

Microstructure and Stability of Non-Protein Stabilized Oil-in-Water Food Emulsions Measured by Optical Methods

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ABSTRACT: The microstructure and stability of oil-in-water emulsions, stabilized with non-protein emulsifiers (sorbitan esters), were analyzed as a function of emulsification time, rotor speed, hydrophilic-lipophilic balance (HLB), and ionic strength. Sauter average dia ($D_{[3,2]}$) were determined from micrographs. Back-scattered light data were analyzed and a method to determine creaming rates of the systems was proposed. Creaming rates showed that the relationship between emulsion stability and HLB was non-linear. Addition of NaCl raised creaming rates, resulting in decreased stability, while micrographs showed the presence of flocs. Results were discussed taking account of interactions present in the system.

Key words: oil-in-water emulsions, emulsion stability, sorbitan esters, creaming kinetics, hydrophilic-lipophilic balance (HLB)

Introduction

THE PRINCIPAL ROLE OF SURFACTANTS IN FOOD EMULSIONS IS TO enhance their formation and stability. There is no single surfactant that is appropriate for every application. Instead, it is necessary to choose the most adequate for each particular case (McClements 1999).

Although sorbitan fatty acid esters (Spans) and the corresponding polyoxyethylene (POE) adducts (Tweens) have applications as emulsifiers in the food industry (Owusu Apenten and Zhu 1996), little research has been developed on the optimization of the mechanical variables in the processing of emulsions stabilized using these nonionic surfactants. It has been pointed out that for emulsions containing a mixture of egg yolk and sucrose stearate as emulsifier, an increase in energy input yields an increase in emulsion stability, lower droplet size, and lower polydispersity (Franco and others 1995). In the case of vegetable protein-stabilized emulsions, an increase in the energy input during emulsification decreases the mean droplet dia of the emulsion and increases the values of the rheological and textural parameters (Franco and others 1998). Franco and others (1997) reported that the inclusion of low molecular weight emulsifiers (sucrose stearate) to egg yolk stabilized emulsions, increased the stability of the systems.

Extensive work has been conducted to analyze the competitive adsorption of proteins and surfactants (Dickinson 1997, 1998). Many dairy-type food colloids such as ice cream or whipped toppings often contain small-molecule surfactants. During homogenization, smaller droplets are generally produced in the presence of surfactants because of a more rapid lowering of the interfacial tension than with milk proteins alone. Most commonly, the competitive adsorption of proteins with surfactants during or after emulsification reduces the protein surface coverage at the oil-water interface (Courthaudon and others 1991). Competitive displacement of individual milk protein fractions by nonionic water-soluble surfactants such as Tween 20 has been reported (Dickinson 1992). The relative extent of protein

removal is reduced when sodium caseinate or skim milk protein was used instead of individual milk protein fractions (Euston and others 1995). Nonionic oil soluble emulsifiers (sorbitan esters and monoglycerides) are generally less effective at displacing milk proteins from the oil-water interface than the nonionic water-soluble emulsifiers (Dickinson and others 1993).

The hydrophilic-lipophilic balance (HLB) is a semi-empirical concept that is widely used for classifying surfactants. The HLB is described by a number that gives an indication of the relative affinity of a surfactant molecule for the oil and aqueous phases. It has long been used to optimize the stability of oil-in-water emulsions (Boyd and others 1972), although the theory does not consider that the presence of other components in the system might also affect the stability of food emulsions (Chow and Ho 1996, McClements 1999).

Visual inspection as a reliable indicator of gravity creaming can only be used once a discernible cream layer (or serum layer) has appeared in the sample; it is only a crude measure of the creaming process, whose results are dependent on the subjectivity of the observer. To overcome this shortcoming, several objective methods have been proposed based on the intensity of light transmitted through a sample (Dickinson and others 1989), magnetic resonance imaging (Pillhofer and others 1993), ultrasonic velocity measurements (Dickinson and others 1994), or electric conductivity (Bani-Jaber and others 2000).

The objectives of the present work are: (1) to analyze the influence of HLB, surfactant concentration, and ionic strength on the microstructure and stability of 40% w/w sunflower oil-in-water emulsions, stabilized with non-protein emulsifiers, and (2) to apply a new methodology that relates light-scattered measurements taken on an optical instrument with the kinetics of the creaming process in emulsions.

