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A KINETIC DESCRIPTION FOR THE DESTABILIZATION PROCESS OF PROTEIN FOAMS

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In the present work, a new kinetic model to describe the protein foam destabilization was determined by the conductimetric method. The second order, two term kinetic of foam destabilization by liquid drainage proposed in the current study was more adequate for describing the destabilization process than those presented until the present, showing the existence of two simultaneous mechanisms of foam destabilization, which predominate alternatively according to foam age. In the different foams formed with the studied proteins, k values corresponding to gravitational drainage were always at least one order of magnitude higher than those corresponding to Ostwald ripening.

Keywords: *Stability, Protein, Kinetic, Drainage, Ostwald ripening.*

INTRODUCTION

The process of foam destabilization results from the tendency of the discontinuous gas phase to form, by approach and fusion of the bubbles, a continuous phase allowing a minimum surface area. This process is opposed by the superficial proteinaceous film, whose properties as an effective mechanical barrier increase with increasing viscoelasticity and rigidity.[1,2]

The mechanisms of foam destabilization are drainage of liquid, collapse by lamellar breakage, and Ostwald ripening.[1–3] The drainage of the liquid is produced first by simple action of the gravity on the liquid forming the bubbles. Later, it is produced by more complex processes arising from the difference in curvature between the Plateau edges and the flat part of the films, which creates a pressure gradient according to the Laplace law.

$$\Delta P \propto \sigma [(1/R_a) - (1/R_b)], \tag{1}$$

where R_a and R_b are the curvature radii of Plateau edges and lamellas, respectively. This pressure difference (ΔP) is the driving force that moves the liquid from the inter-bubble lamellas to the Plateau edges, by a mechanism called capillary suction. Next, the liquid is drained by action of the gravity from the edges of Plateau to the lower portion of the foam.

As lamellas weaken as a consequence of thickness decrease (caused by liquid drainage or evaporation) or the presence of particles, lamellar disruption occurs leading to foam collapse. The Ostwald ripening or maturation is the process resulting from the pressure difference between the bubbles (which can also be calculated from Eq. (1) if R_a and R_b are the radii of curvature of the small and large bubbles, respectively), leading to the growth of large bubbles by gas diffusion from the smaller bubbles through the lamellas.

All of these destabilization mechanisms happen simultaneously and synergically.[1,2] A consequence of these processes is that liquid is drained from the foam to the solution. Foaming stability can be assessed by measuring:

- the percentage of foam volume that remains after a given time,[4,5]
- establishing the volume of drainage to a fixed time,[6] or
- the time for half-drainage after the end of bubbling.[7]

However, in all of these cases, a kinetic model that described the destabilizing mechanism was not established.

Many empirical equations have been used to describe the experimental drainage profile. Different researches[8–10] used first order equations. Others applied second order equations to study foam stability.[1,11,12] On the contrary, some of them have proposed that the mechanism of foam destabilization follows first order biphasic kinetics.[13–15] The objective of the present work was to develop a kinetic that allows to describe the stability of foams formed and stabilized by proteins of different origins and to quantitatively identify the different factors involved in foam stability.

MATERIALS AND METHODS

The following proteins were used: ß-casein, hemoglobin, bovine serum albumin (Sigma Chemical Co., St. Louis, MO, USA), α-lactalbumin, ß-lactoglobulin (Davisco Foods International Inc., Eden Prairie, MN, USA), and glycinin and ß-conglycinin obtained and purified according to Nagano et al.'s method.[16]

Foam formation and stability were studied using the conductimetric method with small modifications[17] (equipment TIAV 2002). Foam was generated by bubbling air through a type G2 sintered glass plate with a 100 ml/min flow until a previously determined volume of foam (60 ml) was obtained. The tests were performed using 10 ml of dispersion of the proteins under study (1 mg/ml in 0.1 M sodium phosphate, pH 8). This foaming device allowed analyzing the formation of foam and stability by conductimetric measurements of the solution, including parameters, such as volume of liquid in the foam (V_{LF}) versus time. The determinations were made on duplicate samples and were tested three times each.

