

ZETA POTENTIAL AND COLOR INVESTIGATIONS OF VEGETABLE OIL BASED EMULSIONS AS ECO-FRIENDLY LUBRICANTS

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Received: June, 17, 2016

Accepted: June, 07, 2017

Abstract: In the past 10 years, the need for biodegradable lubricants has been more and more emphasized. The use of vegetable oils as lubricants offers several advantages. The vegetable oils are biodegradable; thus, the environmental pollution is minimal either during or after their use. The aim of this paper is to presents a preliminary study concerning the influence of some preparation conditions on the stability of vegetable oil-in-water (O/W) emulsions as eco-friendly lubricants stabilized by nonionic surfactant. In this context, vegetable oil-in-water emulsions characteristics where assessed using microscopically observation and zeta potential. In addition, the color of these emulsions can be evaluated. It can be observed that the emulsions tend to stabilize in time.

Keywords: *biodegradable oil, color parameters, oil volume fractions, size analysis, zeta potential*

INTRODUCTION

The accidental leakage of mineral lubricants can be an important source of pollution. Therefore, an alternative for the use of those types of lubricants is a need [1]. During the last years, many researchers studied the replacement of minerals and synthetic lubricants with environmentally friendly lubricants [2, 3].

The lubricants industry challenge is to create biodegradable lubricants with physicochemical properties superior to those based on mineral oil [4, 5].

Due to the fact that are renewable resources vegetable oils (complex mixtures of triglycerides of fatty acids) are typically preferred over synthetic fluids. Furthermore, unlike conventional mineral-based oil emulsions vegetable-oil based emulsions as potential lubricants are biodegradable and non-toxic [6]. Belfit and Shirk showed that oil-in-water emulsions were used as lubricant first in 1940s [7]. The vegetable oil-in-water emulsion has been widely used as lubricant in metalworking such as metal rolling and cutting. Liran et al. [8] considered the film formation ability of emulsion as an important evaluation factor. The film formation mechanism of oil-in-water emulsion was discussed and it is based on the different film forming performances of emulsion with different oil volume percentages (from 0.005 % to 2.5 %).

The vegetable oil emulsions have specific physicochemical properties that may give their advantages for these particular applications. More than that, the emulsions technology has been used to create a diverse range of commercial products, including among others bio-lubricants (pharmaceuticals, foods, cosmetics etc.).

The emulsions are colloidal systems of two immiscible liquid phases: a dispersed phase and a continuous phase. The immiscible phases are usually oil and water. Emulsions are of particular interest as colloidal delivery systems because they can easily be fabricated from grade ingredients using simple processing operations.

Emulsions are thermodynamically unstable systems (the kinetic stability is obtained using an adsorbed layer of surface-active material, i.e., surfactant molecules) [9]. The use of these complex structures that are based on emulsions seems to offer an attractive range of tools to engineer healthier lubricants without compromising the environment. The preparation of stable oil-in-water (O/W) emulsions is essential for the success of production of stable vegetable oil emulsions. The preparation of the vegetable oil based emulsions is a complicated process, which has been widely investigated experimentally. However, many of the sub processes are poorly understood [10].

In this context, few papers analyze the factors affecting stability of emulsions as potential environmentally friendly lubricants. Considering this case, the stability as a notion is very complex, involving both colloidal and chemical stability [1, 2].

Roland et al. [11] studied the stabilization and destabilization of oil-in-water emulsions. It was concluded that all emulsions should first be considered as dispersed systems and overall analyzed in terms of stability. Stability is often related to the zeta potential (ζ) of the system. Its value represents the stability of the dispersed system in a chosen environment.

This work deals with the electrokinetic's aspects of interactions between the dispersed oil drops of O/W emulsions in the presence of non-ionic surfactant in the aqueous phase. Comparing different electrokinetic methods, it can be observed that the results are commonly reduced to a single parameter: ζ potential. Variation of electrokinetic potential in dependence of time was determinate.

The availability of methodologies to study the stability of oil-in-water emulsions is very important. Our previous studies have showed that the stability/instability of some emulsions is dependent on the emulsions droplet size, which is a function of the conditions at which the emulsions has been prepared. Our results showed the optimum emulsification conditions: emulsifier dosage, 1 % (w/w) [12]. So, in present work the vegetable oil based emulsions stability by microscopically observation, zeta potential determination and chromatic parameters were reported.

