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Influence of Egg Yolk/Tween 60 Surfactant Blends on the Behavior of O/W Concentrated Emulsions

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In the Food Industry, oil in water (O/W) emulsions are commonly used or prepared. Egg yolk and monostearates are the most frequently employed surfactants. In this work was evaluated the influence of disperse phase content, and surfactant concentrations on the rheological behavior and mean drop diameter (d_{43}) of concentrated corn oil in water emulsions, which constitute the base for some salad dressings. The samples were prepared using surfactant blends at laboratory scale. The experimental method was based on factorial design 2^3 with central points. The concentration of commercial ethoxylated non-ionic surfactant, *Tween 60*, was established at 2000, 3000, and 4000 ppm, while the active egg yolk concentration varied in 1000, 2500, and 4000 ppm. The dispersed phase (corn oil) concentration was varied in 60, 70, and 80 weight percent. As expected, the increase in the blend surfactant concentration produced a reduction in the emulsion's mean drop diameter. However, this d_{43} reduction not necessarily implied an increase in the viscosity of emulsions. The 60/40 O/W emulsions showed a Newtonian rheological behavior and their viscosities were higher when the egg yolk concentration was greater than *Tween 60* content, regardless the d_{43} increase. Highly concentrated emulsions (70/30 and 80/20) behaved like pseudoplastic fluids. The viscosity of 80/20 O/W emulsions increased proportionally with *Tween 60* increment and d_{43} reduction. While 70/30 O/W emulsions showed an increase in the viscosity when one of the surfactants predominates over the each other. Through the analysis of variance of experimental space, eliminating the non-significant effects, it was determined that d_{43} can be predicted almost by 99% by a lineal model which includes pure variables and their interactions. The model's assumptions of normality, independence, and homocedasticity were satisfied.

1. Introduction

There are a number of products based on emulsions like butter, dressings, and mayonnaise. An emulsion is a mixture of two immiscible liquids stabilized by a surfactant agent. Dressings are oil in water emulsions, where oil constitutes the disperse,

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or internal phase, and water the continuous or extern phase. During storage and consumption, the dressing stability is a relevant property on its quality; therefore a dressing that maintains its properties in time is generally a quality synonym.

Mean drop diameter (d_{32} or d_{43}) and drop size distribution of the disperse phase, viscosity, and stability are some of the properties that can be studied in an emulsion. They are determined by formulation, composition, and mixing conditions. There should be an adequate relationship between these variables to obtain the desirable properties of the final product. It has been established that an optimum drop size, determines better results for viscosity and stability. Generally, while smaller is the drop size the emulsion is more stable and viscous, this is also registered when a narrower drop size distribution is obtained (mono-dispersity).

The egg yolk (EG) has been the most common surfactant in the Food Industry, due to its sensorial and characteristics properties. The combination of lipoproteins and phospholipids (lecithin) provides the appropriate mixture to produce excellent emulsifying properties. The presence of EY in the oil/water interface produces a strong and cohesive film around the oil drops avoiding the coalescence (Kiosseoglou, 2003).

Other surfactants widely used in the Food Industry are monosteareates, specifically the *Tweens* family. They are non ionic and their hydrophilic character could be more selective substituting the different number of polyoxyethylene chains in the hydroxy groups, generating diverse types of *Tween,* such as *Tween* 20, 60, or 80.

The use of other surfactants in combination with egg yolk has been studied by several authors, in order to reduce the cholesterol and lipid levels, to improve the microbiological stability, and to reduce costs of some food products. As general rule, high molecular weight proteins are displaced from the interface by the non ionic surfactants in high concentrations, because their emulsifying effect is more effective (Dickinson *et al*., 1999). In addition, the surfactant can fill the empty spaces in the layers of proteins adsorbed on the interface, or it can interact with proteins to produce a more viscoelastic interfacial layer (Carrera, 2000). The concentration of each surfactant will determine the different interactions that could appear in oil-water emulsion interface.

Previous studies of diluted sunflower oil in water emulsions (35/65), using blends of egg yolk and commercial surfactant *Tween* 20, had demonstrated that viscosity and mean drop diameter of emulsion increase proportionally with the egg yolk/*Tween* 20 weight ratio (Riscardo *et al*., 2003). It is important to mention that emulsion viscosity increased even though the mean drop diameter also augmented. Consequently, it seems clear that droplet size cannot be the only variable which justifies rheological results. Thakur *et al*. (2007) studied diluted emulsions stabilized with lecithin. When they compare the viscosity with mean drop diameter of emulsions, they comment that viscosity increase is only consequence of colloidal interactions. The interactions rise proportionally with the distance reduction between oil drops. In addition, flocculation may constitute a stabilization process if this process is extensive enough to induce droplets to form a structural network which disables droplets movement.

Most of the studies have considered emulsions with low content of disperse phase. In the present work was analyzed the effect of different blends of *Tween* 60/Egg Yolk on the properties of concentrated corn oil in water emulsions with disperse content of 60-80 weight percent (mean drop diameter, drop distribution, and rheological behavior). These emulsions constitute the base of salad dressings.

