Nutrition & Food Science
International Journal
ISSN 2474-767X

Juniper Publishers
key to the Researchers

Mini Review
Volume 11 Issue 3 - January 2023
DOI: 10.19080/NFSIJ.2023.11.555820

Nutri Food Sci Int J

Adsorption and Interfacial Properties of Proteins and its Relationship to Emulsification and Foaming: A Mini Review

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Submission: November 30, 2022; **Published:** January 12, 2023

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Abstract

The interfacial properties of proteins have been extensively studied because of those properties are widely used in many food products, for example breads or cakes, ice-cream, and foamy coffee beverages. Protein interfacial behavior is significantly influenced by protein type, concentration, pH, ionic strength, sonication, and heating. Furthermore, proteins frequently work in conjunction with other substances, and these interactions have an impact on the interfacial properties of proteins. The impact of solution environment and processing techniques on the protein interfacial characteristics has been extensively studied in the past. The whole adsorption process of proteins, including protein diffusion in solutions and adsorption, permeation and rearrangement of protein at the interface has been reviewed in this work. The impact of protein type, solution environment and interfacial type on protein interfacial adsorption kinetics and interfacial swelling rheology have been discussed. Additionally, a summary of the structural characteristics of proteins that adhere readily to the interface has been provided. In addition, this review has important guiding significances for predicting and customizing protein adsorption with different process, so as to obtain varying purpose emulsion or foaming system.

Keywords: Protein; Adsorption; Interface behavior; Interface rheology; Emulsification; Foaming

Introduction

An emulsion is the dispersion of one liquid in the form of small droplets (0.1μm - 10μm) in another insoluble liquid [1]. A Foam, on the other hand, is a system in which bubbles are dispersed in a continuous aqueous phase [2]. Emulsions and foams are widely found in food products such as creams, milk powders, cakes, etc. However, due to their large interfacial areas, both foams and emulsions are thermodynamically unstable systems [3,4]. Surfactants are therefore needed to stabilize emulsions and foams over time. Surfactants are amphiphilic and can adsorb to the air-water and oil-water interfaces, thereby reducing the interfacial tension between the two phases forming foams and emulsions. In this way, they stabilize foams and emulsions by forming films at the interface. Surfactants are generally synthetic small-molecule surfactants, proteins, polysaccharides, polyphenols, and nanoparticles [5]. Synthetic surfactants have been widely used in food due to their functional characteristics, however nowadays, an increasing number of consumers prefer natural and safe food ingredients, hence natural surfactants are gradually gaining attention. Among them, proteins are frequently utilized as food surfactants due to their great functional qualities and high nutritional value.

Since the interfacial properties of proteins form the basis of their functional characteristics, they are crucial to the emergence and stability of emulsions and foams. Proteins are quickly adsorbed to the oil-water and air-water interfaces during the stirring process. After this adsorption, the proteins at the interface go through permeation and rearrangement behavior. Finally, the proteins at the interface interact with one another to form a stable and elastic interfacial film to stabilize oil droplets and foaming [6]. A deep understanding of the interfacial properties of proteins is essential for their use as surfactants in food products to improve food taste [7]. However, proteins' interfacial characteristics, such as hydrophobicity, surface charge, particle size, etc., are directly related to their structure. The structure and interfacial characteristics of proteins can be significantly influenced by factors such as protein type, concentration, pH, temperature, and

ionic strength, which can then alter their functional characteristics. Additionally, different protein treatments used in the preparation of food might alter the structure of proteins and have an impact on their interfacial and functional characteristics [8]. This article is based on a review of the changes in protein structure and interfacial properties as a function of solution environment, food processing methods, and compounding of other substances and discusses the changes in protein structure that facilitate adsorption.

Discussion

Diffusion of proteins to the interface

In the initial stage of protein adsorption, the adsorption is primarily controlled by diffusion. The interfacial tension decreases rapidly during this phase. The diffusion rate can be calculated by Ward and Tordai model [9]:

$$\pi = 2C_0KT\left(\frac{Dt}{3.14}\right)1/2 \qquad (1)$$

where C_0 is the initial protein concentration, K is the Boltzmann constant, T is the absolute temperature, and D is the diffusion coefficient. It has been demonstrated previously that proteins diffuse more quickly at the oil-water interface than at the air-water interface because the oil phase is more attractive to proteins than the air phase [10]. The structural differences between individual proteins lead to differences in their diffusion rates. Loosely structured chain-disordered proteins (e.g., *β*-casein) have a faster diffusion rate than compact globular proteins (e.g., bovine serum proteins) [11]. Due to the higher hydrophobicity of pea proteins, they have a higher diffusion rate in comparison to milk proteins [12]. Polyglycerol polyricinoleate has a smaller molecular weight (MW) than proteins and can adsorb faster to the oil-water interface [13]. According to the Stokes-Einstein diffusion model, the diffusion coefficient is inversely proportional to the molecular size [9]. Many studies have shown that the diffusion rate is driven by the concentration gradient and increases with the increase in the concentration of the bulk phase [14,15]. However, it has also been noted that adsorption barriers and electrostatic repulsion cause the protein diffusion rate to decrease with increasing concentration [16]. In the diffusion phase, in addition to the concentration gradient, chemical potential gradients produced by hydrophobic and electrostatic forces also act as a driving factor for protein diffusion to the interface [8]. Therefore, the solution environment such as pH and ionic strength are also important factors that influence the diffusion of proteins to the interface. For *β*-lactoglobulin and *β*-lactoglobulin aggregates, there is less spatial resistance at a pH close to PI (Isoelectric Point), due to the lower net charge compared to positively or negatively charged particles which can diffuse to the interface faster [17]. However, the lower surface charge near the PI may lead to the formation of protein aggregates of large particles, which reduces the diffusion rate [16,18]. At low ion concentrations, the electrostatic shielding effect of ions accelerates protein adsorption to the interface [16,19,20]. A further increase in ion concentration may lead to an increase in particle size but will decrease the diffusion rate [20]. In the diffusion phase, chemical potential gradients produced by hydrophobic and electrostatic forces also act as a driving factor for protein diffusion to the interface in addition to the concentration gradient [21]. Moreover, ultrasound has been shown to increase the hydrophobicity of proteins and reduce their particle size, which accelerates the diffusion rate of proteins [20,22]. The pace of protein diffusion can be influenced by a variety of interactions with other substances in addition to how the protein is processed. For instance, the maize protein hydrolysate's reduced hydrophobicity following compounding with tannic acid and the high viscosity of xanthan gum both lower the protein's rate of diffusion [15,23]. However, Ali Rafe reported that *β*-lactoglobulin and high methoxyl pectin synergistically interact at the air-water interface to accelerate the K_{diff} of *β*-lactoglobulin [24].

Permeation and rearrangement of protein at the interface

After a short period of diffusion, the protein undergoes permeation and rearrangement behavior at the interface. During this phase, the interfacial tension decreases slowly. A first-order equation can be used to monitor the rates of penetration and rearrangement of adsorbed protein [9]:

$$\ln\left(\frac{\pi f - \pi t}{\pi f - \pi 0}\right) = -K_i t \qquad (2)$$

where $\pi 0$, πt, and π are the interfacial pressures at the beginning, at any time point, and at equilibrium, respectively. The first linear region corresponds to the rate constant of penetration (K_P). The second linear region corresponds to the rate constant of rearrangement (K_R). According to a theory, globular proteins partially denature at the interface and unfold to produce molten globules, which in turn increases interactions with exposed hydrophobic groups and results in a protein with K_R greater than K_P [25]. Also, this theory supports that proteins with flexible conformations are easier to permeate and rearrange behavior at interfaces [14]. Numerous studies have demonstrated that proteins have quicker penetration and rearrangement rates at high concentrations, but after a certain point, due to spatial site resistance, the rate of permeation and rearrangement drops [26,27]. However, at high concentrations, the protein forms a more compact conformation [28]. According to this theory, the permeation and rearrangement rate of protein should be worse at higher concentrations, but this is not the case. This is likely because the concentration gradient's favorable impact on the initial adsorption at the interface outweighs the structure's unfavorable impact on the protein's conformational differences [14]. Proteins also form different conformations at different pHs resulting in differences in adsorption behavior [29]. Zhou et al. reported that the higher hydrophobicity of whey protein isolate at pH 3 resulted in faster permeation and unfolding rates [30]. Tian et al. showed that pH2-shifted *β*-conglycinin resulted in lower permeation and rearrangement rates due to its larger particle size

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[31]. High ionic concentrations hindered the penetration rate of -conglycinin and walnut protein-xanthan gum combinations, likely as a result of attractive interactions between the polyelectrolytes, although the electrostatic shielding effect benefited the rate of rearrangement [16,32]. In addition, it has been previously shown that heating causes proteins to form aggregates and increases electrostatic repulsion between proteins thereby reducing the rate of permeation and rearrangement [30,33,34]. However, in medium ratios, mixes of ovalbumin and lysozyme form an aggregate with lower free energies, enabling faster penetration and rearrangement behavior [35] (Figure 1).