The aim of this work was to study (i) the formation process and the stability of vegetable oil-in-water emulsions as potential bio-lubricants and (ii) chromatic parameters change of such emulsions prepared in the laboratory in time. In particular, the aim was to show that the zeta potential determination is a very good method for vegetable oil emulsions stability evaluation, which to the author's knowledge has not been reported before.

These studies have confirmed that vegetable oil-in-water emulsions as potential environmentally friendly lubricants can be grouped into two states: stable emulsions and unstable emulsions.

The results of this study will be particularly useful for the optimization of emulsification conditions in the case of vegetable oil-in-water emulsions used for eco-friendly lubricant.

MATERIALS AND METHODS

Materials

Sunflower oil was purchased from S.C. Prutul S.A. Galati and had the following characteristics: saponification index 189.1 mg KOH g⁻¹ oil, acidity index 0.02 mg KOH g⁻¹ oil, peroxide index 8.4 mL 0.002 N Na₂S₂O₃ g⁻¹ oil and iodine index 123.2 g iodine per 100 g oil. The emulsifier used is polyoxyethylen (20) sorbitan monostearat, also called Tween 60 supplied by Fluka / Sigma–Aldrich Switzerland. It is a non-ionic hydrophilic emulsifier of HLB 10.2, commonly used in emulsions preparation because of its low toxicity. Sodium phosphate monobasic was purchased from Sigma Chemical Co. (St. Louis, MO). Deionized water, used for all experiments, was produced by a purification chain provided by GFL Hanptschalter, Main Switch.

Emulsions preparation

The preparation of emulsions was similar to the report described by Batista [13] with a slight modification. Concentrated oil-in-water emulsions were prepared by blending 10-30 wt % lipid phase (sunflower oil) with 90 - 70 wt % aqueous phase (1 wt % Tween 60, 10 mM sodium phosphate buffer, pH 7.0) using a high-speed homogenizer (Ultra-Turrax, France). So, emulsions containing various volumetric fractions were prepared. The emulsifier was dispersed under magnetic stirring (10 min, at room temperature) and emulsification was carried out at 2500 rpm for 15 min. Then the mixture was passed through a one stage ultrasonication at 45 % amplitude, 0.05 pulse (Bandelin, Sonopuls, Germany, equipped with a titanium horn (3 mm diameter) mounted at the top of the cylindrical glass cell) for 3 min. The emulsion was obtained by ultrasonication. A good

emulsification is related to an optimum amount of ultrasonic energy according to the procedure of Djenouhat et al. [14]. Diluted emulsions with varying compositions were prepared by diluting concentrated emulsions with aqueous emulsifier solution (1 wt %). All emulsions were placed in cylindrical glass containers (100 mm diameter and 150 mm height), at 4 °C for 24 h. All experiments were performed at 20 °C and replicated at least three times. The experiments were repeated in order to verify the reproducibility of the results.

Microscopic observation of emulsions

Traditionally, the microstructure of emulsions is observed under the microscope 24 hours after the preparation.

The microstructure of selected emulsion (1:1 diluted in Milli-Q (Millipore Corp.) water) was determined with an Olympus BX61 light microscope (Carl Zeiss objective, Germany) equipped with view camera.

Particle size measurements

The mean droplet diameter of vegetable oil-in-water emulsions as potential environmentally friendly lubricants was measured using a dynamic light scattering instrument (Zetasizer Nano series-Zen 3600, Malvern Instruments, Instruments Ltd., United Kingdom). To prevent multiple scattering effects the emulsions were diluted (using a dilution of 1:100) with buffer prior to the analysis. A refractive index ratio of 1.08 (refractive index of oil/refractive index of aqueous phase) was used in the calculations of the particle size distribution. The particle size was obtained as surface-volume mean particle diameter:

$$d_{32} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

where n_i is the number of droplets with a diameter d_i [15].

Determination of zeta potential

The zeta potential (ζ) was determined through dynamic light scattering (ZetaSizer nano series - Nano-ZS - MALVERN, Instruments Ltd., United Kingdom). The instrument measures the direction and velocity of a particle in an applied electrical field via phase analysis light scattering and laser Doppler velocimetry. The calculated electrophoretic mobility is converted into zeta potential values using the Smoluchowski model. The emulsions were diluted 1:10 with phosphate buffer for the dynamic lighter scattering analysis. Measurements were made in triplicate at 20 °C.

