limited drop volume, while for a bubble the diffusion occurs from an infinite volume of the measurement cell to the bubble surface, both having a comparable surface area. Another feature can be seen when the bulk concentration of the protein in the drop or in the solution that surrounds the bubble is low. In such a case the mass of the adsorbed protein or surfactant can be comparable to the mass of protein inside the drop. This can lead to a significant decrease in bulk concentration for the drop experiment while for the bubble this loss of protein in the bulk phase can still be negligible. As a third reason, differences between the water/air and water/oil interfaces are such that they have a significant impact on the protein conformation have to be considered.

First, let us analyze the differences in the diffusion process. For the sake of simplicity, we shall consider the case when the concentration of protein or surfactant in the subsurface layer is close to zero. The problem of surfactant diffusion from an

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infinite bulk to a spherical drop (or bubble) surface was studied in a number of papers.[9−11] For a diffusional adsorption mechanism and a subsurface concentration close to zero, the solution for the dynamic adsorption Γ is given by[10,11]

$$\Gamma = \frac{cDt}{r} + 2c\sqrt{\frac{Dt}{\pi}} \tag{1}$$

where c is the protein (surfactant) bulk concentration, D is the diffusion coefficient, r is the drop radius, and t is the time. The adsorption from inside a spherical drop at its surface of area S can be expressed by an average protein concentration $\bar{c}$ (as a function of time) in the drop bulk of volume V[12]

$$\Gamma = \frac{V}{S}(c - \bar{c}) = \frac{r}{3}(c - \bar{c}) \tag{2}$$

A simple assumption is that during an adsorption process the subsurface concentration is zero. Then the value of the average concentration in the drop is given by[12]

$$\bar{c} = c\sum_{j=1}^{\infty} \frac{6}{\pi^2 j^2} \exp(\pi^2 j^2 \mathrm{Fo}) \tag{3}$$

where $\mathrm{Fo} = Dt/r^2$ is the Fourier number. Another solution of the same equation can also be used for the analysis[13]

$$\frac{\bar{c}}{c} = 1 + 3\mathrm{Fo} - 6\sqrt{\mathrm{Fo}}\left[\frac{1}{\sqrt{\pi}} + 2\sum_{j=1}^{\infty} \mathrm{ierfc}\,\frac{j}{\sqrt{\mathrm{Fo}}}\right] \tag{4}$$

Keeping only the first two terms in (4), one obtains

$$\frac{\bar{c}}{c} = 1 + 3\mathrm{Fo} - 6\sqrt{\frac{\mathrm{Fo}}{\pi}} \tag{5}$$

Substitution of eq 5 into eq 2 results in an expression for the adsorption at the drop surface

$$\Gamma = -\frac{cDt}{r} + 2c\sqrt{\frac{Dt}{\pi}} \tag{6}$$

It can be seen that, as compared to a flat surface (the second term in eqs 1 and 6) the diffusion to a bubble surface from an infinite solution leads to an increased adsorption rate and to larger adsorption values (due to the additional first term in eq 1) at the same adsorption time. On the other hand, the dynamic adsorption is decreased for the diffusion from the drop volume due to the negative sign of the curvature term in eq 6, i.e., the first term on the rhs. If a diffusion coefficient of $D = 10^{-6}$ cm^2/s for β-casein is assumed, the first terms in eqs 1 and 6 become essential (10% and more) when $t > 1000$ s. For surfactants with larger diffusion coefficients, the difference between the two methods becomes significant at shorter times.

Although the derivations of the relationships have been demonstrated only for the beginning of the adsorption process, significant differences in the adsorption rate exist also for the entire process until establishment of the adsorption equilibrium. As we do not need to analyze quantitatively the dynamic surface tensions, a more detailed description of the adsorption process is not necessary here.

Up to now, only the results of calculations are discussed. Let us now look into the experimental data and try to understand the differences obtained from the drop and bubble experiments. The main difference is certainly caused by the loss of protein mass in the drop due to adsorption at the drop surface. Clearly,

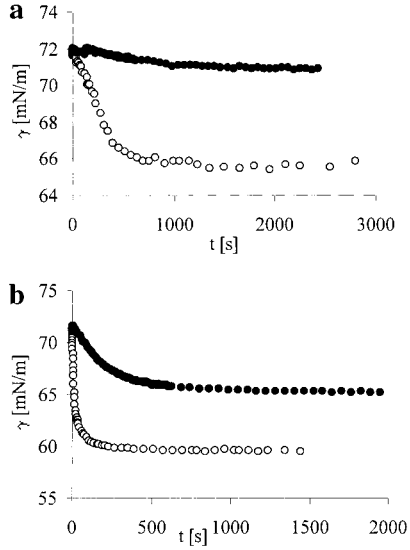

Figure 1. Dynamic surface tension of the $C_{10}EO_8$ solution. Concentration $c = 10^{-9}$ mol/L (a) and 10^{-8} mol/L (b). (●) Data of Ferrari et al.[17], (○) data of Chang et al.[15]