Materials and Methods

COMMERCIAL 100% SUNFLOWER OIL WAS PURCHASED FROM A local supermarket and used without further treatment. The

triglyceride composition of the sunflower oil used was: 11% saturated, 62% polyunsaturated, and 27% monounsaturated fatty acids. Free fatty acid content in the oil was 0.05% expressed as oleic acid. The oil did not contain any antioxidant; phospholipid residue was 5 ppm expressed as inorganic phosphorus. Span™ 60 (S60, sorbitan monostearate), Tween™ 40 (T40, POE sorbitan monopalmitate), and Tween™ 60 (T60, POE sorbitan monostearate) emulsifiers were purchased from Sigma Chemical Co. (St. Louis, Mo., U.S.A.). Analytical grade sodium chloride and sodium azide were used. Distilled and deionized water was used in all solutions and emulsions.

Emulsion preparation

Four separate sets of 40% w/w sunflower oil-in-water emulsions were prepared. As an antimicrobial agent for the laboratory experiments, 0.01% sodium azide was added to the aqueous phase. POE emulsifiers were incorporated to the aqueous phase prior homogenization at room temperature, while S60 was dissolved in the oil phase at 60 °C. The pH of the sample was 6.8, and they were not buffered. An Ultra Turrax T25 (rotor S20-25-NK-196) was used to homogenize the immiscible phases at room temperature. The effect of rotor speed and emulsifying time on emulsion droplet sizes were evaluated in systems containing T40 as surfactant (1% w/oil vol); emulsifying tested conditions were 7800, 11500, and 16300 rpm for 2, 4, and 6 min. All particle size and objective stability measurements were carried out within 5 min after emulsification, unless otherwise stated.

The effect of HLB on emulsion microstructure and stability was studied in a 2nd set of experiments (1% surfactant w/oil vol), varying the HLB value between 14.9 and 4.7 by mixing adequate amounts of T60 and S60. In a 3rd group of experiments, a nearly constant HLB (7.4) was maintained while modifying the total emulsifier content: 0.1, 0.5, 1, and 2% w/oil vol, with a 1 to 1 ratio of T60 to S60. Finally, the 4th set of emulsions contained different amounts of NaCl in the aqueous phase, maintaining a total surfactant content of 1% w/oil vol (50% T60 and 50% S60, HLB = 7.4). The assayed NaCl concentrations were: 0, 0.05, 0.1, and 0.2 M. Emulsifying conditions for these last 3 sets of experiments were 11500 rpm for 4 min.

Droplet Size Determination

Sample droplet size and distribution were measured using a microscope (Zeiss MC80DX microscope equipped with a built in camera). A 40X objective lens calibrated with an objective micrometer and an appropriate software (Global Lab Image, version 2.10) were used. Aliquots of fresh samples were observed after a 1:20 dilution with distilled water. Digitization was based on gray level and the dia was estimated based on the equivalent circular dia. Over 400 droplets were measured to estimate the average droplet size using 5 fields per test.

Sauter average dia ($D[3,2]$) was calculated for each sample as follows:

$$D[3,2] = \frac{\sum_{i=1}^N (n_i d_i^3)}{\sum_{i=1}^N (n_i d_i^2)} \quad (\text{Eq. 1})$$

where d = droplet dia, N = total number of droplets, n_i = number of droplets of d_i dia. The corresponding variances of $D[3,2]$ were calculated (Green and Margerison 1978); the variance is related to the polydispersity of the system. Both $D[3,2]$ and its variance are related to the stability of emulsions when the ratio volume/surface area is important.

Objective stability assessment

A QuickScan™ (Beckman-Coulter Inc., Fullerton, Calif., U.S.A.) instrument was used to analyze stability of emulsions. QuickScan™ is a liquid dispersion optical characterization instrument where the sample to be analyzed is contained in a cylindrical glass measurement cell. The reading head of the instrument is composed of a pulsed near infrared light source ($\lambda = 850$ nm) and 2 synchronous detectors. The transmission detector receives the light, which goes through the sample (0°), while the back-scattering detector receives the light back-scattered by the sample (135°). The head of the instrument scans the entire length of the sample (about 65 μm), acquiring transmission and back-scattering data every 40 μm . Thus, the transmission and back-scattering profiles are obtained as a function of the sample height. An important back-scattering signal (and a very small one in transmission) is observed when dispersions are opaque (droplet-rich); it is the opposite for transparent to turbid dispersions (droplet-depleted).

