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Stability studies of some food emulsions

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Abstract Emulsions, thermodynamically unstable mixtures, are dispersed systems in which one liquid is dispersed as droplets in a second immiscible phase. In most natural and processed foods, the immiscibility of water with lipids is overcomed by dispersing one phase as droplets into the other phase. The oil-in-water emulsions are highly stable. This is because some water-soluble surface-active agents and fine solid mineral particles are often adsorbed onto the oil droplets so that the emulsions are difficult to demulsify. In the present study we have determined some characteristics of oil-in-water emulsions obtained by three different types of oils: sun flower oil, olive oil and corn oil, and we have investigated the stabilization of these emulsions fortified with iron in the presence or in the absence of casein. The solubility, pH values, water and volatile content, free acidity, total fatty matter, iron content and redox potential were measured. It was observed that the increase of emulsions Fe(II) content was associated to the diminution of the system's redox potential.

Keywords: oil-in-water emulsions, iron, casein, stability

1. Introduction

An emulsion consists of two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase). There are two basic forms of emulsion. The first is the oil-in-water (O/W) emulsion in which oil droplets are dispersed and encapsulated within the water column. The second is the water-in-oil (W/O) emulsion in which droplets of water are dispersed and encapsulated within the oil.

Emulsions have found numerous applications in the food industry, cosmetics, medicine, paints, hydraulic fluids, asphalt, polymerization, printing, fiber production, metal and wood processing, etc.

In processed alimentary products, fat and oil often exist as emulsions. In addition to physical properties such as stability of emulsions, lipid oxidation is one of the major issues to be taken into account regarding food, influencing their flavour, odour, and colour [1].

Milk proteins have been widely used as emulsifiers in the food industry. Milk caseins are an example of such natural emulsifiers. Milk contains four different caseins: αs1-, αs2-, b- and k-casein. These proteins not only produce physically stable O/W emulsions, but they are also able to reduce the oxidation of the lipids from the emulsions [2-4].

As all vegetable oils, sunflower oil is composed by triglycerides (98-99%) and other substances representing the unsaponifiable fraction, which are also known as the "minor components" [5].

Corn oil is an effective component in lowering blood cholesterol levels. Corn oil is characterized by high levels of polyunsaturated fats instead of saturated fats, containing about 60% polyunsaturated, 25 to 30% monounsaturated and 10 to 15% saturated fats [6].

Olive oil has been held long time in high regard as a positive factor toward excellent health. The benefits of olive oil have been attributed to its high content of oleic acid which is a monounsaturated fatty acid, (C18:1). In addition, the high levels of natural antioxidants of the olive oil can also improve health. A minimally processed olive oil is composed of two main unsaturated fatty acids, C18:1 and C18:2, along with high levels of tocopherol and phenolic compounds [7].

Iron represents an essential micronutrient for human body. Being incorporated into complex systems like food is, iron confronts the oxidation and precipitation, which could decrease its bioavailability. It is well known that the presence of

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proteins increase iron bioavailability [8-10]. That is why food formulations containing iron and proteins are highly appreciated from a nutritional point of view. In this regard, iron incorporation in edible oil-in–water emulsions in the presence of milk proteins is considered as an objective to be reached.

The aim of the present study is to determine some properties of three types of food emulsions, and to investigate the stabilization with iron supplements of these emulsions, in the presence or in the absence of casein.

2. Experimental

Three types of food emulsions (sun flower oil, corn oil and olive oil) have been used. Certain properties of these emulsions have been determined, such as: pH value, water and volatile substances content, the total fatty mater content, iodine index, acidity index, saponification index and ester index.

2.1. The *pH* value has been determined using a multimeter CONSORT C535. The accuracy of pH determination was +/- 0.01pH.

2.2.Water and volatile substances content

1 g of sample was weighed in a weighing vial. The vial was previously brought to constant mass by heating in an oven at 105 ± 5°C. The vial containing the sample has been placed in an oven at 105±5°C and dried until the mass remained constant. The water content and volatile substances expressed as percentages were calculated using the formula:

Water and volatile substances content, %

$$= \frac{m_2 - m_1}{m} \cdot 100$$

where: m_2 represents the mass of the vial containing the sample before drying, g; m_1 - the mass of the vial containing the sample after drying, g; m – the mass of the sample, g.

