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STABILIZATION OF W/O EMULSIONS USING ECOFRIENDLY EMULSIFIERS

BY

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Abstract. An ecological emulsifier, containing a mixture of fatty acid esters was prepared by the transesterification reaction of sunflower oil with ethanol. The reaction was catalysed by CaO resulted from the calcination of the eggshells. Several emulsions consisting of sunflower oil and water, which differ from each other by the ratio between phases (70% O / 30% W, 60% O / 40% W and 50% O / 50% W) and by the concentration of emulsifier (2%, 4% and 6% respectively with respect to the vegetable oil mass), were prepared. The influence of the emulsifier concentration and of the ratio between phases on the stability of the emulsions were studied. The microscopic images, the stability index values and the turbidity's values showed that the most stable is the emulsion containing 60% O / 40% W and 4% emulsifier.

Keywords: emulsion stability; turbidity; vegetable oil; eggshell; microscopic image.

1. Introduction

Emulsions are applied in various fields including foods, cosmetics, pharmaceuticals, petrochemicals (Albano *et al.*, 2019; Chenglin *et al*., 2011; Ozturk and McClements, 2016). These emulsions are thermodynamically

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unstable and tend to separate into oil and water phases due to the destabilization. Destabilization of emulsions can occur due to various physicochemical processes such as coalescence, flocculation, phase inversion, creaming and sedimentation, Ostwald ripening (Jafari *et al*., 2008; Liang *et al*., 2018; Ushikubo and Cunha, 2014). The stability of the emulsions can be improved by adding of emulsifiers. The emulsifiers lower the surface tension and prevent flocculation by absorption on the droplets surface. Since in recent years the consumer demand for healthy foods made from natural ingredients has increased, the synthetic ingredients have been partially replaced by natural additives. By use of some natural biopolymers such as proteins, polysaccharides and their derivatives (which act as emulsifiers or increase the viscosity) increases the stability of the emulsion (Cheong *et al.*, 2014; Hosseini *et al*., 2015; McClements *et al*., 2017; McClements and Jafari, 2018).

The aim of the paper was (1) to obtain an ecological emulsifier consisting of a mixture of ethyl esters of fatty acids resulted by the transesterification reaction of sunflower oil with ethanol and (2) the preparation and the characterization of some water / oil emulsions by use of the prepared emulsifier.

2. Experimental Part

Materials

Sunflower oil (containing 7% palmitic acid, 30% oleic acid, 57% linolic acid and 5% stearic acid) was purchased from SC GEMITE RO SRL Târgu Neamţ, eggshells were provided by the canteen of the Tudor Vladimirescu student campus in Iaşi, ethyl alcohol was purchased from Chemical Company SA EN.

Obtaining the emulsifier

The emulsifier (consisting of a mixture of ethyl esters of fatty acids) was obtained by the transesterification reaction of sunflower oil with ethanol. CaO obtained by calcining eggshells was used as a catalyst. For this purpose, the eggshells were dried for 24 hours at 60ºC and then were calcined at 900ºC.

Transesterification reaction

The oil was introduced into a 2-necked flask equipped with a condenser. Heating was performed in a thermostatic bath up to 70°C, thereafter the ethyl alcohol was slowly added under stirring. The volume ratio sunflower oil / ethanol was 1: 8. When the temperature of the reaction mixture reached to 70°C, the catalyst was added. The esterification reaction was carried out at 70°C for 6 hours, under stirring (500 rpm). After completion of the reaction the mixture was filtered to remove the catalyst and then was evaporated in vacuum in order to remove the unreacted ethyl alcohol. The reaction mixture containing the fatty acid ethyl esters was used as an emulsifier.

HLB index

The values of the HLB index for the esters of palmitic (EP), oleic (EO) linolic (EL) and stearic (ES) acids were calculated with Griffin's relation (Eq. (1)):

$$HLB=20\cdot\frac{M_h}{M} \qquad (1)$$

wherein: M_h is the mass of the hidrophilic part of the ester and M is the molecular mass of the ester.

