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THERMODYNAMIC AND KINETIC INVESTIGATION OF SUNFLOWER O/W EMULSIONS WITH ADDITION OF CITRAL

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Abstract: *Thermodynamic and kinetic investigations of emulsions prepared with high oleic sunflower oil and addition of 0.1%, 0.2% and 0.3% citral were provided. Thermodynamic parameters as Gibbs free energy, enthalpy and entropy were determined. It was found that emulsions with addition of 0.3% citral and 3% soybean protein isolates are more stable. Particle size in emulsions was determined by optical microscope. The pH values were measured in all emulsions. pH interval was between 5.8–6.1 and after analysis were seen that emulsions exhibited more stability at pH around 6.1. The dynamics of emulsions were investigated at 1 to 15 days as measured of turbidity. The emulsions prepared 0.3% citral and 3% soybean protein presented high turbidity and again determined as more stable.*
Keywords: *Emulsions, Protein stabilizer, Particle sizes, Citral, Thermodynamic, Kinetic.*

INTRODUCTION

Different oils were stabilized with soybean protein isolate (SI) and appears appropriate compound to prepare food emulsions (Krog, M. J., Riisom, T. H., & Larsson, K., 1983). Some foods using emulsions are milk, butter, margarine, soups, mayonnaise, cream liqueurs, sauces, desserts, cream, ice cream and etc. (Dickinson, E., & Stainsby, G., 1982, Dickinson, E., 1992). In foods water-soluble protein and oil phase presented the main phases that form the emulsions. It was established that the emulsions at lower oil concentration were less stable (Ly, M. H., Aguedo, M., Goudot, S., Le, M. L., Cayot, P., Teixeira, J. A., Le, T. M., Belin, J. M., & Wache, Y., 2008). The turbidity of emulsions was investigated (Mikkonen, K. S., Tenkanen, M., Cooke, P., Xu, C., Rita, H., Willfor, S., Holmbom, B., Hicks, K. B., & Yadav, M. P., 2009). They found that, the oil droplets of the emulsion moved upwards due to gravity, which led to the formation of a relatively clear serum layer at the bottom of the cuvette. The turbidity of the emulsion in the bottom part of the cuvette indicates the stability of emulsion. Oil-in-water emulsions prepared with commercial soy protein concentrate were investigated (Roesch, R. R., & Corredig, M., 2002). The protein formed a continuous network and emulsions were stable to creaming. Microstructural observations showed that phase separation occurred in emulsions prepared with high protein concentrations. Emulsions prepared with whey protein were presented (Gancz, K., Alexander, M., & Corredig, M., 2006). At higher concentrations in the range between 0.04 and 0.06% protein it is seen significant changes in the surface of the oil droplets. This changes are affected the droplet-droplet interactions.

Various essential oils are often included in food emulsions in order to increase the quality, which includes improving the aroma-taste complex, their antimicrobial and antioxidant properties and extending the shelf life (Bajpai, V.K. Baek, K.H., & Kang, S.C., 2012; Burt, S., 2004).

These properties of essential oils are due to the various aromatic substances they contain. Citral is an aromatic substance that is a main component of different essential oils and has the smell of lemon (Baser, K., & Buchbauer, G., 2010) and has pronounced biological activities (Huang, D.-H., Wang, C.-C., Yeh, C.-H., Tsai, J.-C., Huang, Y.-T., Li, P.-H., 2018; Samusenko, A., 2008; Shi, C., Zhao, X., Liu, Z., Meng, R., Chen, X., Guo, N., 2016).

In the literature data do not found information of emulsions stabilized with additions of Citral and the scope of this work is to investigate experimentally emulsion stability in O/W emulsions prepared with this addition.

EXPOSITION

Citral was provided by PQ Extra, BBA Aroma Chemicals, London, UK.

Soybean protein isolate (SI) was provided from local commercial network.

High oleic sunflower oil was provided from the commercial network of Plovdiv aria, in 2023.

Emulsions preparations

Eighteen emulsions were prepared with oil phase content of 20 and 30% sunflower oil with high oleic acid content, emulsifier 1, 2 and 3% soybeen protein (SI), aqueous phase – distilled water and citral additive. The phase ratio is presented in the Table 1 and the total amount of all emulsions is 100%. Emulsions 1-6 prepared with 0.1% citral, 7-12 with 0.2% citral and 13-18 with 0.3% citral.

Table 1. Caption Samples, 100% emulsion.