2. Materials and Methods

2.1 Materials

For the emulsions preparation, distilled water (continuous phase) and corn oil (disperse phase) were used. Common egg yolk and a non-ionic surfactant Tween 60 (CS) (polyoxyethylene sorbitan (20EO) monostearate) with HLB=15, were employed as emulsifying agents.

Active egg yolk (AEY) refers to the specific emulsifying egg yolk portion. For its determination it was considered that from the whole yolk, 48% represents dry matter, from the dry matter only 68% contains emulsifying agents corresponding to low density lipoproteins LDL (Guilmineau and Kulozic, 2006). Egg yolk quantity (EY) employed was determined considering the active portion of the yolk, AEY represents 32,64 % of the EY.

2.2 Methods

Emulsions containing different concentrations of Tween 60 and Egg Yolk were prepared at 60/40, 70/30, and 80/20 O/W weight relation (see Table 1). The concentrations of both surfactants were higher than the critical micelle concentration (CMC), obtained in previous experiments. Tween 60 was diluted in distilled water at 333 K, it was cooled down and egg yolk was added. Corn oil was incorporated to the vessel, and it layed still for 1 minute. The mixing system was a rotor-stator homogenizer. The impeller was submerged in the oil phase and the mixing time was 2 minutes at 8000 rpm. Finally, the emulsions were refrigerated at 280 K.

Mean Drop Diameter Measurement: The mean drop diameters and drop size distribution of emulsions were determined by laser light diffraction using a Malvern Mastersizer analyzer. After the measurement, the equipment program generates a report that displays the volume mean drop diameter, d_{43}, which corresponds to the mean arithmetic of the volumetric distribution.

Viscosity Measurement: To determine the rheological behavior of the emulsions it was used a rotational viscometer Brookfield DV+1. The angular velocity could be varied in the range 0 to 100 rpm.

Statistical Analysis: It was developed a factorial design 2^3 with five central points to determine the influence of the variables: concentration of Active Egg Yolk (C_{AEG}), concentration of Commercial Surfactant (C_{SC}) and Disperse Phase content (Φ), on the mean drop diameter (d_{43}). It was necessary to define the coded variables A, B and C (see Eqs. 1, 2 and 3) in two levels, the minimum (-1) and maximum (+1). Each treatment was performed in triplicate to verify the reproducibility, with the exception of central points where the value of the coded variables is zero (0). The analysis of variance (ANOVA) was developed with the program *Design Expert*, the model's assumptions of normality, independence, and homocedasticity were checked. It was considered a probability of a Type I error, α=0,05. The linear effects and the studied factor interactions were considered statistically significant when the probabilities associated with the F-statistics were lower than 0,05 (p = Prob > F < 0,05).

$$A = \frac{\Phi - 0,7}{0,1} \quad (1)$$

$$B = \frac{C_{AEG} - 2500 ppm}{1500 ppm} \quad (2)$$

$$C = \frac{C_{CS} - 3000 ppm}{1000 ppm} \quad (3)$$

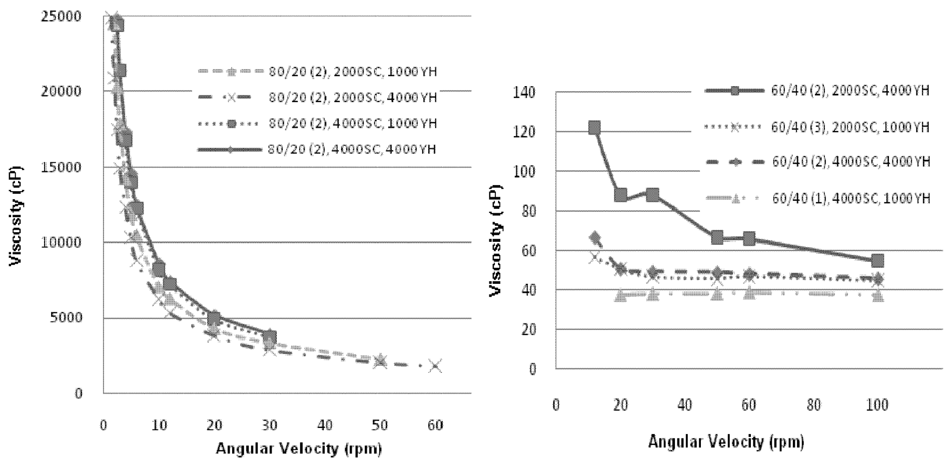
Table 1. Coded variables in the factorial design 2^3 with five central points. Measured mean drop diameters (d_{43})