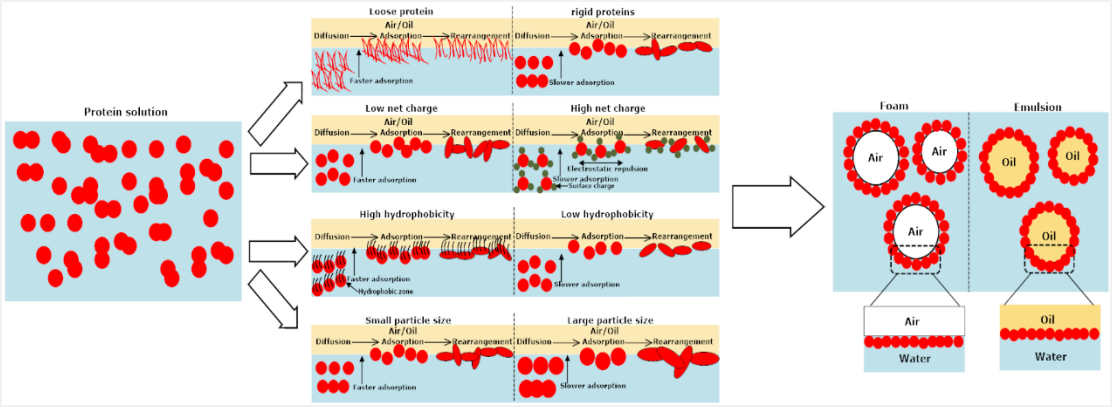

Figure 1: Schematic diagram of adsorption process of proteins at different condition and formation of bubbles or oil in water droplets.

Interfacial dilatational rheology

Interfacial dilatational rheology provides a good response to the mechanical strength of the protein film formed at the interface and the degree of interaction at the interface [36]. Because spherical proteins have greater molecular interactions at the interface, interfacial membranes consisting of flexible proteins (like β-casein) are less flexible than membranes formed of spherical proteins with a rigid structure (like lysozyme) [37,38]. It is important to note that the type of protein leads to differences between interfacial film strengths, and the non-aqueous phase also leads to differences between interfacial film strengths. It has been previously shown that due to salvation, oil-water interfaces form less elastic interfacial films compared to air-water interfaces [39]. In general, as the protein concentration increases more protein molecules tend to adsorb onto the interface to increase the stacking density, thus forming a more powerful membrane [16,40,41]. However, many studies have also pointed out that when the protein concentration continues to increase, the protein molecules become less elastic upon reaching a critical concentration value due to imperfect alignment or blocking by adjacent molecules, resulting in weakened molecular interactions and a consequent decrease in the elasticity of the interfacial membrane [42-44]. The effect of pH on the interfacial modulus of proteins can be attributed primarily to the change in their structure and the effect of surface charge. According to Jose María Ruiz-Alvarez, various charges of the peptides led to a better unfolding of whey protein hydrolysates and blue whiting protein hydrolysates at pH 8 and pH 2, respectively, generating stronger interfacial films at the oil-water interface [45]. Generally, proteins form more rigid interfaces at a pH close to PI, and higher charges reduce the interaction between proteins, forming poor elastic membranes [46-48]. However, similar to diffusion, when the pH approaches PI, the proteins start aggregating which weakens the membrane elasticity [16]. The surface charge of proteins is also dramatically affected by the ionic strength in the solution. The effect of ions on protein swelling modulus depends on pH and increasing the ionic strength at pH away from PI decreases the electrostatic repulsion between protein molecules, while simultaneously increasing the interaction between them and thus increasing the swelling modulus [13]. Xiong et al. investigated the effect of ultrasonic treatment of bound ions on protein interface rheology [20]. After the ultrasound the ovalbumin and ovotransferrin apparently had enhanced intermolecular interactions, forming a more robust film [20,49]. Peanut isolate protein becomes more hydrophobic when heated, which encourages adsorption at the interface and the formation of an interfacial membrane that is more elastic [50]. While many researchers have elaborated on the interfacial rheology of protein complex systems, the majority of the aforementioned studies have solely focused on single protein systems. In accordance with previously published research studies, combining proteins with xanthan gum, chitosan, and cinnamaldehyde improves protein adsorption at the interface and encourages the generation of more elastic protein films while improving the stability of the emulsion [36,51,52].

Conclusion

The effects of different processing methods and environmental conditions on the adsorption kinetics and interfacial swelling

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rheology of proteins have been reviewed. Based on previous studies, it is known that proteins with relatively loose structures can adsorb to the interface faster in comparison to dense spherical proteins, but form less elastic interfacial films. The interfacial affinity of a protein determines the concentration at which its monolayer is saturated, beyond which the diffusion, permeation, and rearrangement rates of the protein as well as the strength of the interfacial membrane are reduced. Since proteins have a high degree of hydrophobicity, those with a low charge and tiny particle size will adsorb at the interface more readily than others with a higher charge and larger particle size. This is crucial for predicting how well proteins would emulsify and foaming. Emulsification and foaming qualities are intimately related to a protein's interfacial activity and the rate at which it adsorbs at the interface. The stability of emulsions and foams is closely correlated with the nature of the interfacial film. We can increase product quality by modifying processing procedures and environmental factors by comprehending the effects of various processing techniques and environments on protein interface and functional properties.

Acknowledgment

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (32060583 and 31660481). The authors would like to thank all the reviewers who participated in the review, as well as Dr. Lei-Yan Wu for providing structural arranging during the preparation of this manuscript.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

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