Once a sample was placed in the instrument, both light profiles were recorded every 5 min; no changes in these profiles would take place during the observing time for a total stable system. The back-scattering profile initially taken ($t = 0$) was considered as the reference to analyze the stability of the system. Figure 1 shows a typical response of the equipment. As creaming takes place, the back-scattered light in the lower region diminishes as it becomes droplet-depleted.

Determination of zeta potential (ζ)

The zeta potential of freshly prepared 40% w/w oil-in-water emulsions containing 1% w/oil vol of a mixture of surfactants (50% T60 + 50% S60, HLB = 7.4) was determined using a Zetasizer 3000HS™ equipment (Malvern Instruments, U.K.).

Statistical Analysis

Statistical analyses were carried out on the averages of the results. Two-way analysis of variance (ANOVA) carried out to study the effect of both agitation speed and emulsification time on $D[3,2]$ and the stability of the system. For simultaneous pairwise comparisons of stability data, the Least Significant Difference

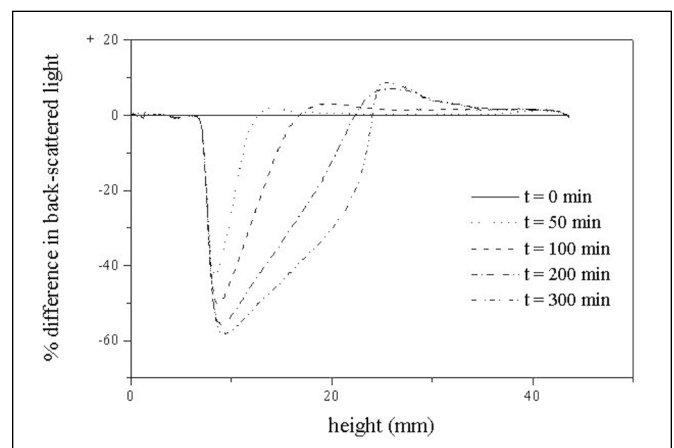


Figure 1—Percentual difference between the back-scattered light with respect to the initial one as a function of sample height at different times (t). Curves correspond to a 40% w/w oil-in-water emulsion with a total 1% w/oil volume emulsifier concentration (0.5% T60 and 0.5% S60, HLB = 7.4).

test (LSD) was chosen. Difference in averages and F tests (ANOVA) were considered significant when the computed probabilities were less than 0.05 ($P < 0.05$). Nonlinear regression analysis was carried out to model the relationship between $D[3,2]$ and HLB and to calculate creaming rates. All statistical procedures were computed using the SYSTAT software (SYSTAT, Inc., Evanston, Ill., U.S.A.).

Results & Discussion

Processing conditions

Table 1 shows the Sauter average dia and its variance for emulsions prepared under different processing conditions with T40 (1% w/oil vol). Figure 2 shows micrographs taken at 2 different rotor speeds; the images of these emulsions showed no aggregates or flocs. An increase of the agitation speed (7800 to 11500 rpm) yielded an important reduction in both droplet size ($D[3,2]$) and variance of $D[3,2]$ (polydispersity of the system). Thus, the larger droplets became rather small in size and less numerous, whereas the number of fine oil droplets appreciably increased and their sizes were not much altered. Nevertheless, a further increase in the agitation speed produced only a slight decrease in the $D[3,2]$ and did not modify the droplet size distribution. These results are in agreement with those reported by Franco and others (1998) for emulsions stabilized by lupin-proteins. The emulsification time did not affect Sauter dia or its variance (between 2 and 6 min). From the results obtained in this set of experiments, processing conditions were chosen for the rest of the study. A rotor speed of 11500 rpm produced a small polydis-

Table 1—Effect of emulsification conditions on Sauter dia ($D[3,2]$) and the corresponding variance (Var $D[3,2]$) in emulsions containing T40 1% w/oil vol.

| Emulsification conditions | | $D[3,2]$ | Var $D[3,2]$ |
|---------------------------|------------------------|-------------------|--------------------------------|
| Agitation speed (rpm) | Emulsification t (min) | (μm) | (μm) ² |
| 7800 | 2 | 41.5 | 6.1 |
| 7800 | 4 | 41.0 | 8.9 |
| 7800 | 6 | 36.7 | 12.0 |
| 11500 | 2 | 23.9 | 1.9 |
| 11500 | 4 | 21.7 | 0.82 |
| 11500 | 6 | 20.2 | 1.6 |
| 16300 | 2 | 21.2 | 3.3 |
| 16300 | 4 | 12.3 | 0.31 |
| 16300 | 6 | 19.3 | 1.1 |

persed system independently of processing time, allowing for a better control of average droplet dia.