2.3. Total fatty matter (TFM)

5 gram of sample has been weighted and transferred into a 250 mL beaker. 100 mL of hot distilled water and 40 mL of 0.5N HNO_3 have been added until the content became slightly acidic. The mixture has been heated in a water bath until fatty acids begun floating as a layer above the solution. Afterwards, the mixture has been suddenly cooled down using an ice water bath in order to solidify and separate the fatty acids. 50 mL of chloroform has been added to the remaining solution and transferred to a separating funnel. After shaking, the solution separated itself into two layers. The bottom layer has been drained. 50 mL of chloroform has been added to the remaining solution in the separating funnel. The fatty acid has been separated and the chloroform has been dissolved again as in the previously case and transferred to the collected fatty matter, weighed in a porcelain dish. The content has been evaporated and the residue has been weighed. From the difference in weight, the percentage of fatty matter in the analyzed samples was calculated using the relation:

$$\%\ of\ fatty\ mater = (B - A) \cdot 100 / m$$

where: A - weight of the porcelain dish; B – weight of the porcelain dish + sample after drying; m – the mass of the sample, g.

2.4. Iodine index

1 g of sample has been weighted and dissolved in 4 mL chloroform into a bottle with glass stopper. 5 mL of 0.1 N alcoholic solution of iodine has been added. The bottle has been held in darkness for 30 minutes, stirring occasionally. 3 mL of KI and 2 mL of water have been added. The solution has been titrated with 0.1 N sodium thiosulfate until it reached a light yellow color. 0.4 mL of starch has been added and titration continued, shaking vigorously until discoloration. A parallel blank determination has been performed. The iodine index value has been calculated using the formula:

$$I = \frac{(V_1 - V_2) \cdot 0{,}01269}{m} \cdot 100$$

where: I – iodine index; V_1 – volume of 0.1 N sodium thiosulfate used in the titration of the blank sample, ml; V_2 - volume of 0.1 N sodium thiosulfate used in the titration of the analysed sample, mL; m - mass of the sample, g; 0.01269 - the number of grams of iodine corresponding to 1 mL 0.1 N sodium thiosulfate.

2.5. Acidity index

5g of sample have been dissolved in 50 mL mixture consisting of equal volumes of ethilic alcohol and ether. The mixture was previously neutralised in the presence of phenolphthalein and after that titrated with KOH 0.1 N in water, until pink color. Acidity index has been calculated according to the formula:

$$I_A = 5,61 \cdot \frac{V}{m}$$

where: I_A – acidity index;
V - volume of 0.1 N KOH in water used in titration, mL; m – mass of sample, g; 5.61 - quantity of KOH, mg, corresponding to 1 mL 0.1 N KOH in water.

Saponification index: 0.5 g of sample has been weighted. The paraffin obtained from the determination of total fat, have been added and placed in a 250 mL conical flask fitted with condenser. 25 mL of benzene and 2.5 mL of potassium hydroxide solution (0.5N) have been added. The mixture was boiled for 2 hours in a water bath with reflux. Immediately after boiling, the solution has been titrated using HCl in the presence of phenolphthalein solution, without cooling. A parallel blank determination has been performed. Saponification index, expressed in milligrams of potassium hydroxide per gram of product, has been calculated using the formula:

$$I_S = \frac{28,055 \cdot (V_1 - V_2)}{m}$$

where: I_S – saponification index;
28.055 - the amount of potassium hydroxide, in mg, corresponding to 1 mL 0.5 N HCl; V_1 – volume of 0.5 N HCl used to titrate the control sample of reagent, ml; V_2 - volume of 0.5 N HCl used to titrate the sample, mL; m - mass of the sample, g.

Ester index has been calculated according to the formula:

$$I_E = I_S - I_A$$

where: I_E –esther index; I_S – saponification index; I_A – acidity index.