No.	Soybeen protein	Oil	Water
1	1	20	79
2	1	30	69
3	2	20	78
4	2	30	68
5	3	20	77
6	3	30	67
7	1	20	79
8	1	30	69
9	2	20	78
10	2	30	68
11	3	20	77
12	3	30	67
13	1	20	79
14	1	30	69
15	2	20	78
16	2	30	68
17	3	20	77
18	3	30	67

Physicochemical, thermodynamic and kinetic properties:

pH

The measured pH values were found between 5.8 and 6.1, which is in relation to their application in food. From the experiment conducted, the results show that emulsions with a pH (approximately 6.1) were associated with higher percentages of oil and with higher stability.

Microscopic observations

Microscopic observation of each emulsion was performed 10 min after its preparation in order to determine the size of the colloidal particles. In the optical micrographs, polydisperse emulsions with different particle sizes from small to large were observed. Their size is a major characteristic of the stability of emulsions. It was found that emulsions with a large particle size are more unstable, as this is related to stronger interactions between them and the occurrence of the coalescence process. As the percentage of oil in the emulsions increases, colloidal particles with smaller sizes are observed and they are associated with a large oil phase, according to a literature source (Kalaydzhiev, H., Gandova, V. D., Ivanova, P., Brandão, T. R., Dessev, T. T., Silva, C. L. M., & Chalova, V. I., 2019). Smaller particles define emulsions as more stable.

Emulsion 1 prepared with 1% soy protein, 20% oil phase and 0.1% citral additive was presented (Fig. 1). The observed colloidal particles were of different sizes. The largest were about

30 μm and reach about 5-6 μm. Emulsions 16 and 18 prepared with 2% and 3% soy protein, 30% oil phase and 0.3% citral additive, respectively were seen (Figs. 2 and 3). The observed colloidal particles for emulsion 16 have unit sizes of about 15 μm and major colloidal particles with sizes between 2-12 μm. For emulsion 18, the colloidal particles observed were with size between 2-8 μm.

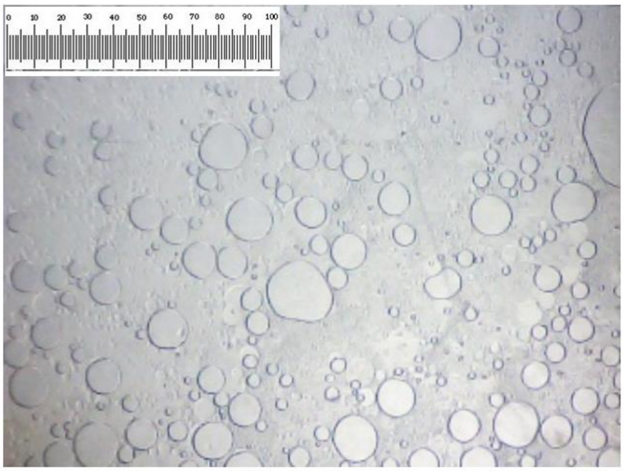

Fig. 1. Microscopic observation of emulsion 1.

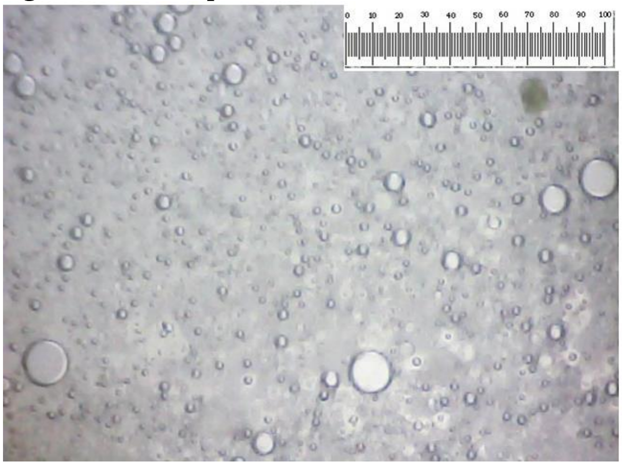

Fig. 2. Microscopic observation of emulsion 16.