Effect of HLB on emulsion microstructure and stability

Increasing the amount of the hydrophilic surfactant (T60), which implies higher HLB, decreased droplet size by reducing interfacial tension (Figure 3).

The variances of $D[3,2]$, which are related to the polydispersity, increased about 6 times when HLB was lowered from 14.9 to 4.7.

Visual inspection was not a suitable method to determine stability of emulsions corresponding to the 2nd and 3rd group of experiments; as an oil-water interface did not appear clearly enough, an objective method was chosen to compare the stability behavior in these cases.

The study of emulsion stability was focused on the measurement and analysis of the creaming rate using QuickScan™, which involved, that as the creaming progressed, the back-scattered light at the bottom layer diminished with time because the emulsion became droplet-depleted. To evaluate the changes in oil concentration along the sample, back-scattered light profiles were integrated in the droplet-depleted zone at any given time. The difference between the average back-scattered light with re-

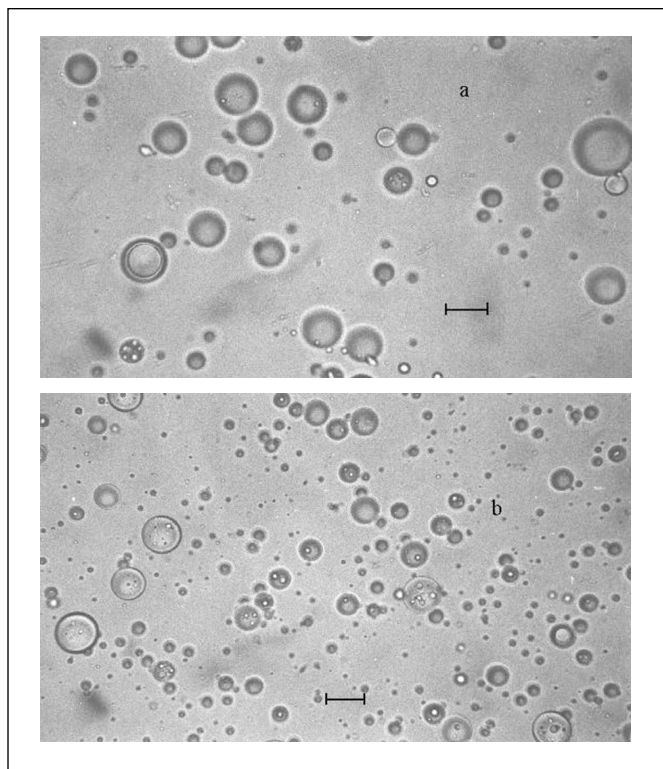


Figure 2—Micrographs of 40% w/w oil-in-water emulsions stabilized with T40 (1% w/oil vol). Emulsifying conditions: (a) 7800 rpm, 6 min. (b) 16300 rpm, 6 min. The bar represents 20 μm .

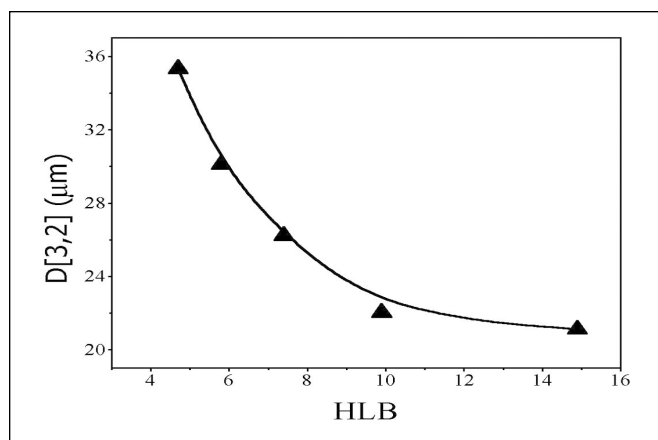


Figure 3—Sauter Diameter ($D[3,2]$) as a function of the hydrophilic-lipophilic balance (HLB) for 40% w/w oil-in-water emulsions with a total 1% w/oil volume emulsifier concentration.

spect to the initial one (time = 0) was defined as Δ_{BS} ; the difference at infinite time (Δ_{BS^∞}) is a measurement of the clarification of the lower region (remnant opacity).