In order to investigate the stability of emulsions, oil in water emulsions have been prepared using three types of oils (sun flower oil, corn oil and olive oil), different quantities of ferrous sulfate (0.2; 0.6, and respectively 1 mg/100mL product) and casein solution 1%. In order to form the emulsion, the mixtures were mixed for 30 minutes.

The equilibrium of the Fe(II)/Fe(III) system has been reached by potentiometrical method. The following equilibrium has been installed in the system:

$$Fe^{3+} + \bar{e} \Leftrightarrow Fe^{2+}$$

Redox potential has been determined for these food emulsions fortified with different amounts of iron in the presence and absence of casein, at various time intervals: immediately after emulsion preparation and after 1, 2, 6, 12 and 24 hours. The measurements have been made using a multimeter instrument type CONSORT C535. The potential and the pH value were determined using a glass electrode. Before the electrode immersion, the solution was homogenised by stirring. The potential and the pH values of the solution have been read directly on the device display. After each reading, the electrode has been washed with distilled water.

3. Results and Discussions

The characteristics of food emulsions used in this study are presented in **Table 1.**

Table 1. The characteristics of food emulsions

Emulsion type/ Characteristic	Sunflower oil	Corn oil	Olive oil
pH value	5	5	5
Water and volatile substances %	4	7	2
Total fatty matter %	99.8	95.6	94.8
Iodine index	1.9	1.64	1.77
Saponification index	28.05	16.83	5.61
Acidity index	8.41	5.61	2.80
Ester index	19.64	11.22	2.81

It has been noticed that corn oil contains the largest amount of water and volatile substances compared to sunflower oil and olive oil. Sunflower oil has a total fat content higher than the others two (corn and olive oil), while the corn oil contains a higher amount of unsaturated fatty acids than the olive and sunflower oils. Olive oil contains fatty acids with higher molecular weight than those contained in sunflower oil and corn oil.

Redox potential variations versus time for emulsions represented by sunflower oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein are presented in **Fig. 1**.

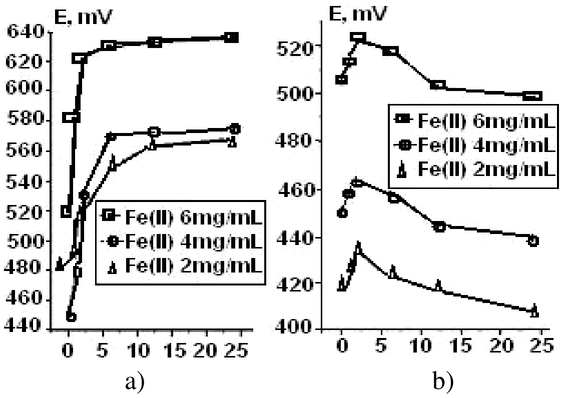

Fig.1. Redox potential variations versus time for emulsions with sunflower oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein.

Redox potential variations for emulsions with corn oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein are presented in **Fig. 2**.

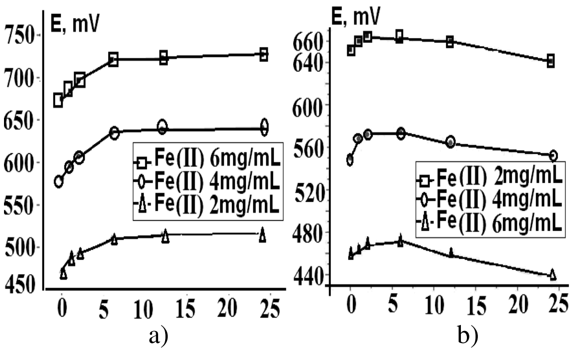

Fig.2. Redox potential variations versus time for emulsions with corn oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein.

Redox potential variations for emulsions with olive oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein are presented in **Fig. 3**.

Redox potential reflects the oxidation state of the system Fe^{2+}/Fe^{3+}, being important for the stability of the system studied. In the absence of casein, redox potential has increased by 50-100 mV for the first 5 hours, and after that, up to 24 hours changed slightly.