RESULTS AND DISCUSSION

Kinetic for the Drainage of Liquid from Foams

Figure 1 depicts the volume of liquid drained from the foam (V_{LDF}) as a function of time for glycinin, one of the studied proteins, which is similar to the behavior of foams
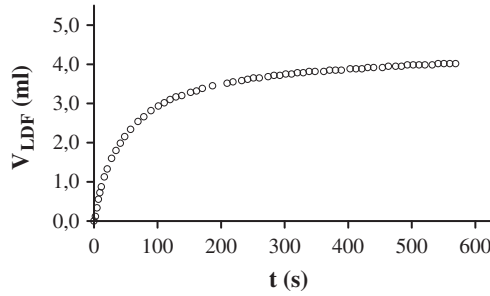
Figure 1 Experimental data of V_{LDF} as a function of time of a glycinin foam. The time 0 is the end of bubbling.

formed by the other proteins. V_{LDF} values were obtained from the data of V_{LF} versus time using $V_{LDF} = V_{LFmax} - V_{LF}$. The equation for describing the drainage profiles using first order kinetics is:[10]

$$V_{LDF}(t) = V_{LFmax}(1 - e^{-kt}), \tag{2}$$

where $V_{LDF}(t)$ is the volume of drained liquid at time t, V_{LFmax} is the maximum volume of drained liquid, and k is the kinetic constant. For second order kinetics, the equation is [12]:

$$V_{LDF}(t) = V_{LFmax}t/(B + t), \tag{3}$$

where $V_{LDF}(t)$ is the volume of drained liquid at time t, V_{LFmax} is the maximum volume of drained liquid, and B is the time needed to drain $V_{LFmax}/2$. Equations (2) and (3) were applied to the experimental data and the parameters were determined by least squares regression. Figure 2 shows the experimental data of one of the studied samples (soy glycinin) and the curves corresponding to the application of both kinetics. Similar graphs were obtained with the other samples under study. It can be seen that the kinetic of second order has a better agreement with the experimental data. In addition, least squares regression performed on the first order equation led to a significantly smaller r^2 (Table 1) than the regression on the second order equation, indicating that the latter is more suitable for describing the draining process.
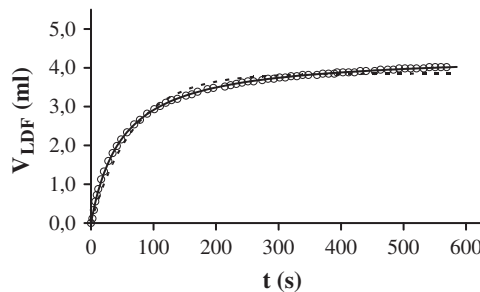

Figure 2 Experimental curve of V_{LDF} as a function of time of a glycinin sample, and curves obtained using data estimated with first order (■■■) and second order (−) equations. The time 0 is the end of bubbling.

Table 1 r^2 values for the different kinetics evaluated.

Protein	First order, monophasic	Second order, monophasic	First order, biphasic	Second order, biphasic
β-Casein	0.969 ± 0.005	0.9997 ± 0.0001	0.9962 ± 0.0006	0.9999 ± 0.0001
α-Lactalbumin	0.978 ± 0.007	0.9972 ± 0.0009	0.995 ± 0.002	0.9976 ± 0.0006
β-Lactoglobulin	0.973 ± 0.002	0.9994 ± 0.0001	0.995 ± 0.003	0.9996 ± 0.0002
Glycinin	0.982 ± 0.002	0.9995 ± 0.0002	0.9970 ± 0.0006	0.9995 ± 0.0001
β-Conglycinin	0.978 ± 0.003	0.9990 ± 0.0001	0.9975 ± 0.0006	0.9998 ± 0.0001
Hemoglobin	0.981 ± 0.002	0.9995 ± 0.0002	0.993 ± 0.003	0.9998 ± 0.0001
Bovine serum albumin	0.981 ± 0.005	0.9991 ± 0.0004	0.996 ± 0.004	0.9995 ± 0.0004

