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# A Kinetic Model for Describing the Effect of Proteins on the Air-Water Interface Tension

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**Abstract:** The main objective of this work was to develop a kinetic model to describe the variation of the surface tension in an air-water interface due to the adsorption of proteins from different origins and to identify quantitatively the relevant parameters. It was considered that the processes of adsorption, unfolding and reordering of the protein molecule in the interface occur simultaneously. The model used in the present work to calculate the surface tension postulates the existence of two simultaneous processes, adsorption and protein rearrangement represented with an equation of first order with two exponential components. The relevant parameter of the equation are $k_a$ and $k_r$—the rate constants of the two first order kinetic phases that correspond to both conformational states of the protein, adsorption and rearrangement during the process of variation of the surface tension, and the amplitude parameters $A_a$ and $A_r$. The results suggest that the kinetic model for the variation of the surface tension of protein solutions proposed in this work, with two simultaneous first order processes, is more appropriate than previous models to describe such variation.

**Key words:** Interface tension, proteins, kinetic model.

## 1. Introduction

The characteristic texture of many food products is due to the existence of a foamy structure (breads, spongy cakes, meringues, ice-creams, mousses, shakes, beer, champagne, etc.) [1]. The structure of most typical foams is formed and stabilized by the presence of proteins adsorbed in the air-solution interface [2]. Graham and Phillips [3] have demonstrated that the most important factor contributing to the foaming capacity of a protein solution is the rate at which the protein can reduce the surface tension, because a new interfacial area is continuously created during beating or bubbling. According to Kitabatake and Doi [4], the foaming capacity of proteins is not related to its equilibrium surface tension, but to the rate of surface tension diminution.

A proper application of surfactant agents like proteins requires a qualitative and quantitative knowledge of the balance and the behaviour of such agents in the interface. Several techniques have been developed to study the dynamic changes of the interface tension. One of most frequently used methods is the drop volume method, which presents several advantages compared to other methods [5].

The creation of a kinetic model for the variation of the surface tension would yield a set of parameters that help to determine which proteins present the most appropriate characteristics. Boutaric and Berthier [6] and Frisch and Al-Madfai [7] have developed kinetic models describing the process of variation of the surface tension due to the adsorption of tensioactives in general, whereas, Graham and Phillips [3], Tornberg [8], Kitabatake and Doi [9] and Kim [10]

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have developed kinetic models to describe the reduction of interfacial tension with time due to the adsorption of proteins in the interface. The objective of the present work was to develop a kinetic model to describe the variation of the surface tension in an air-water interface due to the adsorption of proteins from different origins and to identify quantitatively the relevant parameters.

## 2. Materials and Methods

The following proteins were used: bovine serum albumin, β-casein, hemoglobin and lysozyme from Sigma Chemical Co., α-lactalbumin and β-lactoglobulin from Davisco Foods International Inc., and glycinin and β-conglycinin obtained and purified according to Nagano et al. [11].

The determinations of surface tension ($\sigma$) in the water-air interface were obtained with a dynamic droplet tensiometer (Tracker, IT-Concept; Saint-Clementtes Places, France). Measurements were performed at room temperature (25 ± 3 °C). The aqueous phase (containing proteins) was located in the bucket of the tensiometer and a droplet of 3 μL was formed. The interfacial tension of the interfacial film was evaluated during 120 s; measures were done every second during the first 10 s and then every 10 s. The test was carried out using solutions of the different proteins at 1 mg/mL and pH 7.0, in 0.01 M sodium phosphate. The determinations correspond to duplicates which were also assayed twice.

Data were analyzed by analysis of variances (ANOVA) with $P < 0.05$, and comparison of averages by the test of least significant differences (LSD), using the Statgraphics plus 7.0 software.

