

THE EFFECT OF PROCESSING PARAMETERS ON THE FUNCTIONAL PROPERTIES OF PROTEIN STABILIZED EMULSIONS

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Problems concerning characterization of protein stabilized o/w-emulsions will be discussed. Emphasis will be put on the influence of process variables in the emulsion formation on the functional properties of the emulsions. This will be shown for soybean oil in water emulsions stabilized by whey protein concentrate, sodium caseinate and a soy protein isolate. Different emulsifying techniques have been used as the Ultra-turrax, the Ultra-sonic and the valve homogenizer.

L'INFLUENCE DES PARAMETRES DE PROCÉDÉ SUR LES QUALITÉS FONCTIONNELLES DES ÉMULSIONS STABILISÉES AVEC DE LA PROTÉINE

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Des problèmes concernant la caractéristique des O/W-émulsions stabilisées avec de la protéine sont discutés et particulièrement l'influence des variables de procédé dans la formation de l'émulsion sur les qualités fonctionnelles de l'émulsion. Cette influence est démontrée ici pour de l'huile de soy dans des émulsions d'eau stabilisées avec un concentré de petit-lait-protéine et avec du sodium caseinate et un isolé de protéine de soy. Des techniques différentes sont employées pour l'émulsionnement comme les Ultra-turrax et Ultra-sonic ainsi que l'homogénéisation de soupape.

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DIE EINWIRKUNG DER PROZESSPARAMETER AUF DIE FUNKTIONELLEN EIGENSCHAFTEN DEN PROTEIN-STABILISIERTEN EMULSIONEN

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Probleme bezüglich der Charakteristik der proteinstabilisierten O/W-Emulsionen werden besprochen. Dabei wird besonders die Einwirkung der Prozessvariablen in der Emulsionsbildung auf die funktionellen Eigenschaften der Emulsion berücksichtigt. Die oben genannte Einwirkung bei Sojaöl in Wasseremulsionen, die mit Molkenproteinkonzentrat, Na-Caseinat und einem Sojaproteinisolat stabilisiert sind, wird hier gezeigt und besprochen. Verschiedene technische Emulgierungsmethoden wurden benutzt wie Ultra-Turrax, Ultra-Sonic und die Ventilhomogenisierung.

ВЛИЯНИЕ ПАРАМЕТРОВ ОБРАБОТКИ НА ФУНКЦИОНАЛЬНЫЕ СВОЙСТВА СТАБИЛИЗИРОВАННЫХ ПРОТЕИНОВЫХ ЭМУЛЬСИЙ

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Обсуждаются вопросы, касающиеся характеристики стабилизированных протеиновых эмульсий - м/в. Особенно подчеркивается воздействие переменных в процессе формирования эмульсий на функциональные свойства эмульсий. Это показывается для соевого масла в водных эмульсиях, стабилизированных протеиновым концентратом сыворотки, казеинатом натрия и изолятом соевого протеина. Использовались различные методы эмульгирования как Ultra-turrax, Ultra-sonic и клапанный гомогенизатор.

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INTRODUCTION

The determination of the emulsifying characteristics of proteins has evolved via two main approaches: emulsifying capacity and emulsifying stability measurements.

The method of Swift et al. (1961) to investigate the emulsifying capacity of a protein is to determine the maximum amount of fat emulsified by a protein dispersion. In such a test, oil is added at a given rate to a constantly stirred protein dispersion until the emulsion inverts into a w/o-emulsion, as indicated by a sudden drop in emulsion viscosity. This method has been widely used. Factors such as the blender speed, the rate of oil addition and the equipment design strongly influence the results, why doubts have been raised about the validity of the method. One can also argue if a measure of maximum oil addition is a relevant evaluation of the protein as an emulsifier.

The measurement of the emulsion stability, i.e. the ability to remain durable and unchanged for a serviceable storage time, seems to be a more realistic approach.

The determination of emulsion stability is to quantify the degree of coalescence and/or flocculation. Coalescence can be measured as oil separation, or fat particle counting as a function of time can be registered. The latter method can also be used in order to follow flocculation. Another approach in determining emulsion stability is to observe the extent of creaming, which is the rise of droplets under the influence of gravity. This can be the cause of flocculation or/and coalescence or none of them, as illustrated by figure 1.