Color measurements

The CIE L^* , a^* and b^* parameters were designated as indicators of lightness, redness, and yellowness, respectively (a^* measures the redness when positive, the grayness when zero, and the greenness when negative; b^* measures the yellowness when positive, the

grayness when zero and the blueness when negative). CIE L*a*b* system was derived from the CIE Standard Color Table. Illumination was performed by D65 (an representative CIE illuminant which is intended to represent average daylight and has the equivalent color temperature of 6504 K) and a visual angle of 10 ° [16, 17].

The samples were determined post-preparation, and three measurements were taken from the surface of each sample. The first step in calculating of the dilute emulsion color is to calculate the tristimulus coordinates of the emulsion from its spectral transmittance [18, 19]. The X, Z, Y tristimulus coordinates values can be converted into the L*, a*, b* values of the 1976 CIE Color Space. Equations which define the CIELAB color system are:

$$L^* = 116 \cdot (Y/Y_n)^{1/3} - 16 \quad (2)$$

$$a^* = 500 [(X/X_n)^{1/3} - (Y/Y_n)^{1/3}] \quad (3)$$

$$b^* = 200 [(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}] \quad (4)$$

for $(X/X_n) > 0.008856$; $(Y/Y_n) > 0.008856$; $(Z/Z_n) > 0.008856$; X, Y and Z have the same meaning as in the system CIEXZY (CIE, 1986), and X_n , Y_n și Z_n are white standard components of the appliance to the specified illuminant ($X_n = 94.811$; $Y_n = 100$ și $Z_n = 107.304$) [16].

RESULTS AND DISCUSSION

The influence of vegetable oil volume fraction on the creaming stability of oil-in-water emulsions containing Tween 60 was determined. The emulsions appeared homogeneous and there was no evidence of phase separation due to creaming.

The characteristics of colloidal systems in general are determined by surface properties. In this paper, after 1 day from preparation of emulsions, the decrease in absolute value of the zeta potential from 46.7 mV to 42.7 mV (when oil volume fraction decreased from 0.3 to 0.1) was accompanied by a growth in the effective diameter of emulsion droplets from 182 nm to 253.13 nm. These variations are consistent with those found by Wiacek for some model emulsions [20]. According to Kong et al. [21] the emulsions behavior during their production, processing, and storage is highly dependent on composition.

This experiment shows that after sonication the vegetable oil based emulsions were stable to creaming in time at relatively low oil volume fraction values ($\varphi = 0.2$ and $\varphi = 0.3$). The optimum oil volume fraction for studied emulsions system was $\varphi = 0.3$. Images reveal the presence of some larger droplets after 60 days, probably resulting from the coalescence of smaller droplets. However, after 60 days, the morphology of the emulsion has not changed.

The microscope photographs taken during the storage time provided useful information. Traditionally the emulsions are observed under the optic microscope 24 hours after their preparation. Freshly made emulsions were first diluted by approximately 100 times, and then observed under an optical microscope.

Figure 1 shows typical optical microscopic images in the case of the emulsion with 0.3 volumetric fractions. As evidenced from the optical microscopic images, the storage time has a small influence on the size of the emulsified oil droplets. The optical

microscopic images obtained after 60 days, were similar with those obtained after 1 day of their preparation, indicating again that no coalescence took place.