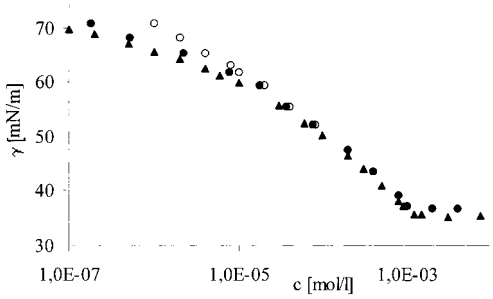

Figure 2. Surface tension isotherm of $C_{10}EO_8$ solutions: (▲) data of Chang et al.[15] (○) data of Ferrari et al.[17] without correction, and (●) with correction.

this effect becomes evident only at low bulk concentrations of a protein or for highly surface-active surfactants. The time required for completion of the diffusion process in the drop can be estimated using the diffusion penetration model.[14] According to this simple model, in any system with any geometry the thickness of the diffusion layer δ can be approximated by $(D\pi t)^{1/2}$. Thus, for the case of a drop the diffusion process will be completed when the thickness of the diffusion layer δ becomes equal to the drop radius r. Exact calculations according to eq 3 show that at $\mathrm{Fo} = 0.34$ the average portion of surface active molecules accumulated at the surface amounts only to 2% of the initial concentration, while for $\mathrm{Fo} = 0.42$ this portion constitutes only 1%.[13] In the above examples for $\delta/r = (\pi\mathrm{Fo})^{1/2}$, one obtains $\delta = 1.03r - 1.4r$. This result agrees well with the penetration model ($\delta = r$). For $D = 10^{-6}$ cm^2/s, the diffusion process in a drop of 1 mm radius will be completed after 3000 s. The data for $C_{10}EO_8$ solutions shown in Figures 1 and 2, which were obtained using bubble and drop methods in ref 15 and refs 16 and 17 respectively, agree with this conclusion perfectly. One can see that, according to eqs 1 and 6, the rate of surface tension decrease for the bubble exceeds significantly that for the drop (Figure 1). However, the equilibrium surface tensions for $C_{10}EO_8$ concentrations above 5×10^{-9} mol/cm^3 are the same for both methods (Figure 2). Only when the concentration of $C_{10}EO_8$ becomes lower than 5×10^{-9} mol/cm^3 is the equilibrium surface tension measured with the drop method higher than that measured with the bubble method. This can be quantitatively described by the decrease in the $C_{10}EO_8$

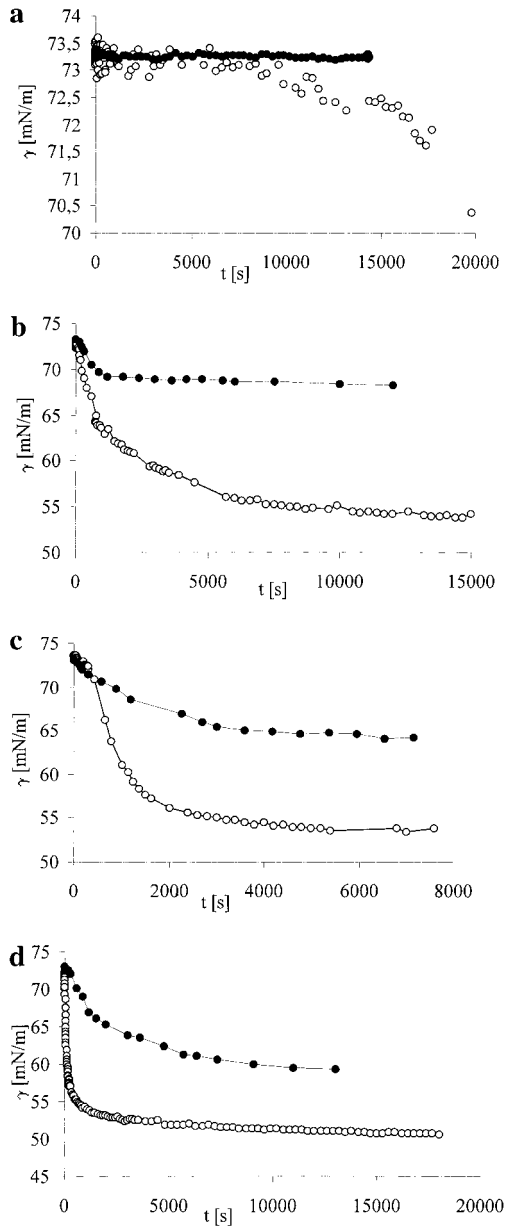

Figure 3. Dynamic surface tension γ of β-casein solutions as a function of time: (a) 5×10^{-9} mol/L, (b) 5×10^{-8} mol/L, (c) 10^{-7} mol/L, (d) 10^{-6} mol/L; (●) drop experiments, (○) bubble experiment.