## 3. Results and Discussion

Fig. 1 shows the variation of surface tension, $\sigma$ versus time for ß-conglycinin, which is representative of the behaviour of all the samples. The graph shows a fast equilibrium value. Boutaric and Berthier [6] reported that the decay rate of the surface tension can be analyzed by means of a first order equation, expressed as:

$$(\sigma_t - \sigma_c)/(\sigma_w - \sigma_c) = e^{-kt} \quad (1)$$

where, $\sigma_c$ is the surface tension at 120 min after starting the modification of the surface, $\sigma_w$ is the surface tension at $t = 0$, which equals the solvent surface tension, $\sigma_t$ is the surface tension at time = $t$ and $k$ is the rate constant. Based on this postulation, Kitabatake and Doi [9] proposed to write the Eq. (1) as:

$$\ln[(\sigma_t - \sigma_c)/(\sigma_w - \sigma_c)] = -kt \quad (2)$$

and to plot $\ln[(\sigma_t - \sigma_c)/(\sigma_w - \sigma_c)]$ versus $t$, where, $k$ can be determined from the slope of the linear portion of the graph. Applying this procedure to the experimental data collected in this work, curves similar to those reported by Kitabatake and Doi [9] were obtained. The curve corresponding to β-conglycinin is shown in Fig. 2. This data processing rejects the first values

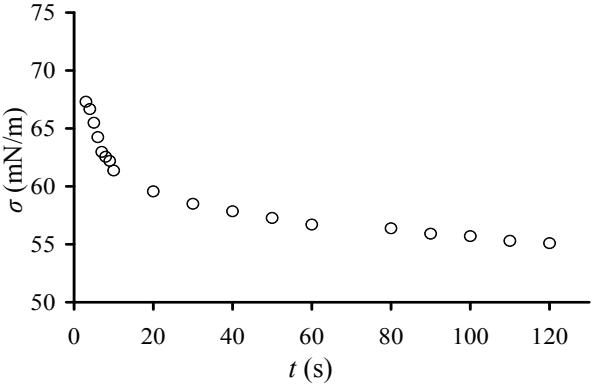


**Fig. 1 Experimental data of $\sigma$ versus $t$ for a solution of β-conglycinin.**

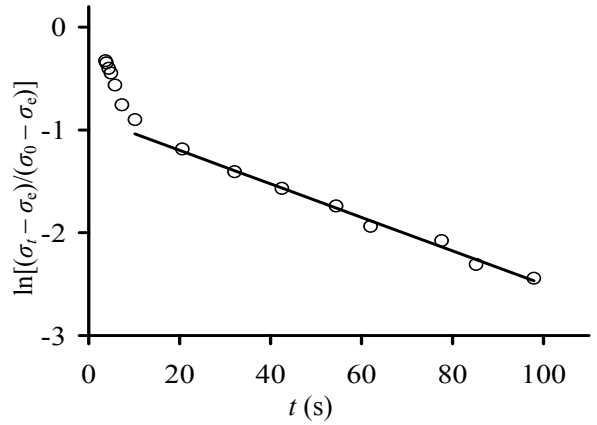


**Fig. 2 Plot of $\ln[(\sigma_t - \sigma_e)/(\sigma_0 - \sigma_e)]$ versus $t$ the experimental data of β-conglicinin (○) and as proposed by Kitabatake and Doi [9], corresponding to β-conglycinin.**

corresponding to the first interval surface tension variation with time, and calculates $k$ considering only the linear section. Based on the work of Frisch and Al-Madfai [7], Graham and Phillips [3] proposed that the kinetics of surface tension modification can be represented by a first order equation expressed as:

$$\ln[(\Pi_{ss} - \Pi_t)/(\Pi_{ss} - \Pi_0)] = -kt \quad (3)$$

Where, $\Pi_{ss}$, $\Pi_t$ and $\Pi_0$ are the values of surface pressure at a constant state, at time = 0, and at time = $t$, respectively, and $k$ is the rate constant. $\Pi$ is the results from:

$$\Pi = \sigma_0 - \sigma_t \quad (4)$$

It can be observed that Eqs. (2) and (3) are equivalent. When Eq. (3) was applied to the experimental data obtained in this work, curves similar to those shown by Graham and Phillips [3] were obtained. The curve shown in Fig. 3a corresponds to β-conglycinin. In agreement with that reported by Graham and Phillips [3], the application of Eq. (3) to the experimental data (graphs $\ln[(\Pi_{ss} - \Pi_t)/(\Pi_{ss} - \Pi_0)]$ versus $t$) yielded two linear portions, thus allowing to identify two rate constants $k_1$ and $k_2$ (Fig. 3a).