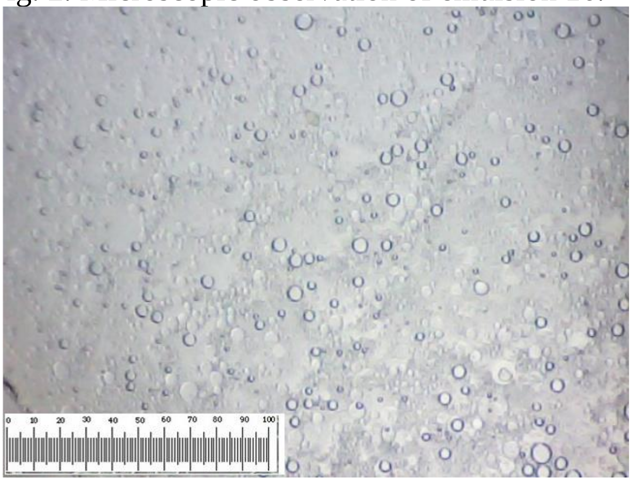

Fig. 3. Microscopic observation of emulsion 18.

The relationship between the oil phase, the water phase and the average size of the colloidal particles is presented (Fig. 4). The largest particle radius for low oil, high water emulsions is about 27.34 to 30 μm. As the oil phase increases, the average colloidal particle size decreases to about 8.7 μm.

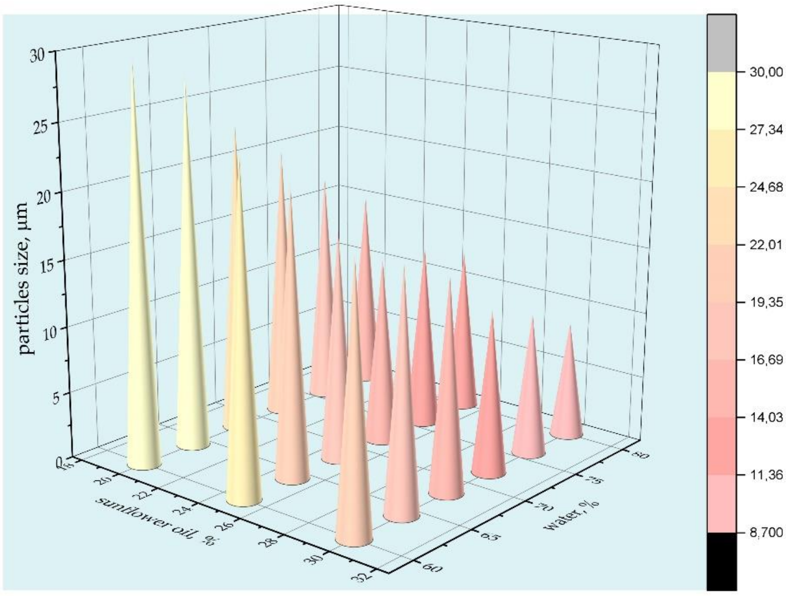

Fig. 4. Dependence between amount of oil phase, water phase and particles size of emulsions.

Thermodynamic properties

The thermodynamic parameters Gibbs free energy, enthalpy and entropy were calculated for all emulsions. They are indicators of the stability of a system and are related to the thermal effect and establishment of equilibrium in it.

Table 2. Linear equations of absorption dependence on concentration of emulsions 1-18 prepared with sunflower oil with high oleic acid content and addition of citral.

№	equations
$y = a + b * x$	
1	$y = 0.308+ 0.749*x$, $R^2 = 0.994$
2	$y = 0.558+ 0.566*x$, $R^2 = 0.991$
3	$y = 0.314+ 0.582*x$, $R^2 = 0.992$
4	$y = 0.291+ 0.665*x$, $R^2 = 0.998$
5	$y = 0.388+ 0.697*x$, $R^2 = 0.993$
6	$y = 0.412+ 0.586*x$, $R^2 = 0.989$
7	$y = -0.002+ 0.960*x$, $R^2 = 0.980$
8	$y = -0.073+ 1.349*x$, $R^2 = 0.998$
9	$y = 0.039+ 1.052*x$, $R^2 = 0.993$
10	$y = -0.007+ 1.259*x$, $R^2 = 0.995$
11	$y = 0.108+ 0.996*x$, $R^2 = 0.999$
12	$y = 0.162+ 0.822*x$, $R^2 = 0.998$
13	$y = 0.266+ 0.907*x$, $R^2 = 0.988$
14	$y = 0.156+ 1.133*x$, $R^2 = 0.999$
15	$y = 0.039+ 0.925*x$, $R^2 = 0.997$
16	$y = 0.348+ 0.815*x$, $R^2 = 0.998$
17	$y = 0.132+ 1.154*x$, $R^2 = 0.992$
18	$y = 0.268+ 0.887*x$, $R^2 = 0.981$

The equilibrium constant of the dispersion process of separation of the two phases was calculated. Positive values of this parameter are observed in all emulsions. To determine the values of this constant, a linear regression model of the dependence of absorption on the concentration of a series of solutions prepared by the dilution method was used for all emulsions (Kendrow, C., Baum, J. C., & Marzzacco, C. J., 2009). The obtained equations are presented in Table 2. High correlation coefficients (R^2 = 0.981 to 0.999) indicate a good correlation of the values obtained as a result of an experiment.