In the presence of casein, the potential has increased for the first 2 hours, and after significantly decreases, indicating the stabilization of low iron status, as a result of fixation of Fe (II) by casein.

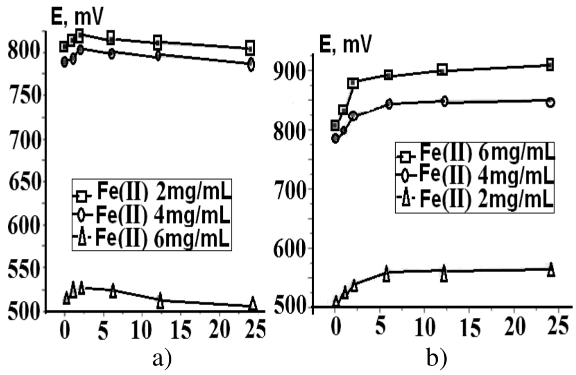

Fig.3. Redox potential variations versus time for emulsions with olive oil fortified with different amounts of iron sulphate in the presence (a) and absence (b) of casein.

Increasing iron concentration in emulsions with added casein minimises the redox potential of the system due to the fixation of iron ions by casein.

pH values obtained for emulsions fortified with different amounts of iron (II) in the absence and the presence of casein are presented in **Fig. 4** and **Fig. 5.**

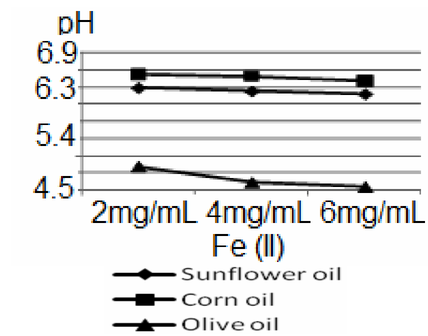

Fig.4. pH values obtained for emulsions fortified with different amounts of iron (II) in the absence of casein

Protein solubility depends on the pH of the solution. Proteins can be loaded with positive charge at low pH and negative charge, at high pH, by terminal $-NH_2$ or -COOH groups.

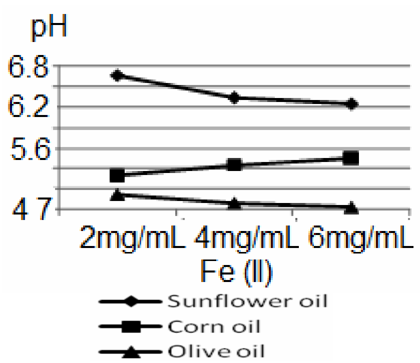

Fig.5. pH values obtained for emulsions fortified with different amounts of iron (II) in the presence of casein.

Isoelectric point is reached when the protein has the lowest solubility and hence the emulsion will be unstable. It can be noticed from figures 4 and 5 that in both cases, in the absence or in the presence of casein, only olive oil has a pH value near the isoelectric point of casein (4.6), which indicates that the emulsion based on olive oil is the most unstable.

However, the presence of casein induces an increased stability for the emulsion based on sunflower oil, compared to the other two emulsions.

4. Conclusions

Based on our research conducted on food oils and emulsions prepared with them, the following conclusions were formulated:

- corn oil contains the largest amount of water and volatile substances compared to sunflower oil and olive oil;
- sunflower oil has a total fat content higher than the other two oils (corn and olive oil);
- corn oil has a higher amount of unsaturated fatty acids than olive and sunflower oils;
- olive oil contains fatty acids with higher molecular weight than those contained in sunflower oil and corn oil;
- the addition of casein to the emulsions with an increased iron concentration, minimizes the redox potential of the system due to the fixation of iron ions by casein;
- in the absence and in the presence of casein, only olive oil has a pH value near the isoelectric point of casein (4.6), which indicates that the emulsion based on olive oil is the most unstable;
- the presence of casein induces an increased stability for the emulsion based on sunflower oil, compared to the other two studied emulsions.

This study provides new data regarding the quality of sunflower, corn and olive oils and contributes to the understanding of the role of casein and iron in the stability of food emulsions.

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