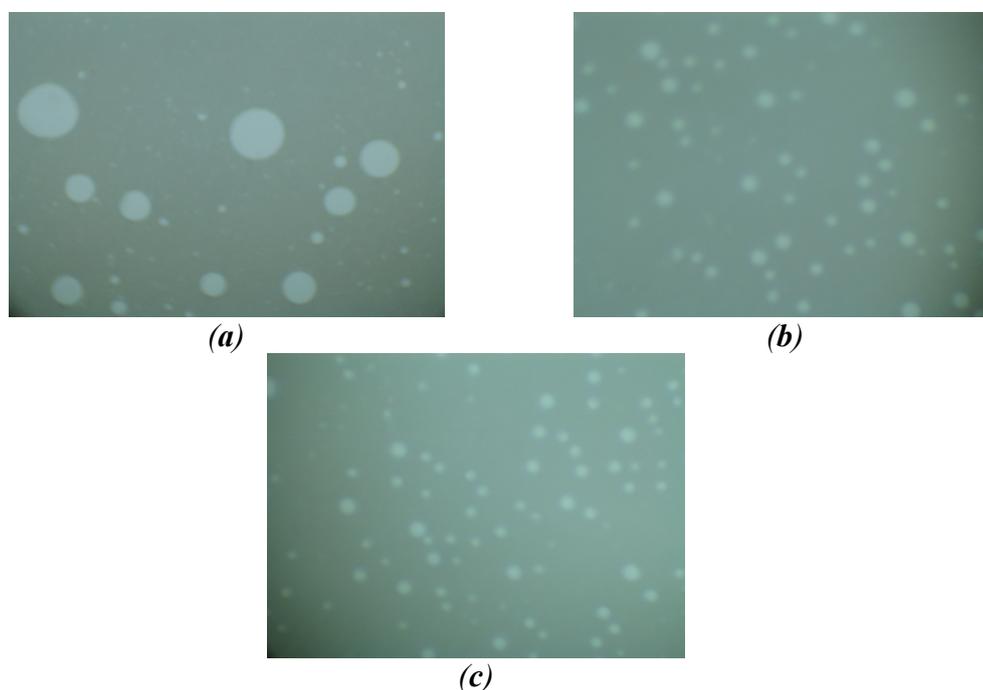


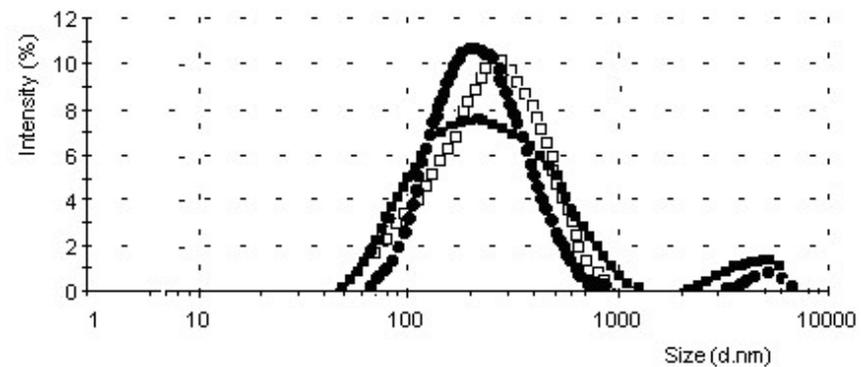
Figure 1. Microscopic view of vegetable oil based emulsions, after 1 day (a), 30 days (b) and 60 days (c) storage at 4 °C (400 × magnifications)

The small changing effective diameter of the droplets as a function of time resulted from coalescence of the droplets and their flotation to the oil-in-water emulsion surface [22].