If the creaming process (monitored through the changes of D_{BS}) follows a 1st order kinetics, it becomes:

$$d(\Delta_{BS})/dt = k(\Delta_{BS} - \Delta_{BS^\infty}) \quad (\text{Eq. 2})$$

where t is the elapsed time in min and k is a rate constant proportional to the rate of destabilization. Integrating Eq. 2 between $t = 0$ (where $\Delta_{BS} = 0$) and a given time t , the following was obtained:

$$\Delta_{BS} = \Delta_{BS^\infty} (1 - \exp(-k.t)) \quad (\text{Eq. 3})$$

Equation 3 was fitted to the experimental curves of Δ_{BS} against time by nonlinear regression analysis. A very good agreement between measured and calculated results was obtained (Figure 4).

As can be observed in Table 2, systems with higher HLB showed lower k values and higher stability. The increase in droplet size and polydispersity when S60 content was raised does not seem to be large enough to produce such a noticeable effect on stability. If the creaming rate had been affected by coalescence, the optical method (Quick Scan) would have shown negative values of the difference between the average back-scattered light with respect to the initial one at the top of the tube; however these results were not observed in our tested systems (Figure 1). Boyd and others (1972), working with nujol oil-in-water emulsions, stated that HLB and chemical constitution of the emulsifiers exerted a large influence on the rate of coalescence of emulsions containing blends of Span and Tween emulsifiers. O/W emulsions showed regions of minimal coalescence at HLB = 12. On the other hand, Chow and Ho (1996) did not find a synergistic effect between T40 and Span 40TM using palm oil-in-water emulsions. They observed that as HLB increased, coalescence decreased and attributed these results to the presence of natural emulsifiers in the oil.

Results can be explained in terms of the influence of the sur-

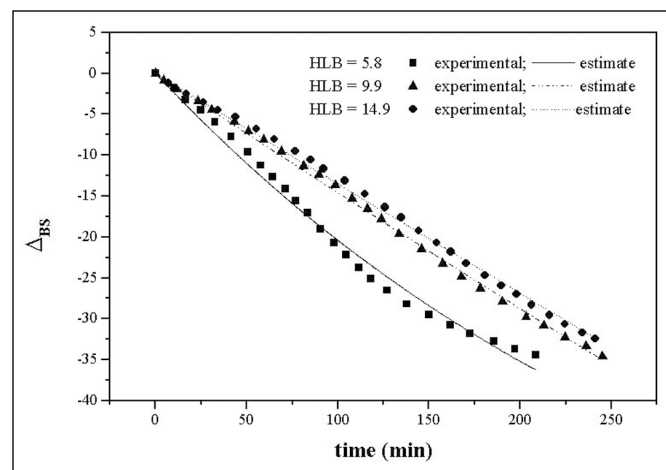


Figure 4—Difference between the average back-scattered light with respect to the initial one (Δ_{BS}) as a function of time in 40% w/w oil-in-water emulsions with a total 1% w/oil volume emulsifier concentration. Symbols correspond to experimental data and curves show predicted results for HLB = 5.8, 9.9, and 14.9.

Table 2 – Effect of HLB on creaming rate of emulsions stabilized with T60 and S60 mixtures (total surfactant concentration 1% w/oil vol).

| HLBCreaming rate | $k \times 10^4 \text{ (min}^{-1}\text{)}^a$ |
|-------------------------|---|
| 4.7 [100 % S60] | 39.0 (1.0) |
| 5.8 [25% T60 + 75% S60] | 32.0 (1.0) |
| 7.4 [50% T60 + 50% S60] | 4.6 (0.05) |
| 9.9 [75% T60 + 25% S60] | 2.83 (0.01) |
| 14.9 [100% w/w T60] | 0.97 (0.01) |

^a: standard deviation between parentheses

factants on the nature of the droplet-droplet interactions. Non-ionic emulsifiers may stabilize food emulsions through short-range steric forces, which are sufficiently strong to prevent droplets from getting close enough to aggregate (polymeric steric interaction). As HLB decreased, the number of hydrophilic head groups that protruded into the aqueous phase and prevented the droplets of coming together decreased. When the continuous phase surrounding the droplets is a poor solvent, such as water for S60, the surfactant molecules prefer to be surrounded by themselves. The increase in concentration of S60 molecules in the interpenetration zone is thermodynamically favorable because it increases the number of polymer-polymer contacts and therefore leads to an attractive interaction between the droplets (McClements 1999).