Although the same stability test has been used by several authors it is difficult to compare the results, due to the fact that the formation of the emulsions is made differently. When evaluating a protein as an emulsion stabilizer, the parameters governing the emulsion formation should be considered, in order to get comparable results. The aim of this presentation is to show the strong influence of process variables in emulsion formation on the stability of protein stabilized emulsions. Three protein systems with distinctly different properties, namely soybean protein isolate, sodium caseinate and whey protein concentrate (WPC) have been used. The effect of three different types of emulsifying equipment, an ultra-turrax (U-T), a valve homogenizer (V-H) and an ultrasonic apparatus (U-S) has been studied. Only low-viscosity milk or creamlike emulsions (fat content 40%) as a model system are considered in this investigation.

MATERIALS

Soy protein isolate

Promine-D (Central Soya) a commercially available sodium soybean proteinate. Analysis: protein (N x 6.25) 86.7% (dry weight), solubility in distilled water at pH 7 denoted as (0 - 7), 54%.

CASEINATE

Spray blend caseinate (DMV, Holland) a commercially available sodium caseinate. Analysis: protein (N x 6.37) 89.3% (dry weight), solubility in distilled water and in 0.2 M sodium chloride solution at pH 7, denoted as (0 - 7) and (0.2 - 7), is 97.4% and 95.4%, respectively.

Whey protein concentrate (WPC)

WPC concentrated by ultrafiltration was used. Analysis: protein (N x 6.25) 61.7% (dry weight), solubility in distilled water and in 0.2 M sodium chloride solution at pH 7, denoted as (0 - 7) and (0.2 - 7) is 100% and 98.2%, respectively.

Soybean oil

Soybean oil (AB Karlshamns Oljefabriker, Karlshamn, Sweden) commercially available was used. Analysis: fatty acid composition C 18:2 53.3%, C 18:1 23.0%, C 16 10.8%.

METHODS

Preparation of samples

Protein dispersions composed of 2.5% (w/w) based on the protein content and distilled water or 0.2 M sodium chloride solutions were made with the Sorvall Omni-mixer. pH was adjusted with 0.2 M NaOH or 0.2 M HCl. In each aliquot amounts of protein dispersion and soybean oil were added directly to attain 40% oil by weight.

Emulsion formation

A quantity of 50 grams was emulsified in a circulating system, consisting of a gear pump, plastic tubings, a refrigerating system and an emulsifying apparatus. The emulsifying part could be varied from an ultra-turrax

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(U-T) to an ultrasonic (U-S) device and a valve-homogenizer (V-H). When using a valve-homogenizer as emulsifying equipment no gear pump was needed (Tornberg and Lundh). The flow rate of the emulsion in the circulating system was controlled to be equal to 250 ± 25 ml/min.

Cooling was performed during all the emulsification procedures to a final temperature of the emulsion of about 25°C . All emulsions were made in duplicate, and the reproducibility is on average $\pm 5\%$ SR.

Emulsion characterization

The measurement of the extent of creaming was used as a rapid test for estimating emulsion stability. The stability rating (SR) was determined on the basis of the change of percent of fat in the aqueous lower phase after creaming. The following equation was used:

$$\text{SR} = \frac{100 - F_{\text{test}}}{100 - F_{\text{original}}} \times 100 \quad (\%)$$

F_{test} is the percent of fat of the bottom 5 ml of the sample, and F_{original} is the initial percent of fat of the whole sample. Before the test, 30 grams of the emulsion were stored for 24 hours at 20°C . After storage the aliquots were centrifuged at low speed (1000 rpm) for 15 minutes. After centrifugation of the emulsion 5 ml of the aqueous lower phase was carefully removed with a syringe for fat determination by the Gerber method.

RESULTS AND DISCUSSION

Effect of different emulsifying equipments

Differently processed WPC (0.2 - 7)-emulsions show clearly the importance of the emulsifying equipment. In figure 2, where the emulsion stabilities obtained have been plotted as a function of the emulsification time, this is illustrated for differing emulsifying techniques working at various intensities. Stability ratings from 3 up to 95% can be achieved. It can be seen from the graph that U-T-emulsification at a speed of 18000 rpm is not as effective as sonication or valve homogenization. Comparing the latter methods, valve homogenization for WPC (0.2 - 7)-emulsions is a better method of emulsifying at low intensities than emulsifying with the ultrasonic device, whereas the same stability level is attained at higher intensity input for both the equipments. Mulder and Walstra (1974) pointed out that mixers usually employed in emulsification give fat globules of order of $10 \mu\text{m}$, whereas the effect per unit of volume (energy density) generated in the valve homogenizer and in the ultrasonic produces very small particles, predominantly less than $1 \mu\text{m}$. Making meat emulsions globules as large as $200 \mu\text{m}$ can be observed (van den Oord, 1973), why the energy density in a bowl chopper is very low compared to that in the emulsifying apparatus used in this investigation. Moreover, a meat emulsion is not a "true" emulsion, consisting of additional structures such as gel and suspension, and no direct correlations can be made with the results shown here. Another complexity arises due to the fact that the fat in meat products is partly solid and surrounded by cell membranes (van den Oord, 1973). Only when the liquid part of the fat is pressed out from the cell tissue during chopping emulsification takes place. Under these conditions protein additives can act as emulsifiers, and processing conditions will probably influence the results in the same way as shown here.