This approach establishes the existence of two different successive kinetics during the modification of surface tension (or surface pressure). After an initial period during which the surface tension diminishes at a certain rate, a rate change occurs, which can be detected as a modification of the rate constant. Graham and Phillips [3] correlated the slope change with the fact that protein concentration in the interface ($\Gamma$) reaches a balance. Consequently, two phases would take place, the first one with the constant $k_1$ while $\Gamma$ increases, and the second one with the constant $k_2$ when $\Gamma$ is constant. The first phase would be related with the adsorption, penetration and potential unfolding of the protein molecule in the interface, while the second phase would be related with the rearrangement of protein molecules once the adsorption has ended. Tornberg et al. [12] agreed with Graham and Phillips [3] indicating that the rate of

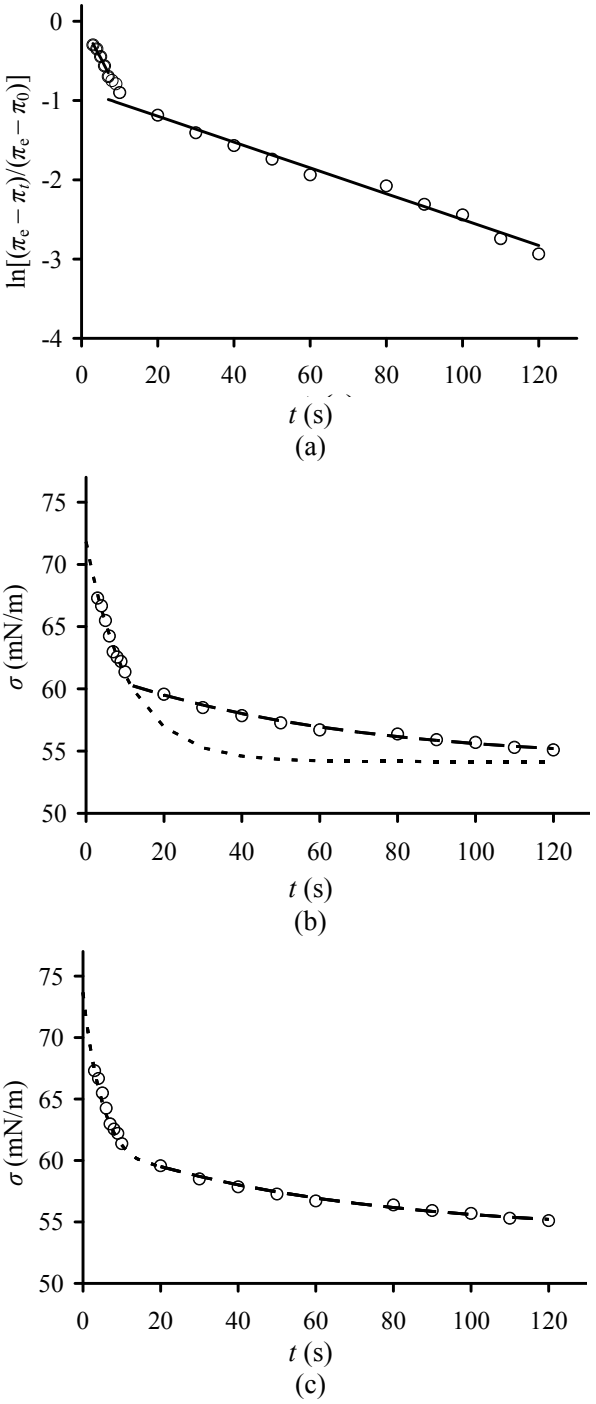


**Fig. 3 (a) $\ln[(\pi_e - \pi_t)/(\pi_e - \pi_0)]$ versus $t$ of the experimental data of β-conglicinin (○) and as proposed by Graham and Phillips [3] corresponding to β-conglycinin; (b) variation of surface tension versus time in the two stages represented by Eqs. (5) (. .) and (6) (— —) according to Graham and Phillips [3]; (c) variation of surface tension versus time in the two stages represented by the modified Eq. (5) ($\sigma_e = \sigma_{e1}$) (. .) and Eq. (6) (— —) according to Graham and Phillips [3], corresponding to ß-conglycinin.**

diminution of the interface tension of proteins could be evaluated through three consecutive stages: the diffusion of protein molecules, the adsorption to the interface, and the unfolding of the already adsorbed molecules. The proteins with a surface activity appropriate for foam elaboration must have three attributes: (1) to adsorb quickly to the interface; (2) to unfold and to reorient themselves quickly in the interface; (3) to have the capacity, once located and oriented in the interface, to interact with neighbouring molecules and to form a strong viscoelastic film, able to support the mechanical and thermal movements [13, 14]. For these reasons, the proposal of Graham and Phillips [3] about the existence of two different kinetic during the modification of the surface tension is adequate. The mathematical expression for the variation of the surface tension versus time according to this model would include two first order equations:

$$\sigma_1 = (\sigma_0 - \sigma_e) A_1 e^{-k_1 t} + \sigma_e \quad (5)$$

$$\sigma_2 = (\sigma_0 - \sigma_e) A_2 e^{-k_2 t} + \sigma_e \quad (6)$$

where, $\sigma_1$ corresponds to the first phase, related to the adsorption and possible unfolding of the protein molecule in the interface, and $\sigma_2$ corresponds to the second phase, related to the reordering of protein molecules after the adsorption has stopped. $A_1$ and $A_2$ represent amplitude parameters corresponding to each stage.

The graphical representation of the variation of the surface tension versus time according to the postulate of Graham and Phillips [3] is shown in the Fig. 3b. According to this mathematical model, the surface tension in the equilibrium is the same for both stages (Eq. (5) and Fig. 3b). Thus, although two successive kinetic stages are proposed, the first of which would take place until protein adsorption stops, and the $\sigma_e$ measured at the end of the process is used to calculate the rate constant corresponding to this stage. This implies that the process of surface tension diminution due to adsorption would continue even after the second stage, corresponding to molecular rearrangement, has started. It can be seen that there is a contradiction between the conceptual and the mathematical models. A possible solution could be to solve Eq. (3) considering for the first stage a $\Pi_{ss}$ value corresponding to the $\Pi$ value that would be obtained when $\Gamma$ reaches the equilibrium. In Graham and Phillips [3], this value would coincide with the slope change in the $\ln[(\pi_e - \pi_t)/(\pi_e - \pi_0)]$ versus time plot (Fig. 3a). With this approach, different values for $A_1$ and $k_1$ would be obtained. In Eq. (5), $\sigma_e$ should be replaced with $\sigma_{e1}$ corresponding to the slope change already mentioned, which must be experimentally measured. The surface tension versus the time for the two stages is that represented in Fig. 3c.