Our results suggest that T60 stabilized emulsions produce the slowest creaming rates. According to reported data (Dickinson 1997) it should be pointed out that if emulsions are stabilized by dairy proteins, T60 would be the most effective competitor, among the systems studied in this work, in displacing the protein from the surface interface. Industrial formulations take advantage of this competitive adsorption in the preparation of whipable emulsions such as ice cream mix or whipped cream since the weakening of protein-fat binding causes agglomeration of fat globules, which leads to products with high melt resistance and a smooth texture (Goff and Jordan 1989).

Effect of total surfactant concentration

Creaming rate and droplet size distribution were analyzed as functions of the total emulsifier concentration, which was varied between 0.1 to 2% w/oil vol, combining equal weights of T60 and S60 (Table 3) with a HLB value close to 7.4. Table 3 shows that when total emulsifier concentration increased, the stability of the emulsion was higher, tending to asymptotic values when concentrations approached 2% w/v. From the creaming rate values shown in Table 2 and 3, it is clear that, in the range of concentrations assayed, the effect of HLB on the emulsions stability is much more important than the total amount of surfactant used.

Stability of emulsions at different ionic strengths

Sodium chloride (0.05 to 0.2 M) was added to the aqueous phase emulsions containing 40% w/w with 1% emulsifiers (w/oil vol, 0.5% T60 and 0.5% S60) to analyze the effects on stability and droplet size distributions. The presence of NaCl modified the behaviour of the emulsion systems with respect to the control samples without salt (Table 4); a sharp interphase between the creaming zone and the particle-free serum below was clearly visible with the naked eye after a few min. The effect of NaCl was also noticeable in the shape of the back-scattered light profiles. The back-scattered light decreased sharply at the bottom of the

tube, remained constant, then increased abruptly again at the interface between the serum and creamed layers (Figure 5). The emulsion stability decreased when NaCl concentration increased, although the D[3,2] did not vary significantly. Polymeric steric interactions are one of the most important stabilizing mechanisms in food emulsions, however, some emulsions are stabilized by a combination of steric and electrostatic interactions. The presence of NaCl in the aqueous phase of the emulsions stabilized by nonionic surfactants can influence the interactions between droplets by the following main mechanisms: (1) Ions can screen electrostatic interactions. In the presence of electrolyte the thickness of the double electric layer that surrounded the oil droplets was reduced, decreasing electrostatic repulsion between droplets to a point that it could no longer prevent flocculation and creaming. In other words, the neutralization of the surface charge occurs at shorter distances when the concentration of the opposite charge in the surrounding solution increases, thus allowing droplet aggregation. (2) Salts alter structural organization of water influencing the strength of the hydrophobic associations, altering the way in which surfactants pack together in a mixed interface (McClements 1999).

On 40% w/w oil-in-water emulsions containing 1% w/oil vol of surfactant the measured zeta potential value (ζ) was -59 mV for T60. When a mixture of equal parts of T60 and S60 was used as emulsifier, ζ was -57 mV. Even though the used emulsifiers were nonionic, charge may arise from small amounts of natural surface active materials in the oil (such as free fatty acids and phospholipids) located at the oil/water interphase. Measurements in the emulsion containing 1% w/oil vol T60 and 0.1M NaCl showed a marked decrease of the ζ value (-5.8 mV). The decrease of the zeta potential in the presence of NaCl can be explained on the basis of the electrostatic interaction mechanism described previously. The measured ζ -values agree with data reported in literature by Aizawa and others (2000) for POE sorbitan fatty acid esters, such as Tween 85 and Tween 40, having a zeta potential of -43.68 mV and -41.28 mV, respectively.