Table 1
HLB Values of the Fatty Acid Esters

Ester	M_h	M	HLB
Ethyl Linolate	44	308	2.857
Ethyl Palmitate	44	284	3.099
Ethyl Oleate	44	310	2.834
Ethyl Stearate	44	312	2.821

Since the emulsifier is a mixture of esters, the total HLB index was calculated with the relation (Eq. (2)):

$$HLB_{mixture}=\sum f_i\cdot HLB_i \qquad (2)$$

where: f_i – represents the gravimetric fraction of the component i with the hydrophilic lipophilic balance value HLB_i

According to the Eq. (2) the hydrophilic lipophilic balance value of the emulsifier used in the experiments is $HLB_{mixture}$ = 2.836.

Preparation of the emulsions

The W / O type emulsions were prepared as follows: the emulsifier was dissolved in the oily phase and then the distilled water was added dropwise. The mixture was stirred (stirring speed 1000 rpm) for 15 min at room temperature. The influence of the emulsifier concentration and the ratio between the two phases on the stability of the emulsions were analysed.

Microscopic evaluation of the emulsions

Microscopic evaluation of the prepared emulsions was carried out using the KRUSS optical microscope and the microscopic images were transferred for computerized analysis using a photo- digital camera (Nikon, Coolpix P 5100).

3. Results and Discussion

The emulsions were characterized by visual observation, by optical microscopy, by the stability index and by turbidimetric analysis.

Visual monitoring of the emulsions

The variation of the stability over time of the analysed emulsions is illustrated in the photographic images shown in Fig. 1-5.

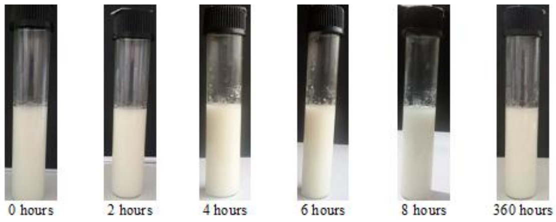

Fig. 1 – Overall appearance of the emulsions consisting of 50% O and 50% W (4% emulsifier).

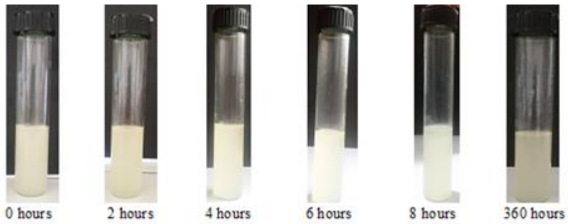

Fig. 2 – Overall appearance of the emulsions consisting of 60% O and 40% W (4% emulsifier).

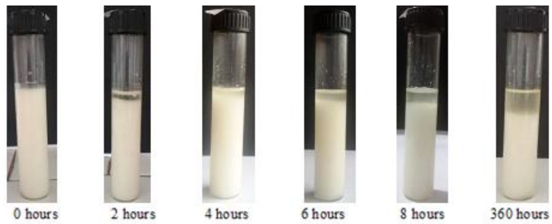

Fig. 3 – Overall appearance of the emulsions consisting of 70% O and 30% W (4% emulsifier).

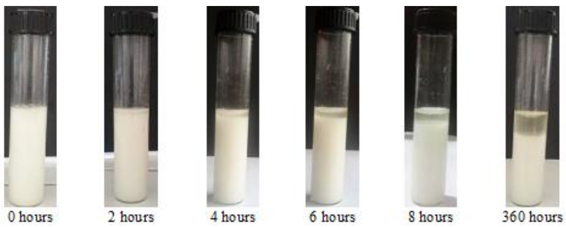

Fig. 4 – Overall appearance of the emulsions consisting of 60% O and 40% W (2% emulsifier).

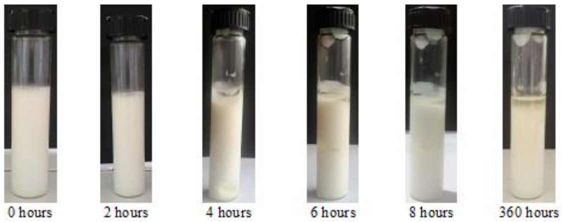

Fig. 5 – Overall appearance of the emulsions consisting of 60% O and 40% W (6% emulsifier).