Fainerman et al. [15] proposed that the surface pressure could be expressed as:

$$\Pi = (RT/\omega_\Sigma) \times [\ln(1 - \Gamma_{\Sigma\omega_\Sigma})] \quad (7)$$

where, $R$ is universal gas constant, $T$ is the thermodynamic temperature and

$$\Gamma_\Sigma = \Sigma_{\Gamma i} \quad (8)$$

$\Gamma_\Sigma$ is the total adsorption of the protein, the sum of all the adsorption states, and $\omega_\Sigma$ is the mean partial molar surface, which is determined as proposed by Lucassen-Reynders [16] for mixtures of surfactants, calculating the weighted average using the interface concentration at the different adsorption states.

$$\omega_\Sigma = (\Sigma \omega_i \Gamma_i)/\Gamma_\Sigma \quad (9)$$

Then the processes of adsorption, unfolding and reordering of the protein molecule in the interface must happen simultaneously. In the present work it was considered that if the changes of surface tension in the interface are due to the presence of protein in its different conformational states, the kinetics of the variation of the surface tension must be directly related to the kinetics of variation of the conformational states of the protein. Then the surface tension at a certain moment can be expressed as:

$$\sigma_t = \sigma_0 - \Sigma f_i P_i \quad (10)$$

where, the $f_i$ factors indicate the correlation between surface tension and protein concentration in the interface in its different conformational states. Considering that, as proposed by Graham and Phillips

[3], the conformational changes of a protein during adsorption in the interface are two, these can be represented as:

$$P_s \xrightarrow{\text{adsorption}} P_1 \xrightarrow{\text{rearrangement}} P_2$$

where, $P_s$ is the dispersed protein and $P_1$ and $P_2$ are different conformational states of the protein in the interface. The variation of $P_1$ versus time corresponds to a first order kinetic [17] and can be expressed as:

$$P_1 = k_1/(k_2 - k_1)P_{so}\,e^{-k_1 t} - k_1/(k_2 - k_1)\,P_{so}\,e^{-k_2 t} + P_{1o}\,e^{-k_2 t} \quad (11)$$

where, $P_{1o}$ is $P_1$ initial. The variation of $P_2$ as a function of time can be expressed as:

$$P_2 = P_{so} + P_{1o} + P_{2o} - P_s - P_1 \quad (12)$$

where, $P_{2o}$ is $P_2$ initial and $P_{so}$ is the maximum amount of protein in the solution necessary to saturate the interface and $P_s$ is the part of $P_{so}$ that still has not reached the surface. Replacing Eq. (12) in Eq. (11) and reordering the terms, the expression for $P_2$ is:

$$P_2 = P_{so} + P_{1o} + P_{2o} - P_{so}\,e^{-k_1 t} - (k_1/(k_2 - k_1)\,P_{so}\,e^{-k_1 t} + (k_1/(k_2 - k_1)P_{so}\,e^{-k_2 t} - P_{1o}\,e^{-k_2 t} \quad (13)$$

Eq. (10) can then be written as:

$$\sigma_t = \sigma_0 - f_1[k_1/(k_2 - k_1)\,P_{so}\,e^{-k_1 t} - k_1/(k_2 - k_1)\,P_{so}\,e^{-k_2 t} + P_{1o}\,e^{-k_2 t}] + f_2[P_{so} - P_{so}\,e^{-k_1 t} + P_{1o} + k_1/(k_2 - k_1)\,P_{so}\,e^{-k_2 t} - k_1/(k_2 - k_1)\,P_{so}\,e^{-k_1 t} - P_{1o}\,e^{-k_2 t} + P_{2o}] \quad (14)$$

Taking into account the nature of protein effects on surface tension, $f_2$ was expected to be greater than $f_1$, meaning that the effect of the unfolded protein is larger than the effect of the protein in the surface before unfolding. Also, taking into account the results of previous models, $k_2$ was expected to be smaller than $k_1$, which means that the unfolding or reordering processes are slower than diffusion to the surface. According to these assumptions, and considering that the adsorption, the unfolding and the reordering of proteins in the interface are the main causes of the decrease of the surface tension, it is logical to assume that these processes happen simultaneously during surface tension diminution. In addition, considering that previous adsorption is necessary for surface tension to diminish due to protein reordering, it is reasonable to attribute $k_1$, which predominates in the initial period, to the adsorption of proteins in the air-water interface. Therefore, Eq. (14) can be expressed as