Micrographs taken immediately after emulsification (Figure 6) showed the presence of numerous flocs in the systems with

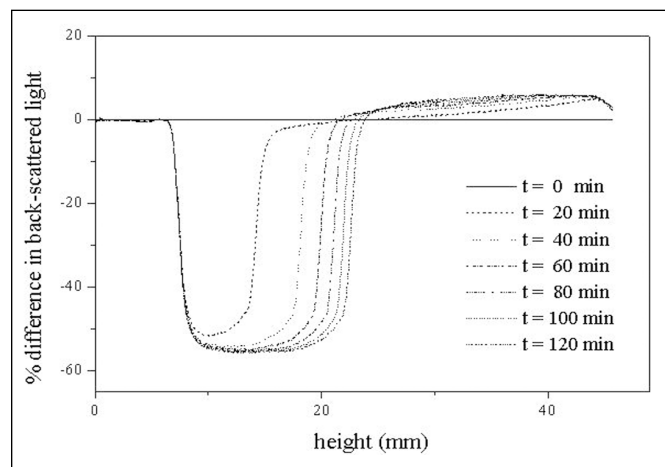


Figure 5—Percent difference between the back-scattered light with respect to the initial one as a function of sample height at different times (t). Curves correspond to a 40% w/w oil-in-water emulsion with a total 1% w/oil volume emulsifier concentration (0.5% T60 and 0.5% S60, HLB = 7.4) and 0.1 M NaCl.

Table 3—Effect of total surfactant concentration on D[3,2] and creaming rate of emulsions stabilized with 1:1 T60 and S60 mixtures

| Total surfactant concentration % (weight of surfactant/oil vol) | D[3,2] (μm) | Creaming rate $k \times 10^4$ (min^{-1}) ^a |
|---|--------------------------|--|
| 0.1 (HLB = 7.4) | 26.2 | 6.51 (0.05) |
| 0.5 (HLB = 7.0) | 27.7 | 5.30 (0.03) |
| 1.0 (HLB = 7.4) | 26.2 | 4.56 (0.05) |
| 2.0 (HLB = 7.4) | 20.5 | 3.46 (0.01) |

^a: standard deviation between parentheses

Table 4—Effect of salt concentration and ionic strength (I) on creaming rate of emulsions 40% w/w with a total 1% w/oil volume emulsifier concentration (0.5% T60 and 0.5% S60, HLB = 7.4).

| Salt concentration and ionic strength (I) | D[3,2] (μm) | Creaming rate $k \times 10^4$ (min^{-1}) ^a |
|---|--------------------------|--|
| 0 M NaCl, I = 0 | 26.2 | 4.6 (0.05) |
| 0.05M NaCl, I = 0.05 | 25.6 | 128.0 (4.0) |
| 0.1M NaCl, I = 0.1 | 29.6 | 266.0 (5.0) |
| 0.2M NaCl, I = 0.2 | 27.3 | 242.0 (4.0) |

^a: standard deviation between parentheses

salt added besides the shape of the back scattered light profiles also indicate a highly flocculated system.

Conclusion

CREAMING RATES WERE EVALUATED USING AN OPTICAL METHOD; a 1st order kinetic model was considered to analyze experimental data, obtaining a good agreement between experimental results and the proposed model. The main advantage of the optical technique is its simplicity and speed of operation, which allows to reliably compare the stability of different systems.

The effect of HLB in the 40% w/w oil in water emulsions on Sauter dia of oil droplets as well as on creaming rates was not linear. Higher HLB values led to a higher emulsion stability that can be attributed to polymeric steric interactions. Sodium chloride decreased emulsion stability by reducing electrostatic repulsion between droplets.

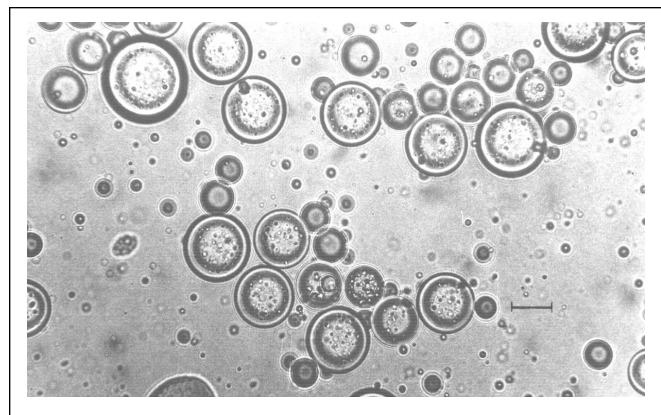


Figure 6—Flocculated oil droplets of a 40% w/w oil-in-water emulsion with 1% emulsifiers (w/oil vol, 0.5% T60 and 0.5% S60) containing 0.2M NaCl in the aqueous phase. The bar represents 20 μm .