bulk concentration within the drop. The correction of the bulk concentration with respect to the equilibrium adsorption using eq 2 and the $C_{10}EO_8$ adsorption isotherm equation derived in ref 17 results in perfect agreement of the two surface tension isotherms, as one can see in Figure 2.

The results for β-casein obtained using the two methods are in many aspects similar to those found for $C_{10}EO_8$. However, for the protein a number of significant additional features exist, which can be attributed to the peculiar properties of the protein molecule.

The dynamic surface tensions of β-casein concentrations of 5×10^{-9}, 5×10^{-8}, 10^{-7} and 10^{-6} mol/L are shown in Figure 3a−d. As one can see, the results from the two methods differ significantly. For the bubble the surface tension decrease starts much earlier. The surface tensions at long times, and hence the equilibrium surface tension from the bubble experiment, are lower than those from the drop. However, the establishment of a quasi-equilibrium for the drop method is more rapid at low β-casein concentrations (cf. Figure 3b), while at higher β-casein concentrations this process is more rapid for the bubble method (cf. Figure 3d). This essential difference between concentrated solutions of proteins and surfactants will be discussed below in more detail.

The behavior of β-casein solutions of low concentration ($c < 10^{-7}$ mol/L) is quite similar to that of $C_{10}EO_8$ solutions. We note that at low initial concentrations and high adsorption activity, which is typical for proteins, the final bulk concentration in the drop can become significantly lower than the initial one. By comparing the results obtained by the drop and bubble experiments one can estimate the value of the protein adsorption.

The theory of protein adsorption proposed in refs 18−20 assumes that multiple states of the protein molecule can exist in the surface layer. The partial molar area per molecule for any particular ith state is different from that of the neighboring states ($i \pm 1$) by the increment value $\Delta\omega$. This increment depends on the flexibility of the molecular chain and can, in principle, be extremely small. The range over which the partial molar area can vary is confined to certain minimum and maximum values, ω_{min} and ω_{max}, respectively. Therefore, $\omega_{max} = \omega_{min} + (n - 1)\Delta\omega$, where n is the number of states. The composition of the surface layer is controlled by the surface pressure (or by the total adsorption of all states). The most important characteristic of the model, the ratio of the adsorption in the ith state to the total adsorption, can be rigorously derived from a thermodynamic consideration of the chemical potentials for all possible states of protein molecules within the surface layer. For the most simple case, when the adsorption activity of the protein molecule is assumed to be equal in all states, and by neglecting the contribution of surface layer nonideality, the following relationship is obtained[19,20]

$$\Gamma_i = \Gamma_\Sigma \frac{\exp\left[-\dfrac{(i-1)\Pi\omega_1}{RT}\right]}{\sum_{j=1}^{n} \exp\left[-\dfrac{(j-1)\Pi\omega_1}{RT}\right]} \tag{7}$$

Here Γ_i and Γ_Σ are the adsorptions in the ith state and the total adsorption of all possible states, respectively; $\omega_1 = \omega_{min}$, Π is the surface pressure, R is the gas constant, and T is the temperature. It follows from eq 7 that with the increase in pressure Π, adsorption states possessing higher molar area are replaced by those of smaller areas, and the adsorption layer thickness increases. It follows from the theory presented in ref 19 that the main contribution to the surface pressure comes from the interion interaction, i.e., from the electric double layer which arises due to the significant unbound local charge of the protein molecules. The main equations of the model are the equation of state

$$\Pi = -\frac{RT}{\omega_\Sigma}[\ln(1 - \Gamma_\Sigma\omega_\Sigma) - a_{el}\Gamma_\Sigma^2\omega_\Sigma^2] \tag{8}$$

and the adsorption isotherm

$$bc = \frac{\Gamma_1\omega_\Sigma}{(1 - \Gamma_\Sigma\omega_\Sigma)^{\omega_1/\omega_\Sigma}} \tag{9}$$

The parameter b is an equilibrium constant, c is the bulk concentration of the protein, a_{el} is the interion interaction parameter, and ω_Σ is the mean molar area defined as the weighted average over all states of protein molecules in the surface layer

$$\omega_\Sigma = \omega_1 \frac{\sum_{i=1}^{n} i \exp\left(-\frac{i\Pi\omega_1}{RT}\right)}{\sum_{i=1}^{n} \exp\left(-\frac{i\Pi\omega_1}{RT}\right)} \qquad (10)$$

Among the parameters which enter eqs 8−10, only a_{el} can be varied to achieve a best fit with experimental data, because other parameters ω_{max}, ω_1, and $\Delta\omega$ are determined by the geometric dimensions of the protein molecule and its flexibility.