$$\sigma_0 - \sigma_t = f_a\,[k_a/(k_r - k_a)\,P_{so}\,e^{-k_a t} - k_a/(k_r - k_a)P_{so}\,e^{-k_r t} + P_{1o}\,e^{-k_r t}] + f_r\,[P_{so} - P_{so}\,e^{-k_a t} + P_{1o} + k_a/(k_r - k_a)\,P_{so}\,e^{-k_r t} - k_a/(k_r - k_a)\,P_{so}\,e^{-k_a t} - P_{1o}\,e^{-k_r t} + P_{2o}] \quad (15)$$

where, $k_a$ and $k_r$ are the first order rate constants for the adsorption and reordering processes of the proteins in the air-water interface, respectively, and $f_a$ and $f_r$ are the factors that correlate the surface tension with the concentration of the protein in its different conformational states.

Fig. 4 depicts the total variation of the surface tension and the variation due to each of the two conformational states according to the proposed kinetic model represented by Eq. (15). It can be seen that the effect of surface tension decline due to each of the conformational states is simultaneous, but one of them is initially dominant and then lowers until it has no effect, while the other state prevails at the final stages. During the initial period, the decrease of surface tension would be due mainly to protein adsorption, which prevails over the process of reordering at the interface. But as a larger amount of

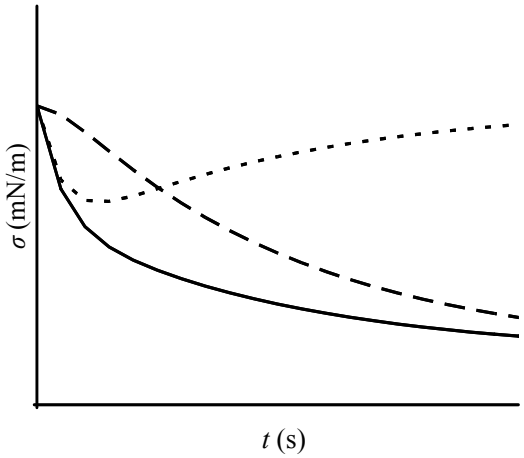


**Fig. 4 Variation of surface tension vs. time, corresponding to: total variation (—) and the two stages represented in Eq. (15), variation due to adsorbed protein (– –), variation due to adsorbed and reordered protein (- -).**

adsorbed protein changes its conformational state, its interface concentration diminishes. Therefore, the same occurs with its effect on the decrease of the surface tension, which becomes less and less important until getting null. It is in this process that the interface concentration of proteins in a rearranged conformational state becomes preponderant and so does its contribution to the decrease of surface tension. This mechanism assumes that the process of unfolding of the proteins in the surface is either irreversible or is an equilibrium strongly displaced to the unfolded state.

By reordering the terms, Eq. (15) can be written as:

$$\sigma_0 - \sigma_t = [(f_a - f_r)P_{so}k_a/(k_r - k_a) - f_rP_{so}]\,e^{-k_a t} + [(f_r - f_a)P_{so}k_a/(k_r - k_a) + (f_a - f_r)P_{1o}]\,e^{-k_r t} + f_rP_{so} + f_rP_{1o} + f_rP_{2o} \quad (16)$$

Based on this last expression and considering the conditions $f_r > f_a$, and $k_r < k_a$ to be fulfilled, it was considered more convenient to describe the process of modification of the surface tension with an equation of first order but with two exponential components, as follows:

$$\sigma_t = A_a e^{-k_a t} + A_r e^{-k_r t} + \sigma_e \quad (17)$$

where, $k_a$ and $k_r$ are the rate constants of the two first order kinetic phases that correspond to both conformational states of the protein during the process of variation of the surface tension, whereas $A_a$ and $A_r$ are amplitude parameters. The simplification of the mathematical expression allows an easier estimation of the kinetic constants $k_a$ and $k_r$. These were estimated by means of least squares regressions (Table 1), but it is