A proportional relationship between the equilibrium constant and Gibbs energy is observed. The larger equilibrium constant, which grows in positive values and the smaller Gibbs energy, which grows in negative values and this is an indication of a more stable colloidal system. The relationship between the equilibrium constant and the Gibbs energy is presented (Fig. 5). It shows that emulsions with an equilibrium constant of 6.4 to about 6.9 have the lowest Gibbs energy values, which defines them as the most stable.

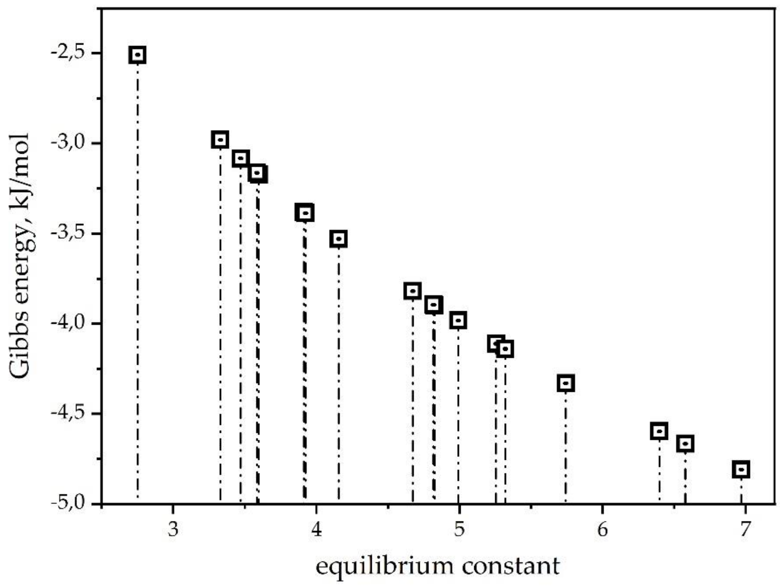

Fig. 5. Dependence between equilibrium constant and Gibbs energy of emulsions 1 - 18.

Gibbs free energy can be used as a criterion for emulsion stability. Strong negative values were observed in emulsions 5, 6, 11, 12, 17 and 18. The highest value was in emulsion 18, equal to -4.809 kJ/mol, followed by emulsions 6 and 17, which showed values of Gibbs free energy -4.597 kJ/mol and -4.597 kJ/mol, respectively. These results were related to the fact that these emulsions were prepared with a higher amount of oil and soy protein and emulsion 18 had the highest amount of citral at 0.3%.

It was established during the conducted research that the Gibbs energy is affected by the change of the oil and water phases. Emulsions prepared with a larger oil phase are more stable and have lower Gibbs energy values. The relationship between Gibbs energy, the oil and water phases is presented (Fig. 6).

Besides the Gibbs energy, the values of the other two thermodynamic parameters enthalpy and entropy were also calculated. Negative enthalpy and small negative entropy values are observed. At negative enthalpy, the process is defined as exothermic. Entropy is related to the rapid phase separation of emulsions and this leads to difficulties in determining the direction of the process.