Effect of emulsifying time and intensity

The emulsification procedure will also drastically change, when varying the emulsifying intensity and time. The curves in figure 2 show that prolonged emulsification gives more stable emulsions up to a certain stability range, after which it levels out. Maximum stability attained varies according to emulsifying equipment and intensity applied. In figures 3, 5 and 6 the stability rating has been plotted as a function of emulsifying time using a valve-homogenizer and the same type of curves appears for the different proteins. But the stability limit achieved in these cases also depends on the protein and on variables such as pH and ionic strength.

The intensity dependence on emulsion stability is made quite evident in figure 4, where the ultrasonic power supply, marked with arbitrary units from 1 to 10, has been varied. The resulting emulsion stabilities are plotted for WPC (0 - 7), WPC (0.2 - 7) and Promine-D (0 - 7)-emulsions. For all the three protein stabilized emulsions the emulsifying was performed during 2 minutes. It can be seen from the figure that at a certain emulsification intensity there is a sharp increase in stability rating, which levels out with additional power supply, i.e. there is nothing to gain in emulsion stability with increasing emulsifying intensity as long as a certain intensity limit has been passed. But this limit depends on the protein and conditions used.

Effect of protein and protein conditions

In figures 3, 5 and 6 valve-homogenization has been applied to different proteins, and the resulting stability ratings are presented as a function of the emulsifying time. The curves in figure 3 were obtained at a constant pressure of 11 ± 2 kp/cm². As can be seen from this figure caseinate (0.2 - 7) only reaches a stability rating around 15% when emulsified for 9.5 minutes, whereas the other proteins investigated WPC (0 - 7), WPC (0.2 - 7) and Promine-D (0 - 7) achieve a SR of 60 - 70%.

Increasing the ionic strength of the WPC does not change the emulsifying behaviour drastically, which can be judged from figures 3, 4 and 6, although WPC (0 - 7) is always somewhat better.

Promine-D (0 - 7) is a good emulsifier, which is apparent from figures 3 and 4. It is most evident in figure 4, where the need of sonication intensity is low compared to that of the WPC product in reaching a stability of for

example 80%.

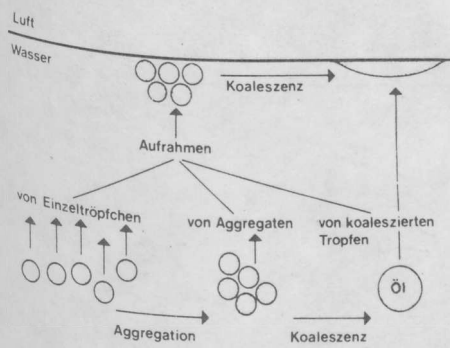
The susceptibility to increasing pressure in valve homogenization has been investigated for the caseinate and the WPC at different ionic strength. The results are presented in figures 5 and 6. In figure 5 the pressures applied are 75 and 150 kp/cm^2 , and in figure 6 also an additional pressure of 11 kp/cm^2 has been investigated. Contrary to the WPC, the emulsifying properties of the caseinate improve drastically when adding salt at pH 7. The curves in figure 5 clearly show that caseinate (0 - 7) needs a pressure drop of 150 kp/cm^2 and an emulsifying time up to 7 minutes to reach a SR around 95%, whereas caseinate (0.2 - 7) only demands 75 kp/cm^2 as pressure applied, and emulsifying for 3 minutes to achieve the same level of stability. It is also shown in figures 5 and 6 that there is no need to increase the pressure above 75 kp/cm^2 when making WPC (0 - 7) and caseinate (0.2 - 7) emulsions, as the curves representing a pressure drop of 75 and 150 kp/cm^2 coincide in both cases. A little change in ionic strength can give rise to completely differently emulsifying behaviour as in the case of caseinate. Therefore, even a subtle recipe modification can give unexpected results.