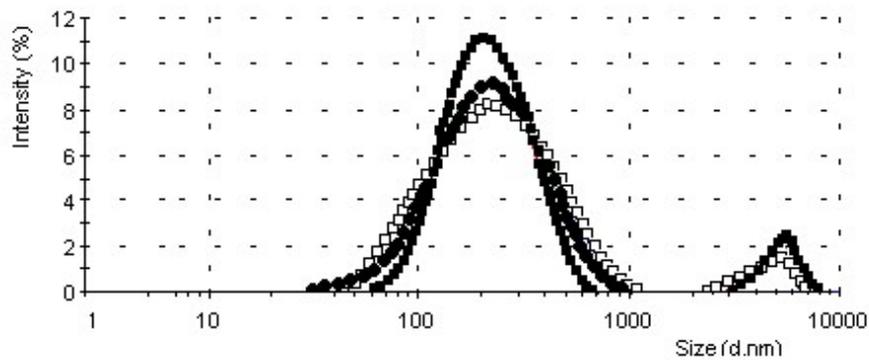
Droplet size distributions

Many emulsified systems are often characterized by size analysis and zeta potential measurements [21]. In the case of emulsions, droplet size is considered often as the most important parameter. As droplet size decreases, significantly increased surface area compared to volume. Thus, the characteristics of emulsions and colloidal systems in general are determined by surface properties. To describe the differences between the various emulsion droplet sizes, the results are presented as their distributions. All emulsions made were stored at 4 °C for 60 days and particle size was measured in order to detect stability, since an increase of particle size will give an indication of coalescence and instability [20]. According to experimental data, we concluded that the emulsions as potential environmentally friendly lubricants with 0.1 vegetal oil volume fraction have relatively large droplet sizes compared to the emulsions containing 0.2 or 0.3 oil volume fractions. The serum volume fraction (creaming stability of oil-in-water emulsions was determined by measuring the height of the serum layer formed at the bottom of the emulsions after 24 h storage at 4 °C and the results were expressed in term of the serum volume fraction) of emulsions increased as oil volume fraction increased from 0.1 to 0.3. As the oil volume fraction increased further, serum volume fraction decreased (results not shown).

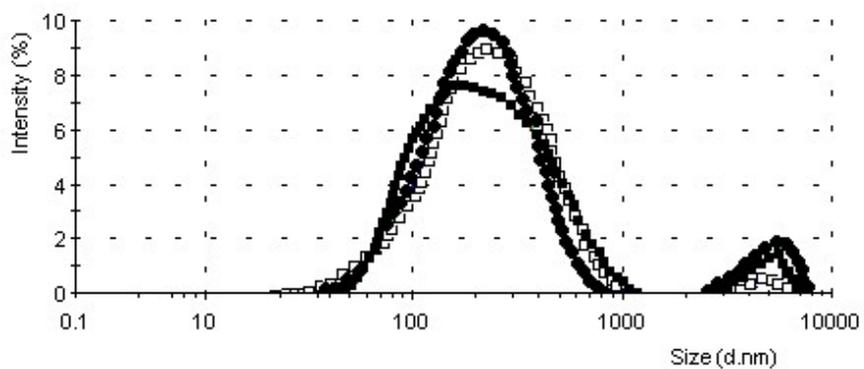
Figure 2 shows droplet size distribution curves for studied emulsions. As evidenced from the optical microscopic images, the storage time has a small influence on the size of the emulsified oil droplets. These observations are in good agreement with the results obtained from the droplet-size distribution determined by dynamic light scattering experiments. On the other hand, as can be observed, droplet size distributions are quite similar in all cases.



(a)



(b)



(c)

Symbols: ■: $t = 1$ day; ●: $t = 30$ days; □: $t = 60$ days

Figure 2. Stability versus time studies of vegetable oil -in-water emulsions prepared with 1 wt% of emulsifier Tween 60: evolution of the droplet size distribution in intensity from $t=1$ to $t = 60$ days for emulsion with $\phi = 0.1$ (a), $\phi = 0.2$ (b) and $\phi = 0.3$ (c)

The size distribution analysis show that in the studied emulsions mostly there are two populations of the droplets and only one is large (principal). In emulsion with 0.1 oil volume fraction ($\varphi = 0.1$, Figure 2a), 1-day-old emulsion (effective diameter 253.13 nm) consisted of a principal population around 250 nm and a very small one (negligible) around 5800 nm. The polydispersity value (dimensionless unit) was 0.196, which shows that the system is of nearly narrow distribution.

For analogous emulsion, in which 0.2 vegetable oil volume fraction was present (effective diameter 205 nm, (Figure 2b), 1 day after its preparation also two populations were present, the principal population around 200 nm and a very small one around 5800 nm (negligible). In 30 days, another two population were detected (only one large), thus giving the effective diameter 205.7 nm.

In the case of the emulsion with 0.3 vegetable oil volume fraction two population (principal population appear around 180 nm and one very small population appear around 5800 nm) were detected, thus giving the effective diameter 182 nm. In this case, after 1 day from preparation of emulsion the droplet diameter decreases by about 28.1% compared to the reference. So, from the size distribution analysis it appeared that in the investigated emulsions usually one small population of the droplets was remarkable.

On the other hand, the droplet size distributions and characteristics of the emulsions did not change significantly during the storage. In all cases, the increase of storage time caused a slight increase in effective droplet diameter (this parameter was determined as a function of time, after 1, 30 and 60 days since the moment of the emulsion preparation). Initial droplet sizes increased with storage time for over the entire range of emulsions tested. The small changing effective diameter of the droplets as a function of time resulted from coalescence of the droplets and their flotation to the oil-in-water emulsion surface. For example, in the cases of the emulsion with 0.3 vegetable oil volume fraction, from 182 nm (1 day old emulsion) to 186.3 nm (60 days old emulsion); this changing effective diameter of the droplets as a function of time is visualized in Figure 2c. This increase in the effective diameter shows that the coalesced droplets are still present in the bulk emulsion for 60 days.