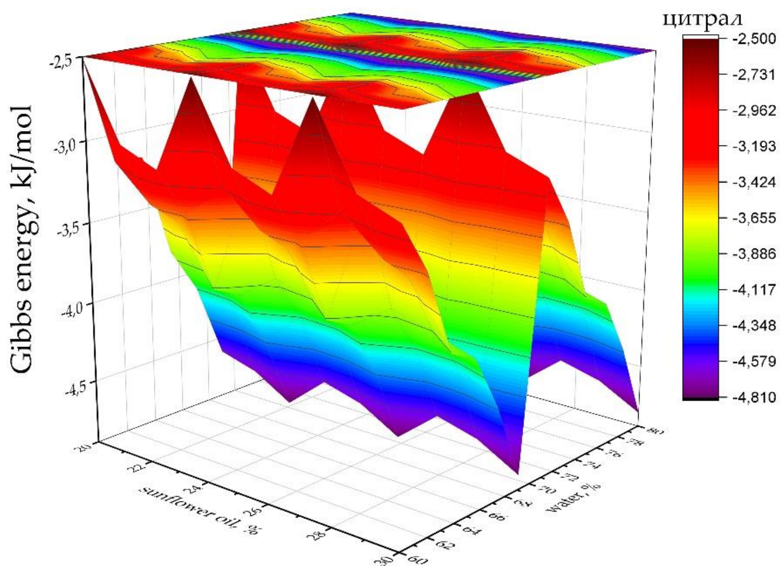

Fig. 6. Dependence between Gibbs energy, oil and water phases of emulsions.

In Table 3 the values of all thermodynamic parameters of the investigated emulsions are presented.

Table 3. Thermodynamic parameters Gibbs energy, enthalpy and entropy

No. of emulsions	Gibbs energy, kJ/mol	Enthalpy, kJ/mol	Entropy, kJ/(mol.K)
1	-2.508 ± 0.008	-18.432 ± 0.104	-0.053 ± 0.003
2	-3.163 ± 0.016	-18.716 ± 0.117	-0.052 ± 0.001
3	-3.172 ± 0.011	-18.721 ± 0.122	-0.052 ± 0.001
4	-3.819 ± 0.009	-19.005 ± 0.095	-0.051 ± 0.005
5	-4.117 ± 0.011	-19.128 ± 0.111	-0.050 ± 0.002
6	-4.597 ± 0.014	-19.339 ± 0.093	-0.049 ± 0.007
7	-2.979 ± 0.009	-18.637 ± 0.107	-0.052 ± 0.004
8	-3.378 ± 0.007	-18.814 ± 0.117	-0.052 ± 0.001
9	-3.529 ± 0.012	-18.876 ± 0.126	-0.051 ± 0.001
10	-3.895 ± 0.015	-19.034 ± 0.084	-0.051 ± 0.005
11	-4.141 ± 0.011	-19.141 ± 0.121	-0.050 ± 0.003
12	-4.666 ± 0.016	-19.369 ± 0.113	-0.049 ± 0.008
13	-3.083 ± 0.012	-18.682 ± 0.092	-0.052 ± 0.002
14	-3.386 ± 0.013	-18.814 ± 0.114	-0.052 ± 0.005
15	-3.899 ± 0.008	-19.036 ± 0.106	-0.051 ± 0.001
16	-3.983 ± 0.011	-19.073 ± 0.117	-0.051 ± 0.002
17	-4.332 ± 0.013	-19.224 ± 0.112	-0.049 ± 0.004
18	-4.809 ± 0.018	-19.431 ± 0.104	-0.049 ± 0.001

Kinetic properties

The dynamics of emulsions were followed for 15 days to determine their turbidity. Spectrophotometric measurements of the aqueous phase of each emulsion were performed during the storage period.

When conducting the experiment, high turbidity was observed in emulsions prepared with 30% of oil. High turbidity is associated with a large amount of oil phase, which is evidence of stability of the respective emulsion.

In the studies carried out, turbidity varied on different days of the storage period, but in general it decreased.

The turbiditie of emulsions 1-6 are presented are presented (Fig. 7). They showed a tendency for high turbidity during the first to fifth day of storage. For emulsions 1 and 3 a sharp drop in turbidity was observed on the sixth day and it reached 6. In emulsion 5, just opposite on the sixth day the turbidity rises to 9. The highest turbidity remained for emulsion 6, which was prepared with 30% oil, 3% soy protein and 0.1% citral.