**Table 1 $k_a$, $k_r$ and $k_a/k_r$ values corresponding to the different protein dispersions studied.**

| Protein | $k_a \times 10$ | $k_r \times 10^3$ | $k_a/k_r$ |
|---|---|---|---|
| α-lactalbumin | 2.6 ± 0.2 | 7.2 ± 0.9 | 36 |
| β-lactoglobulin | 3.6 ± 0.1 | 4.5 ± 0.2 | 80 |
| β-casein | 3.3 ± 0.5 | 4.7 ± 0.9 | 70 |
| β-conglycinin | 1.6 ± 0.2 | 6.4 ± 0.3 | 25 |
| Glycinin | 0.9 ± 0.2 | 4.4 ± 0.4 | 20 |
| Hemoglobin | 1.9 ± 0.4 | 8.1 ± 0.9 | 23 |
| Lysozyme | 0.6 ± 0.2 | 2.7 ± 0.9 | 22 |
| Bovine serum albumin | 2.7 ± 0.1 | 6.5 ± 0.6 | 41 |

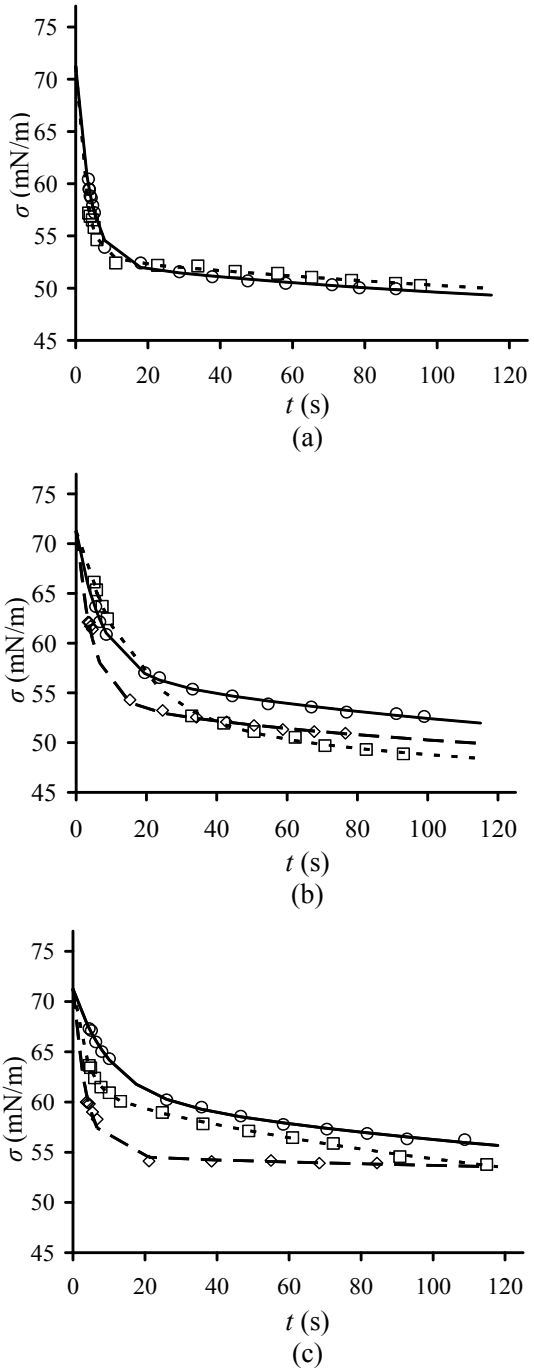


**Fig. 5 (a) Curves of surface tension versus time of the experimental data for α-lactalbumin (○) and β-lactoglobulin (□), and the respective curves considered according to Eq. (16) for the same data; (b) curves of surface tension versus time of the experimental data for β-conglycinin (○), glycinin (□) and hemoglobin (◊), and the respective estimated curves based on Eq. (16); (c) curves of surface tension versus time for the experimental data of lysozyme (○), bovine serum albumin (□) and β-casein (◊), and the respective estimated curves based on Eq. (16) for the same data.**

necessary to note that the full description of the physicochemical process would be correctly described only by Eq. (15).