	Coded Variables			Natural Variables			d_{43} (μm)	
Treatment	A	B	C	Φ	Conc. AEY ppm	Conc. CS ppm	Average (μm)	σ (μm)
1	-1	-1	-1	60/40	1000	2000	24,20	0,97
2	+1	-1	-1	80/20	1000	2000	12,82	0,82
3	-1	+1	-1	60/40	4000	2000	17,20	0,45
4	+1	+1	-1	80/20	4000	2000	8,60	0,90
5	-1	-1	+1	60/40	1000	4000	19,39	0,63
6	+1	-1	+1	80/20	1000	4000	7,05	0,16
7	-1	+1	+1	60/40	4000	4000	14,14	0,32
8	+1	+1	+1	80/20	4000	4000	6,29	0,24
9	0	0	0	70/30	2500	3000		
10	0	0	0	70/30	2500	3000		
11	0	0	0	70/30	2500	3000		
12	0	0	0	70/30	2500	3000		
13	0	0	0	70/30	2500	3000	11,95	0,29

3. Results and Discussion

Table 1 shows the average of d_{43} values measured with the Malvern Mastersizer and the corresponding standard deviation (σ). The central point treatments were elaborated only one time, and Table 1 presents the average of the five emulsions. The mean drop diameters decrease inversely proportional to the dispersed phase concentration. The increase of surfactants concentration in the emulsions prepared with 80% of oil (80/20) produced a decrease in the d_{43} values, more viscous emulsions, and narrow drop size distributions. The effect of active egg yolk was more evident in the emulsions prepared with low concentration of commercial surfactant (2000 ppm); the d_{43} difference between treatments 6 and 8 was 11% (see Table 1), while the d_{43} of treatments 2 and 4 showed a difference of 33%. The molecules of both surfactants compete for the adsorption on the interface; the commercial surfactant has a small molecule than egg yolk, which promotes the diffusion along the continuous phase, then when high concentrations of both are used, the CS adsorbs easily due to its better emulsifying properties. When the CS concentration is 2000 ppm, exist enough space on the drop and the adsorption of both surfactants is promoted. The viscosity increases inversely proportional to d_{43} decrease, and the 80/20 emulsions showed pseudoplastic behavior (see Fig. 1a).

For emulsions low concentrated (60/40) the tendency of results was similar, the increase in the surfactant concentrations produced low d_{43} values. However, in this case the influence of active egg yolk was more evident; the increase of this surfactant produced a 27% of change in the d_{43} values of emulsions prepared with 4000 ppm of CS (see treatments 5 and 7 in Table 1). In addition, the increase of AEG produced more viscous emulsions, even though in some cases the d_{43} values were bigger; this result is similar to the one reported by Riscardo *et al.* (2003). For diluted emulsions the drop size is bigger, increasing the adsorption of egg yolk on the interface, which affects the colloidal interactions. The 60/40 O/W emulsions presented a transition between Newtonian and pseudoplastic behavior (see Fig. 1b). The emulsions O/W corresponding to central points, 70/30 (treatments 9-13), were pseudoplastic. At 20 rpm the viscosities of 60/40 emulsions were almost fifty times lower than the viscosities of 80/20 emulsions.



(a) (b)

Figure 1: Viscosity of O/W emulsions prepared with different concentrations of surfactants (a) 60/40; (b) 80/20

The result of analysis of variance of d_{43} factorial design is showed in Table 2. The coded pure variables A, B, C, and their interactions AB and BC, were significant. It was determined a correlation (Eq. 4) between the value of d_{43} and the variables: oil weight fraction, AEG and CS concentration, and the combination of some of these variables. The linear regression of factorial design reported an adjusted R^2 value of 0,944, and R^2

value of 0,9974. The R^2 value is an indicator of how well the model fit the experimental data.

Table 2. ANOVA for the factorial design of d_{43}

Parameter	Square Sum	DF	Mean Square	F Value	Prob > F
Model	280,57	6	46,76	323,25	<0,0001
A	201,30	1	201,30	1391,57	<0,0001
B	37,28	1	37,28	257,72	<0,0001
C	31,96	1	31,96	220,93	<0,0001
AB	6,68	1	6,68	46,17	0,0011
AC	3,612e-3	1	3,612e-3	0,025	0,8806
BC	3,34	1	3,34	23,10	0,0049
Curvature	9,51	1	9,51	65,76	0,0005
Residuals	0,72	5	0,14		
Lack of fit	0,38	1	0,38	4,50	0,1013
Pure error	0,34	4	0,085		

$$d_{43} = 13{,}7125 - 5{,}0150\text{A} - 2{,}1600\text{B} - 1{,}9975\text{C} + 0{,}9075\text{AB} - 0{,}0150\text{AC} + 0{,}6400\text{BC} \qquad (4)$$

The lower d_{43} value is obtained when maximum values (+1) of coded variables A, B, and C (disperse phase content, AEY and CS concentration) are used. However, for the most concentrated emulsions with 4000 ppm of CS the egg yolk concentration could be reduced, promoting the elaboration of products with lower contents of cholesterol and lesser costs. In addition, is possible to reduce the internal phase proportion, because 70/30 emulsions showed acceptable viscosities and d_{43} values.

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