The equilibrium surface tensions of the β-casein solutions were obtained by extrapolation of the dynamic tensions to $t \rightarrow \infty$ in coordinates $\sigma - t^{-1/2}$ or $\sigma - t^{-1}$. The data obtained using the bubble method are in good agreement with the data of Graham and Phillips[21] (cf. Figure 4). At the same time, the data obtained from the drop method plotted as a function of the initial protein concentration, give lower values of the surface pressure Π for all the β-casein concentrations. It seems, however, that only for $c < 10^{-7}$ mol/L this effect can be ascribed to the redistribution of the protein between the bulk and the drop surface. As one can see from eq 2, the average protein concentration in the drop after the establishment of adsorption equilibrium is lower than the initial one. Comparing the values of the initial and final concentration, one can determine the adsorption of β-casein from eq 2. For these theoretical calculations we first determined the isotherm parameters using the data of Graham and Phillips,[21] and the results of the bubble experiments. For the thermodynamic model given by eqs 8−10, the following optimum values of the adsorption isotherm parameters were obtained: $\omega_{max} = 80$ nm^2, $\omega_{min} = 5$ nm^2, $\Delta\omega = 1$ nm^2, $b = 3.25 \times 10^6$ L/mol, and $a_{el} = 120$. For the drop experiments, the values of $\bar{c}$ calculated from eq 2 were found to be close to zero for all concentrations $c < 10^{-7}$ mol/L. Therefore, for β-casein concentrations $c < 10^{-7}$ mol/L the drop method does not allow one to obtain a corrected dependence of Π on c.

On the other hand, at $c \gg \bar{c}$ another option for a direct determination of protein adsorption arises. For this condition, the expression which describes the mass balance of protein in a drop, eq 2, yields $c \cong \Gamma(S/V)$. Therefore, the β-casein adsorption can be calculated directly from the initial protein concentration in a drop. In Figure 5 the experimental data of Graham and Phillips[21] are presented in the form of the Π dependence on Γ. Note that in ref 21 the adsorption Γ was determined independently by radioactivity and ellipsometry methods. The figure also contains the results obtained from our experiments at concentrations $c \gg \bar{c}$.

It is seen that the values of β-casein adsorption calculated from the mass balance condition are in perfect agreement with the results directly measured in ref 21.

At the same time, when the initial concentration of the protein within the drop exceeds 5×10^{-7} mol/L, the loss of mass caused by adsorption is rather small. Therefore, the loss of protein molecules is insufficient to explain the higher values of Π for $c > 5 \times 10^{-7}$ mol/L obtained from the drop method as compared with the bubble method and the data reported in ref 21 for a flat surface.

Equation 7 indicates that in the equilibrium state, a definite distribution of the adsorptions of protein molecules over all possible states exists, which depends on the surface pressure or total adsorption. It follows from eq 7 that for low Π and Γ_Σ values, the most probable state of the molecule is that corresponding to the highest possible ω value. It means that if the process of β-casein adsorption is very slow, then at low Π-values the β-casein molecules have sufficient time to become completely unfolded and spread over the solution/air interface. If the adsorption proceeds further on, and Π becomes higher, then for the equilibrium monolayer the states with ω lower than ω_{max}, which corresponds to $\Pi \approx 0$, will be more probable. In Figure 6 the portions of β-casein molecules which possess $\omega = \omega_1$, $\omega = \omega_1 + \Delta\omega$, $\omega = \omega_1 + 4\Delta\omega$, and $\omega = \omega_1 + 9\Delta\omega$ are plotted as a function of Π. It is seen that with the increase in pressure, only the portion of molecules with $\omega = \omega_1$ becomes higher, while the relative portions of the molecules in other states acquire some maximum values and then turn lower.