The curves of surface tension versus time for the different proteins under study are shown in Figs. 5a-5c curves (markers), as well as the curves (lines) for the equation adjusted for the same experimental data. It can be seen that the adjustment obtained is good. The proposed model correlates well with the experimental data in the whole range of the variation of surface tension versus time. The application of the biphasic first order equation to the experimental data presented a good adjustment, with $r^2$ in an interval between 0.995-0.998 (Table 1). According to Damodaran [18], the most critical requirement for the formation of foam during whipping or homogenization is the fast reduction of the free energy (interfacial tension) of the newly formed interface. Although a fast protein adsorption is needed to facilitate this reduction in surface tension, this is not a rate limiting step for the speed under dynamic flow conditions. The rate-limiting is the rapidity with which the protein undergoes conformational rearrangements and reorientation in the interface and its effect on the decrease of interfacial tension. Studies made by Xu and Damodaran [19, 20] and Annad and Damodaran [21] about the relative differences among the abilities of β-casein, bovine serum albumin and lysozyme to decrease the superficial tension during their adsorption in the water-air interface, demonstrated that among these structurally very different proteins, the rate of increase of the surface pressure (or the rate of decreasing of the surface tension) is proportional to the rate of increase of the surface concentration. In the case of the β-casein, both the surface pressure and the surface concentration reached their equilibrium values simultaneously [20], suggesting that the β-casein could unfold completely, reorient and reduce the interface tension as soon as it reached the surface. Annad and Damodaran [21] found that, in the case of bovine serum albumin, the surface pressure did not reach the stationary state and increased continuously, even after the surface concentration reached the value of stationary state. This would suggest that the unfolding and the rearrangement of the bovine serum albumin are not as fast as in the case of the β-casein, but still continue after the saturated layers have formed in the interface. The change in the surface pressure with lysozyme solutions was slower than with bovine serum albumin [19-21]. In addition, as it happened with the later protein, the surface pressure of the lysozyme solution did not reach the stationary state until after a long time, even after the superficial concentration had reached a stationary state, indicating that the rate of conformational change at the surface was very slow. It is important to emphasize that although the surface concentrations of bovine serum albumin and lysozyme were very similar after a long adsorption time, surface pressure values were very different. This difference reflects a differential capacity of these globular proteins to unfold and reorient in the interface and to reduce the interface tension.

The results obtained in the present work agree with those of other authors, which have been described above. It can be seen that for ß-casein, $k_a$ was significantly higher than $k_r$ ($k_a/k_r$ = 70) (Table 1), indicating that the most important contribution to the rate of reduction of surface tension was due to the adsorption process. The $k_a$ value of ß-casein was significantly higher than that of bovine serum albumin (Table 1), indicating that the rate of adsorption process of the later protein was slower and its $k_a/k_r$ ratio was significantly lower (Table 1). This would indicate that the reduction of the surface tension during the process of reordering of the bovine serum albumin in the interface continued and contributed more than in the case of β-casein. As shown in Fig. 5c, the reduction of surface tension, mainly during the initial phase of dissolution, was larger for bovine serum albumin than for lysozyme. It is necessary to take into account that in the present work the

reduction of surface tension had to happen much faster that in the studies of Xu and Damodaran [19, 20] and Annad and Damodaran [21], since protein concentrations were three orders of magnitude higher. Therefore, the larger reduction of surface tension in the initial period with the dissolution of bovine serum albumin may be due to the fact that the $k_a$ value of this protein was significantly higher than that of lysozyme.

## 4. Conclusions

The model used in the present work fits well with the experimental data for different proteins in the whole time interval, showing that there are not two consecutive stages but two parallel phenomena. In summary, the results suggest that the kinetic model for the variation of the surface tension of protein solutions proposed in this work, with two simultaneous first order processes, is more appropriate than previous models to describe such variation.

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