Some authors found that foams prepared by bubbling from dispersions of high protein content presented sigmoideal liquid drainage curves,[18] for which they proposed the following kinetic equation:

$$V_{LDF}(t) = V_{LDFmax} t^n / (c + t^n), \qquad (4)$$

where n parameters are introduced as exponentials of t and c in Eq. (3). In this equation, n is characteristic of the sigmoideal behavior of the drainage kinetics curve, and c is related to the mean drainage time according to the following expression:

$$B = c^{1/n}. \qquad (5)$$

As in the current study, none of the curves of V_{LDF} as a function of time for the studied proteins had a sigmoideal shape; the use of this equation was not considered adequate. The method here used for studying foam stability allows determining the maximum volume of liquid incorporated by the foam (V_{LFmax}). In every case, the maximum volume of drained liquid (V_{LDFmax}) determined by the use of first order and second order kinetics did not agree with the experimental V_{LFmax} values. The latter was higher, since the V_{LDFmax}/V_{LFmax} ratio was lower than 1. These findings allow two hypotheses: first, not all of the liquid incorporated by the foam is drained and these foams would be infinitely stable; and, second, the retained liquid drains by a mechanism different from the initial one. The latter hypothesis seems more reasonable and, therefore, the second order kinetics would not describe adequately the destabilization behavior of foams by liquid drainage.

Some authors[13–15] have proposed that the destabilization mechanism of foams follows biphasic first order kinetics, suggesting the involvement of two microscopic processes in foam destabilization. Such kinetics could be expressed as:

$$V_{LDF}(t) = Q_g \exp(-k_g t) + Q_d \exp(-k_d t), \qquad (6)$$

where $V_{LDF}(t)$ is the volume of liquid drained at t time, k_g and k_d are first order rates constants for the gravitational drainage and gas diffusion processes, respectively, and Q_g and Q_d are the respective amplitude parameters. Once the parameters of Eq. (6) are determined by least squares regression of the experimental data, a close inspection of Fig. 3 and the calculated r^2 values reveal that the adjustment using this kinetic is poorer than that achieved with the second order equation. Notwithstanding, the lack of agreement between
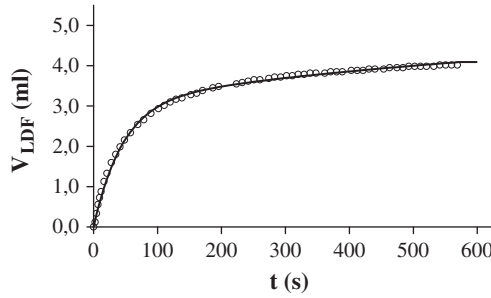
Figure 3 Experimental data (○) of V_{LDF} as a function of time of glycinin sample, and the corresponding curve (−) of values estimated with a biphasic first order kinetic as proposed by Yu and Damodaran (1991). The time 0 is the end of bubbling.

Table 2 Estimated values of the relationship V_{LDFmax}/V_{LFmax} in the different kinetics studied.

Protein	Kinetic			
	First order, monophasic	Second order, monophasic	First order, biphasic	Second order, biphasic
β-Casein	0.82	0.91	1	1
α-Lactalbumin	0.85	0.93	1	1
β-Lactoglobulin	0.79	0.88	1	1
Glycinin	0.79	0.90	1	1
β-Conglycinin	0.70	0.81	1	1
Hemoglobin	0.84	0.93	1	1
Bovine serum albumin	0.81	0.92	1	1

the volume of liquid incorporated by the foam and the volume of drained liquid no longer exists (Table 2).