Returning again to Figure 3, one can see that for the drop method, at any concentration, the adsorption process proceeds more slowly than for the bubble method. Thus, at low Π values the probability for the β-casein molecule to exist in a completely unfolded state is higher, as compared to the bubble method. However, for medium and high Π values, according to eq 7,

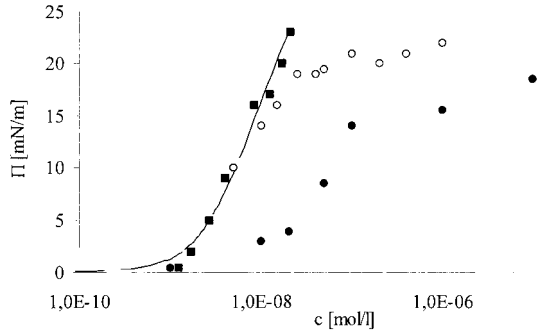

Figure 4. Surface pressure isotherm of β-casein: data of Graham and Phillips[21] (■), obtained from pendent bubble (○), obtained from pendent drop (●); theoretical line corresponds to present bubble experiments and data of Graham and Phillips.

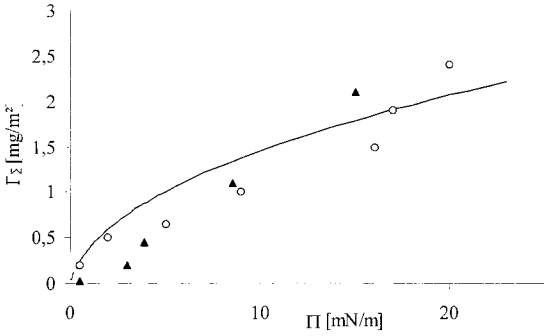

Figure 5. Adsorption of β-casein at the water/air interface as a function of surface pressure Π: (○) data of Graham and Phillips,[21] (▲) present data.

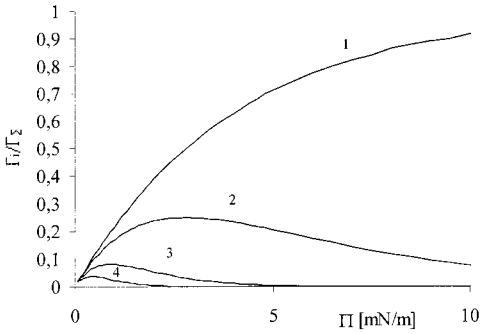

Figure 6. Adsorption of proteins at the water/air interface as a function of surface pressure Π calculated according to the theoretical model of eq 7: $\omega_i = 5$ (1), $\omega_i = 6$ (2), $\omega_i = 9$ (3), $\omega_i = 14$ (4) nm^2/molecule; $\omega_1 = 5$ nm^2/molecule, $\Delta\omega = 1$ nm^2/molecule, $T = 293$ K.

one can expect that a folding of molecules, which were previously unfolded, can happen (cf. Figure 6). This segment-by-segment folding process is quite slow, and can be described by a theory developed elsewhere.[19,20]

As the adsorption at large Π increases only due to the decrease in ω, the more unfolded the molecules of β-casein in the surface layer are, the slower this process will be. It is quite possible that the transition between the states $n\omega_1 \rightarrow (n-1)\omega_1$ is so slow that equilibrium cannot be achieved in a finite time interval.

For the bubble method, the initial adsorption rate is always higher than for the drop method, and therefore β-casein molecules have no time to complete the unfolding process. Therefore, they do not need to be subsequently folded up at medium and large Π values. This results in the fact that not only the dynamic surface pressures but also the equilibrium (or, more precisely, the quasi-equilibrium) pressures measured with the bubble method in the concentration range of $c = 10^{-7}-10^{-5}$ mol/L are higher than those values measured with the drop method.

Conclusions

Comparing the two methods, axisymmetric drop and bubble shape analysis, one can conclude that the use of bubbles enables one to obtain real equilibrium surface tension values of protein solutions, although the establishment of equilibrium requires rather long time. The time necessary to achieve the diffusion equilibrium could be reduced by induced convection in the solution bulk. In the drop method the equilibrium state is established relatively rapidly while the protein concentration in the solution is decreasing due to loss of protein by adsorption. A simultaneous use of both methods seems to be especially effective. A comparison of the results allows to estimate the adsorption of a protein or surfactant of extremely high adsorption activity, i.e., at extremely low bulk concentrations. Another interesting experiment can be performed by varying the drop radius. In this case the adsorption can be calculated from the change in the ratio $V/S = r/3$.

As the quantitative description of dynamics of protein adsorption is still on a very low level, experiments have been started with highly surface active surfactants adsorbing in a concentration range very similar to that of β-casein. In this way, it will be possible to separate the effect of surfactant loss due to adsorption from the effect of conformational changes so that the difference in the adsorption rate to bubble and drop surfaces, respectively, can be analyzed quantitatively.

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