Determination of the emulsion stability index

The obtained emulsions were introduced in glass tubes with 1.5 cm in diameter and their evolution over time (15 days) was evaluated. The term of emulsion stability refers to the ability of an emulsion to retain its properties unchanged over a period of time. The slower these properties change, the more stable the emulsion is. Emulsion stability is influenced by several parameters such as the surfactant concentration and the phase ratio.

The stability index of the emulsion (expressed as a percentage %) was calculated as the ratio between the height of the emulsion at time t and the total height of the emulsion at time 0. The results obtained are presented in Table 2 and Table 3.

Table 2

The Influence of the Ratio between the Two Phases on the Stability of the Emulsion

Composition of emulsion (emulsifier amount)	Emulsion stability (%) after various lengths of time								
	0 hours	2 hours	4 hours	8 hours	24 hours	48 hours	72 hours	144 hours	360 hours
50% W+50% O (4% emulsifier)	100	100	98	94	92	90	88	87	87
40% W+60% O (4% emulsifier)	100	100	100	100	100	100	100	100	100
30% W+70% O (4% emulsifier)	100	84	78	63	61	60	60	59	59

Table 3

The Influence of the Emulsifier Concentration on the Stability of the Emulsion

Emulsion (40% W + 60% O)	Emulsion stability (%) after various lengths of time								
	0 hours	2 hours	4 hours	8 hours	24 hours	48 hours	72 hours	144 hours	360 hours
Emulsifier (2%)	100	96	75	61	60	60	60	60	60
Emulsifier (6%)	100	100	100	84	77	76	76	76	76

From observing the overall appearance of the emulsions and from the analysis of the variation of the values of the stability index in time it is observed that the stability of the emulsions is influenced both by the ratio between the two phases of the emulsion and by the emulsifier concentration used to preparate the emulsions. For the same emulsifier concentration (4%) the most stable are the emulsions containing 60% oil and 40% water (the phases do not separate even after 30 days of storage). The least stable are the emulsions containing 70% oil and 30% water (phase separation occurs after 2 hours). As far concerns the influence of the emulsifier concentration used in the preparation of emulsions containing 60% oil and 40% water, it is observed that the most stable are the emulsions containing 4% emulsifier, and the least stable are the emulsions containing 2% emulsifier (the separation of the phases occurs after 4 hours from preparation).

Microscopic evaluation of the emulsions

Microscopic images of the emulsions 24 hours after their preparation are shown in Fig. 6 and Fig. 7.

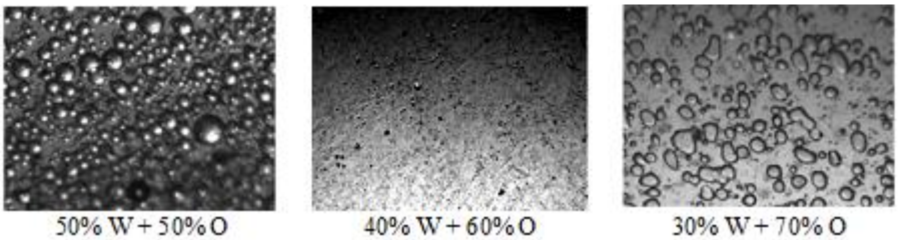

Fig. 6 – Microscopic images for W/O emulsions containing 4% emulgator.

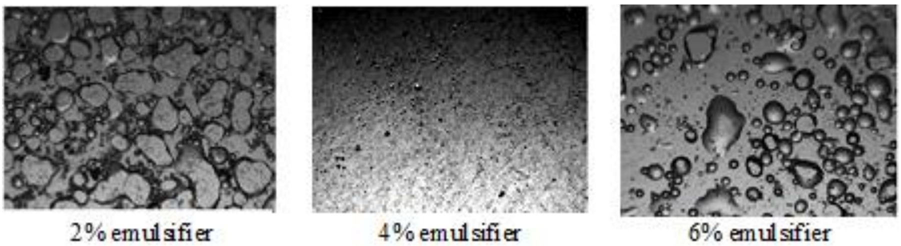

Fig. 7 – Microscopic images for W/O emulsions containing 40% W + 60% O.