The mechanisms for foam destabilization are liquid drainage (as a consequence of gravity force and liquid transfer from the inter-bubble lamella to the Plateau border), foam collapse by lamellar rupture, and Ostwald ripening or maturation. Foam collapse is usually a consequence of liquid drainage, and Ostwald ripening also involves liquid drainage.[2] Therefore, it is reasonable to consider the existence of two different processes for liquid drainage from foam, one due to liquid drainage itself and the other due to Ostwald ripening. On the other hand, it has been shown that the second order kinetic proposed by Elizalde et al.[12] fits well with the experimental data. Considering this, it was deemed appropriate to propose the following biphasic second order kinetic:

$$V_{LDF}(t) = V_{gmax}t/(B_g + t) + V_{dmax}t/(B_d + t), \qquad (7)$$

where $V_{LDF}(t)$ is the volume of liquid drained at t time, V_{gmax} corresponds to the maximum liquid volume released by gravitational drainage, B_g corresponds to the time required to drain $V_{gmax}/2$, V_{dmax} corresponds to the maximum volume of liquid drained by gas diffusion, and B_d corresponds to the time required to drain $V_{dmax}/2$.

Figure 4 depicts the drainage curve according to Eq. (7), together with experimental data. The adjustment by least square regression of the biphasic second order equation,
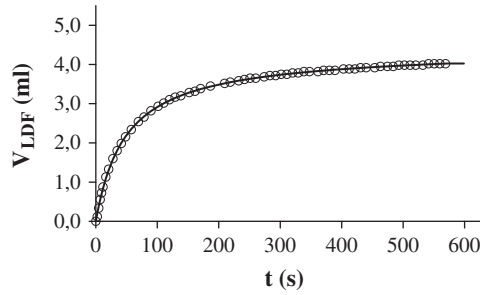
Figure 4 Experimental data (○) of V_{LDF} versus time of a glycinin sample, and the corresponding curve (−) of values estimated with a biphasic second order kinetic according to equation 7. The time 0 is the end of bubbling.

corresponding to Eq. (7), yielded in most cases an r^2 significantly higher than that achieved with the second order equation, except for glycinin foams for which no significant difference in r^2 was observed. An important finding is that the sum of V_{gmax} plus V_{dmax}, equivalent to V_{LDFmax}, is concordant with V_{LFmax} (Table 2). Therefore, Eq. (7) would be an appropriate and satisfactory kinetic for describing liquid drainage from foams. Since Eq. (3) represents second order kinetics, it can also be expressed as:

$$V_{LDF}(t) = V_{LDFmax}^2 kt/(V_{LDFmax}kt + 1), \tag{8}$$

where k is the velocity constant. Similarly, the biphasic second order kinetic (Eq. 7) can be represented as:

$$V_{LDF}(t) = V_{gmax}^2 k_g t/(V_{gmax}k_g t + 1) + V_{dmax}^2 k_d t + 1), \tag{9}$$

where k_g is the rate constant corresponding to the gravitational drainage process, and k_d is the rate constant corresponding to the process of gas diffusion or disproportionation. The parameter B is intrinsic to the process only for first order kinetics and does not depend on the characteristics of the particular system, such as, for example, initial conditions.

$$B = \ln 2/k. \tag{10}$$

For phenomena with a kinetic order different from one, however, B depends not only on the phenomenon itself, but also on the initial conditions of the system. For a reaction of order two, considering a foam destabilization process, B can be expressed as:

$$B = 1/(kV_{LFmax}). \tag{11}$$

In contrast, for any kinetic type, the constant (k) depends only on the phenomenon under study. In consequence, while the mean drainage time B is frequently used because of its dimensions and because it provides an easy physical perception of the phenomenon, k is the adequate parameter for describing a phenomenon with second order kinetics as is the case of foam destabilization.

Once the adequacy of the biphasic second order kinetic was established for foam stabilization, it was necessary to determine which of the equation terms corresponded to
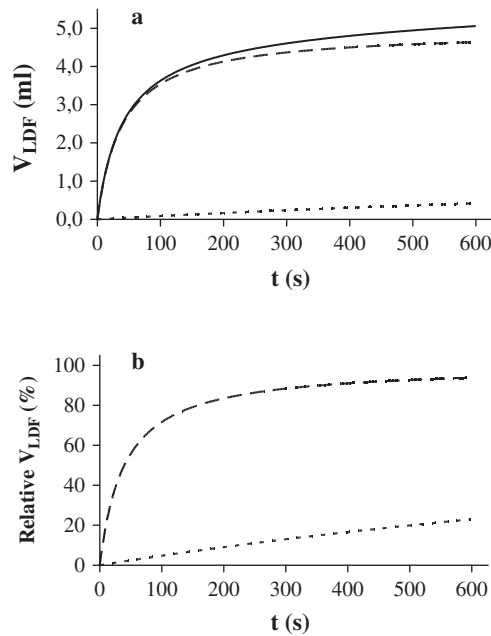
Figure 5 (a) Volume of liquid drained from a β-conglycinin foam as a function of the time of the whole destabilization process (—), the destabilization due to gravitational drainage (–), and the destabilization due to disproportionation (– –). (b) Relative volume of liquid drained from a β-conglycinin foam as a function of the time of destabilization due to gravitational drainage ($V_g.100/V_{gmax}$) (–), and destabilization due to disproportionation ($V_d.100/V_{dmax}$) (– –). The time 0 is the end of bubbling.