CONCLUSIONS

This investigation has shown the importance of process variables, as emulsifying equipment and emulsifying time and intensity, and their influence on the properties of protein stabilized emulsions. To be able to control an industrial process, involving emulsion formation with a protein as a stabilizer, these parameters must be considered.

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Figure 1. Schematic representation of emulsion instability.

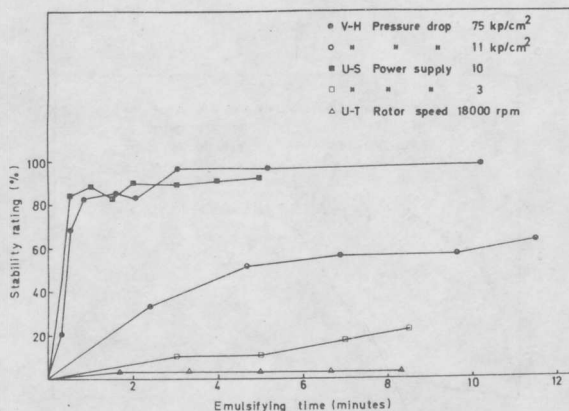


Figure 2. Stability rating of WPC (0.2 - 7) emulsions as a function of the emulsifying time, when emulsified with differing emulsifying apparatus working at various intensities.

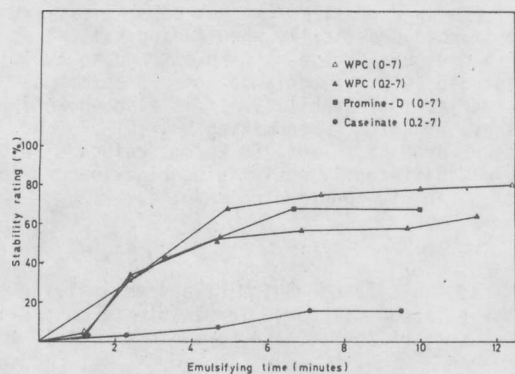


Figure 3. Stability rating of different protein stabilized emulsions as a function of the emulsifying time when valve-homogenized at a constant pressure of $11 - 2 \text{ kp/cm}^2$

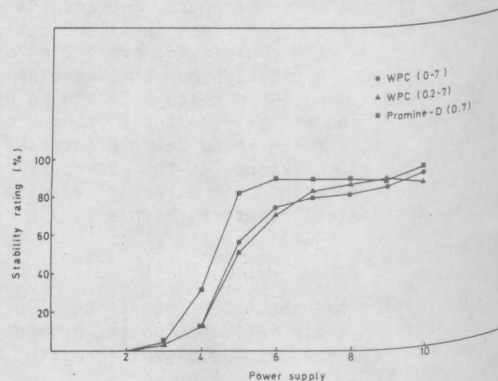


Figure 4. Stability rating of different protein stabilized emulsions as a function of the ultrasonic power supply.

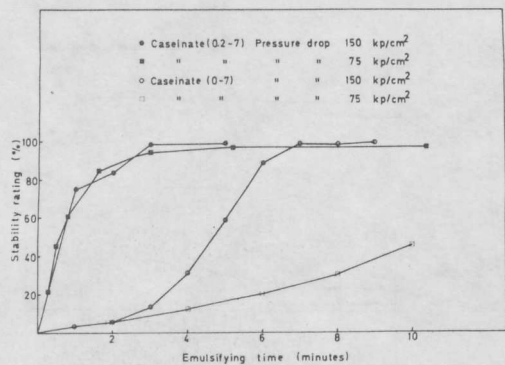


Figure 5. Stability rating achieved, when valve-homogenizing caseinate (0 - 7) and caseinate (0.2- 7) emulsions at different pressures, as a function of the emulsifying time.

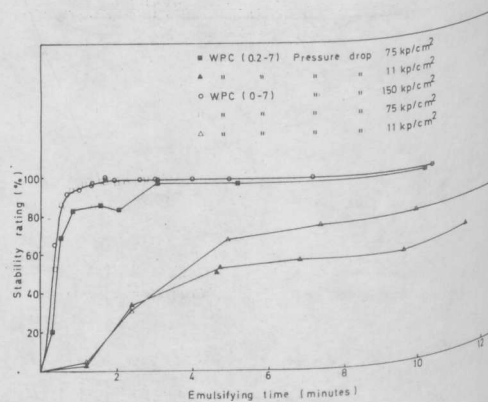


Figure 6. Stability rating achieved, when valve-homogenizing WPC (0 - 7) and WPC (0.2 - 7) emulsions at different pressures, as a function of the emulsifying time.