References

- Aizawa H, Tsutsumi M, Masaki T, Liu XQ, Watanabe Y, Nabetani H, Nakajima N, Ichikawa S, Ihara H, Sano Y. 2000. Difference in dispersed properties of O/W emulsion prepared with polyoxyethylene [20] sorbitan monopalmitate (Tween 40) or polyoxyethylene [20] sorbitan trioleate (Tween 85). *J Jpn Soc Food Sci Tech* 47(7):487-495.
- Bani-Jaber A, McGuire J, Ayres JW, Daeschel MA. 2000. Efficacy of the antimicrobial peptide nisin in emulsifying oil in water. *J Food Sci* 65(3):502-506.
- Boyd J, Parkinson C, Sherman P. 1972. Factors affecting emulsion stability, and the HLB concept. *J Colloid Interface Sci* 41(2):359-370.
- Chow MC, Ho CC. 1996. Properties of palm-oil-in-water emulsions: Effects of mixed emulsifiers. *J Am Oil Chem Soc* 73:47-53.
- Courthaudon JL, Dickinson E, Christie WW. 1991. Competitive adsorption of lecithin and β -casein in oil in water emulsions. *J Agric Food Chem* 39(8):1365-1368.
- Dickinson E, Murray BS, Stainsby G. 1989. A rapid routine method for monitoring creaming behavior in small samples of food emulsions. *Lebensm-Wiss Technol* 22:25-28.
- Dickinson E, Tanai S. 1992. Protein displacement from the emulsion droplet surface by oil-soluble and water-soluble surfactants. *J Agric Food Chem* 40(2):179-183.
- Dickinson E, Owusu RK, Tan S, Williams A. 1993. Oil-soluble surfactants have little effect on the competitive adsorption of α -lactalbumin and β -lactoglobulin in emulsions. *J Food Sci* 54(2):295-298.
- Dickinson E, Ma J, Povey MJW. 1994. Creaming of concentrated oil-in-water emulsions containing xanthan. *Food Hydrocoll* 8(5):481-497.
- Dickinson E. 1997. Properties of emulsions stabilized with milk proteins: overview of some recent developments. *J Dairy Sci* 80(10):2607-2619.
- Dickinson E. 1998. Proteins at interfaces and in emulsions: stability, rheology and interactions. *J Chem Soc, Farad Trans* 94(12):1657-1669.
- Euston S, Singh H, Munro PA, Dalgleish D. 1995. Competitive adsorption between sodium caseinate and oil-soluble and water-soluble surfactants in oil-in-water emulsions. *J Food Sci* 60(5):1124-1131.
- Franco JM, Guerrero A, Gallegos C. 1995. Rheology and processing of salad dressing emulsions. *Rheol Acta* 34:513-524.
- Franco JM, Berjano M, Gallegos C. 1997. Linear viscoelasticity of salad dressing emulsions. *J Agric Food Chem* 45(3):713-719.
- Franco JM, Raymundo A, Sousa I, Gallegos C. 1998. Influence of processing variables on the rheological and textural properties of lupin protein-stabilized emulsions. *J Agric Food Chem* 46:3109-3115.
- Goff HD, Jordan WK. 1989. Action of emulsifiers in promoting fat destabilization during the manufacture of ice cream. *J Dairy Sci* 72:18-29.
- Green JM, Margerison D. 1978. Statistical treatment of experimental data. Elsevier Scientific Pub. Co. 64-92 pp.
- McClemens DJ. 1999. Food Emulsions: Principles, Practice and Techniques. Florida: CRC Press. 104, 196 p.
- Owusu Apenten RK, Zhu QH. 1996. Interfacial parameters for selected Spans and Tweens at the hydrocarbon-water interface. *Food Hydrocoll* 10(1):27-30.
- Pilhofer GM, McCarthy MJ, Kauten RJ, German JB. 1993. Phase separation in optically opaque emulsions. *J. Food Eng* 20:369-380.
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