the parameters of the liquid drainage process (V_g and k_g) and which corresponded to the Ostwald ripening (V_d and k_d).

    Figure 5a depicts the volume of liquid drained from β-conglycinin foam as a function of the time of the two destabilization processes considered in Eq. (9), as well as the volume of liquid drained during the whole destabilization process. It can be observed that one of the processes predominates initially and approaches much faster than the other to the maximum volume of drained liquid. The graph in Fig. 5b shows that at 600 s, after the beginning of the destabilization process, one of the processes is associated with 94% drainage of the maximum volume, while the other represents only 23%. Table 3 shows that k values corresponding to one of the processes are always significantly higher (at least one

Table 3 k_g and k_d values and V_g and V_d proportions in foams formed from dispersions of the studied proteins.

Protein	$k_g \times 10^3$ (1/ml.s)	$k_d \times 10^4$ (1/ml.s)	V_g (%)	V_d (%)
β-Casein	3.9 ± 0.4	3.5 ± 0.5	0.89 ± 0.01	0.11 ± 0.01
α-Lactalbumin	4.9 ± 0.5	5.8 ± 0.9	0.91 ± 0.04	0.09 ± 0.04
β-Lactoglobulin	3.8 ± 0.3	2.2 ± 0.7	0.86 ± 0.01	0.14 ± 0.01
Glycinin	5.3 ± 0.3	3.7 ± 0.9	0.87 ± 0.02	0.13 ± 0.02
β-Conglycinina	4.7 ± 0.8	3.6 ± 0.6	0.74 ± 0.01	0.26 ± 0.01
Hemoglobin	3.6 ± 0.3	4.6 ± 0.8	0.90 ± 0.01	0.10 ± 0.01
Bovine serum albumin	2.8 ± 0.4	6.6 ± 0.9	0.87 ± 0.02	0.13 ± 0.02

order of magnitude) than those corresponding to the second process. In addition, there is a predominance of drained volume values of the process showing the lower k.

Regarding Eq. (6), Monsalve and Schechter[13] have considered that the first term corresponds to gravitational drainage, while the second term corresponds to gas diffusion among bubbles. This was corroborated by Yu and Damodaran,[15] who argued that the magnitude of foam decline by gas diffusion among bubbles is significant only for lamellar thickness lower than a critical value, and that it is reasonable to attribute to gravitational drainage the initial phase of first order indicated in Eq. (6). Therefore, in this case, it is reasonable to attribute to gravitational drainage the phase predominating in the initial period, represented in Eq. (9), and to attribute the second phase, of lower incidence, to the liquid drainage produced by Ostwald ripening.

CONCLUSION

The second order, two term kinetic model of foam destabilization by liquid drainage proposed in the current study was more adequate for describing the destabilization process than those presented until present, showing the existence of two simultaneous mechanisms of foam destabilization, which predominate alternatively according to foam age. The kinetic constant k is the appropriate parameter for comparing the stabilizing properties of different proteins, since it is not influenced by the initial volume of liquid in the foam. In the different foams formed with the studied proteins, k values corresponding to gravitational drainage were always at least one order of magnitude higher than those corresponding to Ostwald ripening. In addition, relative volumes of liquid drained by gravitational processes predominate.

ACKNOWLEDGMENTS

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