Figure 2b shows that the measured droplet-size distribution for the emulsion with 0.2 vegetable oil volume fraction remains largely unchanged over the 60 days storage period (the effective droplet diameters are: 205.0 nm after 1 day, 205.7 nm after 30 days and 206.3 nm after 60 days) indicating that there was a limited degree of droplet aggregation.

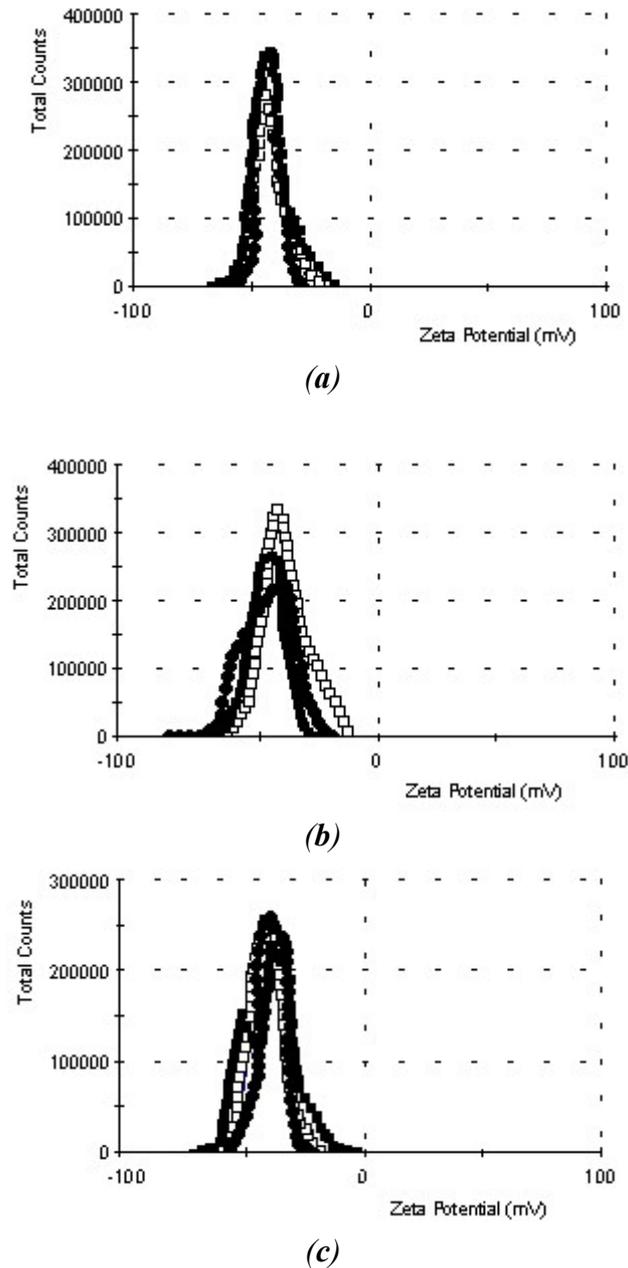
This study has shown that stable vegetable oil-in-water emulsions as eco-friendly lubricants with 0.3 oil volume fraction can be prepared using a simple method that utilizes standard preparation procedures (homogenization and ultrasonication). These emulsions may be relatively good models for lubricants industry such as biodegradable lubricants.

Zeta potential

Emulsion stability is ensured by the zeta potential, which measures the surface charge of droplets. Thus, the change of the zeta potential constitutes important information about the conditions of the interface which determines the life of the emulsion droplets. Electrostatic aggregative stability depends on the electrokinetic potential which characterizes the droplets electrostatic repulsion.

The origin of electric charge and potential at the oil droplet of the emulsions are still not well understood.

Evaluation of the electrical charge of emulsion droplets stabilized by Tween 60 at pH 7.00 by determining the zeta potential is shown in Figure 3.