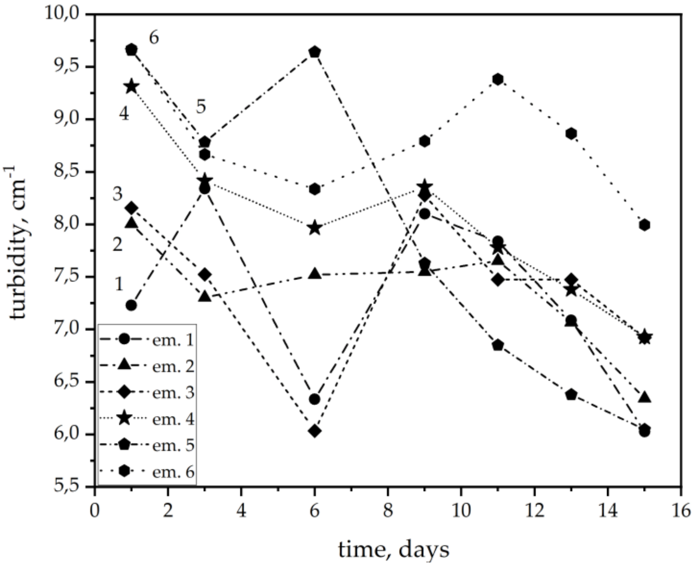

Fig. 7. Relationship between storage time and turbidity of emulsions 1-6.

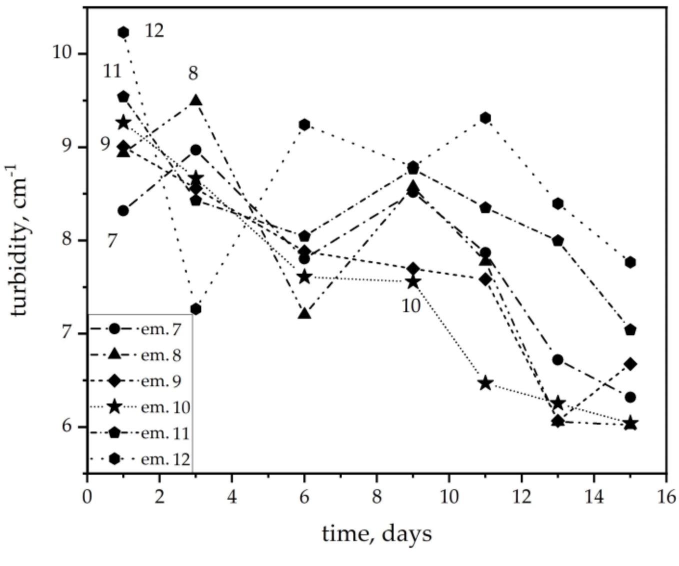

Fig. 8. Relationship between storage time and turbidity of emulsions 7-12.

The turbidities of emulsions 7-12 are presented (Fig. 8). In them, the tendency for high turbidity at the beginning of the studied period is observed. On the eighth day, the turbidity started to decrease, remaining higher only for emulsions 11 and 12. In emulsion 11, it reaches about 7.5 in eleven day and in emulsion 12 to about 9.2.

Graphical presentation of turbidities of emulsions 13-18 was seen (Fig. 9). During their storage, emulsion 18 shows the highest turbidity, which is preserved over time and at eleven day it is about 9.5. For the other emulsions, the turbidities decrease proportionally with time.

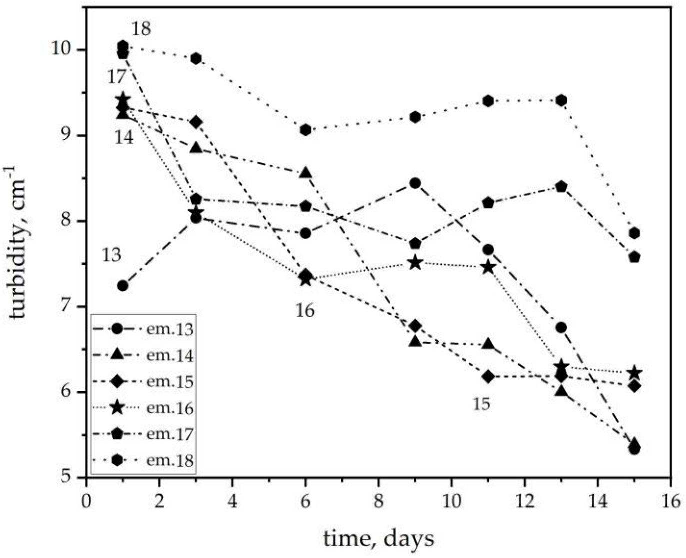

Fig. 9. Relationship between storage time and turbidity of emulsions 13-18.

CONCLUSION

The interactions between soybean protein isolate and other components were studied to understand the stability of food emulsions with addition of 0.1, 0.2 and 0.3% citral. The emulsion stability was determined by optical microscope, measured of turbidity of emulsions and by determined the thermodynamic parameters. Finally, the all results show that the emulsions prepared with high oil %, 3% soybean protein isolate and 0.3% citral exhibit increase of emulsion stability.

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