From the presented images it can be concluded that the smallest dimensions for the particles of the dispersed phase and respectively the highest degree of dispersibility are obtained in the case of the emulsion containing 60% oil and 40% water and a concentration of 4% emulsifier.

Turbidimetric evaluation of the emulsions

Turbidity measurements were also used to assess the stability of the emulsion (Aizawa, 2014). The proposed method for determining turbidity is based on the principle of measuring the transmittance of the light that passes through the analysed emulsion. The Lambert-Beer law was used to correlate the transmittance with the length of the path travelled by light through the emulsion (the width of the spectrophotometric cuvette wherein the emulsion is found).

$$\tau \cdot 1 = 2.303 \cdot A \tag{3}$$

wherein: τ is the turbidity of the emulsion; l – represents the width of the spectrophotometer cuvette (the thickness of the emulsion layer penetrated by UV radiation); A – represents the absorbance of the emulsions read on a UV spectrophotometer at a wavelength of 205 nm.

In order to determine the absorbances 0.2 mL of sample extracted from the lower layer was diluted with distilled water to a volume ratio of 1:500 and stirred vigorously for 5 minutes.

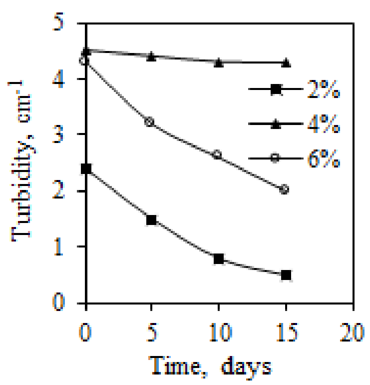

Fig. 8 – The influence of the emulsifier concentration on the emulsion turbidity.

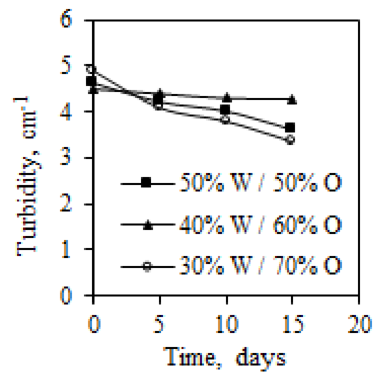

Fig. 9 – The influence of the ratio between the two phases on the emulsion turbidity.

The lowest variation in time of the turbidity values (Fig. 8 and Fig. 9) indicates in this case too, that the most stable emulsion is the one consisting of 60% oil / 40% water and an emulsifier concentration of 4%.

3. Conclusions

The results obtained show that the obtained mixture of fatty acid esters is capable to stabilize the emulsions and can therefore be suitable as a natural emulsifier for obtaining stable emulsions. The stability of the emulsions is influenced by both the emulsifier concentration and the ratio between the two phases. For the same emulsifier concentration (4%), the most unstable is the emulsion containing 70% oil and 30% water, and for the emulsions that contain the same ratio between the two phases (60% oil and 40% water), the most unstable is the emulsion containing 2% emulsifier. The most stable is the emulsion containing 60% oil and 40% water and an emulsifier concentration of 4%.

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STABILIZAREA EMULSIILOR A/U UTILIZÂND EMULGATORI ECOLOGICI

(Rezumat)

S-a preparat un emulgator ecologic, conţinând un amestec de esteri ai acizilor grași, prin reacția de transesterificare a uleiului de floarea soarelui cu etanol. Reacția a fost catalizată de CaO rezultat prin calcinarea cojilor de ouă. Au fost preparate mai multe emulsii formate din ulei de floarea soarelui și apă, care diferă între ele prin raportul dintre faze (70% U / 30% A, 60% U / 40% A și respectiv 50% U / 50% A) și prin concentrația de emulgator (2%, 4% și respectiv 6% în raport cu masa uleiului). S-au studiat influența concentrației de emulgator și a raportului dintre faze asupra stabilității emulsiei. Imaginile microscopice, valorile indicilor de stabilitate și valorile turbidității au arătat că cea mai stabilă este emulsia care conține 60% U/40% A și 4% emulgator.