Symbols: ■: $t = 1$ day; ●: $t = 30$ days; □: $t = 60$ days
Note that some sample symbols are obscured by others

Figure 3. Zeta potential distribution on the surface of oil droplets-in-water emulsion with vegetable oil volume fraction, $\varphi = 0.1$ (a), $\varphi = 0.2$ (b) and $\varphi = 0.3$ (c)

When the zeta potential is relatively high (25 mV or more, absolute value) the repulsive forces exceed the attractive London forces. The particles are dispersed and the system is deflocculated.

The results obtained for vegetable oil based emulsions are consistent with those presented in literature [23].

On the other hand, when the zeta potential is low (less than 25 mV, absolute value), the attractive forces exceed the repulsive forces, and the particles come together leading to flocculation [11, 24].

Zeta potential is nowadays mainly determined by measuring the electrophoretic mobility of the dispersed particles in a charged field but other instruments can be used for this purpose: electrophoretic mass transport analyzer, streaming current detector, and electrokinetic sonic amplitude device.

The data indicate that for 0.1 vegetable oil volume fraction case, electrical charge of emulsion droplets was around - 42 mV (as a result of three experimental determinations: -42.7 (1 day), -42.3 (30 days) and -41.9 mV (60 days), Figure 3 (a).

It is interesting to note that although the emulsion droplets were stabilized by a nonionic surfactant (Tween 60), they have considerable negative charge (-42.7 mV). Measurement of electric charge in such a situation can be attributed to adsorption of HO^- ions (high pH) of water. It is also possible that some of the electrical charge of emulsion oil droplets that occur from free fatty acids and phospholipids present in sunflower oil used to prepare the emulsion.

Figure 3 (b, c) shows the zeta potential of emulsion with $\varphi = 0.2$ and $\varphi = 0.3$. As shown in this figure, the absolute zeta potential values of these emulsions were higher than emulsion with down volume fraction in the presence of Tween 60.

This may be due to the presence of some specific chromophores in the interfacial layer surrounding the oil droplets which can lead to different charge on the droplet surface.

Experimental data obtained for zeta potential value of the emulsion with oil volume fraction $\varphi = 0.2$ indicates that negative electrokinetic potential varies as follows: 45.86 mV (1 day), 44.66 mV (30 days) and 44.06 mV (60 days) (Figure 3 (b)).

In accordance with the experimental data presented in Figure 3 (c) by the utilization of volume oil fraction $\varphi = 0.3$ in oil-in-water emulsion, electrokinetic potential negative increase from baseline of 42.7 mV (emulsion no. 1) to 46.7 mV (1 day), 45.06 mV (30 days) and 44.73 mV (60 days). This can be explained by the contribution of unsaturated acids from vegetable oil.

These measurements suggested that the amount of vegetable oil and surfactant could form a more negative electrostatic potential, which would result in a strong repulsive force between the droplets.

The small differences observed in the stability of the emulsions as eco-friendly lubricants to droplet aggregation and creaming can be attributed to the influence of vegetable oil volume fraction on the colloidal interactions between the droplets. Therefore, in the emulsions with $\varphi = 0.2$ and $\varphi = 0.3$, it seems that the electrical charge on the emulsion droplets is sufficiently large to prevent droplet flocculation.

On the other hand, the emulsion with $\varphi = 0.2$ is less stable to droplet aggregation after 60 day of storage time, which may be attributed to the fact that there is a relatively low electrical charge on the droplets compared to emulsion with $\varphi = 0.3$.

Zeta potentials are generally related to factors that may influence the emulsion stability.

Color measurements

The chemical stability was readily observable through the color of vegetable oil-in-water emulsions (Figure 4), which was not affected by storage time (difference by perceivable color was small).

The Figure 4, shows the results obtained for objective color evaluation carried out in CIE systems by L^* , a^* and b^* parameters. On the other hand, the impact of droplet concentration on the color coordinates of oil-in-water emulsions are shown in Figure 4. L^* , a^* and b^* values of oil-in-water emulsions as eco-friendly lubricants with different oil volume fractions were calculated from its spectral transmittance (dilute emulsions) using equations (2 - 4).

The dependence of emulsion color on droplet concentration is affected by the vegetable oil volume fractions.

In accordance with the experimental data the emulsions lightness (L^*) decreases (Figure 4a) while the parameters a^* , b^* decrease and increase, respectively, (Figure 4b) as the droplet concentration increased. L^* parameter decreased for emulsion with three units approximately.

Emulsion lightness decreased with increasing oil volume fraction because more light was scattered by the droplets and therefore less light was transmitted through the oil-in-water emulsions.

The fraction of light transmitted through a dilute emulsion depends on the scattering of light by the droplets and the absorption of light by any chromophores from vegetable oil [25 - 27].

The a^* and b^* chromatic parameters of the emulsions to the variation of the oil volume fraction was also sensitive. As would be expected, the presence of more vegetable oil had a pronounced influence on the chromaticness (a^* and b^*) of the emulsions. Thus, the redness ($-\Delta a^*$) of the emulsions decreased with increasing oil volume fraction.

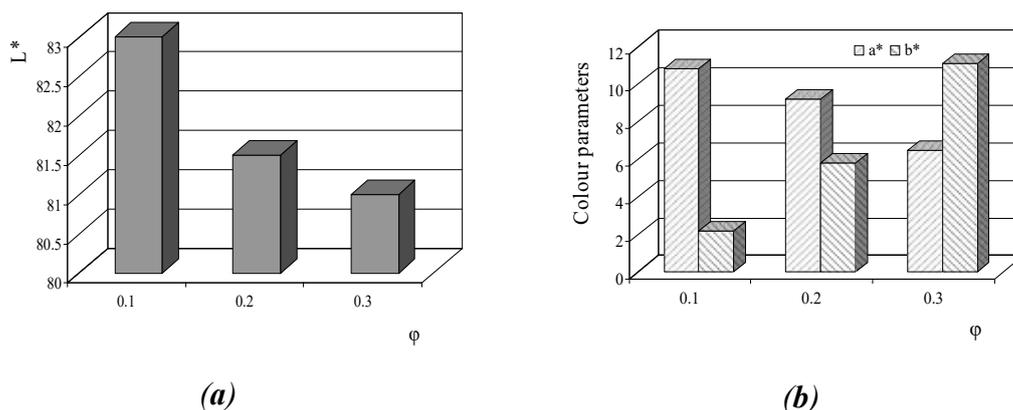


Figure 4. Experimental results on the influence of droplet concentration on the color coordinates L^* (a), a^* and b^* (b) of vegetable oil-in-water emulsions after 1 day of storage

The yellowness of the emulsions containing more vegetable oil increased ($+\Delta b^*$) with increasing droplet concentration (Figure 4b) which highlights that the b^* values were dominated by the presence of the droplets.

The emulsions become lightly more yellow in the presence of more vegetable oil because the unsaturated acid molecules selectively absorbed less yellow light than blue light.

Also, a^* and b^* parameters of the emulsion as eco-friendly lubricant with $\phi = 0.3$ under study are little sensitive to changes in droplet radius with storage time (results not shown). Therefore, stable emulsions containing 30 wt % vegetable oil were obtained.

CONCLUSIONS

The use of some stable vegetable oil based emulsions as lubrication in engineering application is reported. All the experimental studies indicate that stable vegetable oil-in-water emulsions can be obtained with nonionic surfactant.

Coalescence and aggregation of the emulsion droplets were not observed over a period of 60 days.

Results obtained from experimental measurements show that drops all studied emulsions are well dispersed during the experiments. Emulsions are more stable and smaller in droplet size when they contained 30 wt % vegetable oil. In addition, the microscopic observations show no significant differences of this emulsion 1 day after preparation and after 60 days.

Experimental research on the relationship between zeta potential and emulsions stability proves efficacy of zeta potential in the analysis of emulsions stability. Also, zeta potential is an effective way to determine the vegetable oil based emulsions stability and that is correlated with droplet size.

More than that, the experimental results indicate that color measurement is a good complementary method to evaluate the stability of vegetable oil-in-water emulsions as bio-lubricants. Therefore, during the study, chromatic parameters for oil-in-water emulsions show that emulsion with 0.1 or 0.2 volumetric fractions is more sensitive, in terms of color development, than the 0.3 one. However, the vegetable oil based emulsions as eco-friendly lubricants have a good color stability.

To sum up, this study demonstrates that stable oil-in-water emulsions as potential lubricants can be prepared using a simple method that utilizes standard preparation procedures (homogenization and ultrasonication). On the other hand, color of the emulsions is a very important parameter during or after their use as lubricants.

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