

UDC 544.72.05

MANK V.V., POLONSKA T. A.
National University of Food Technologies

SYNERGISTIC EFFECTS RESEARCH IN THE SYSTEM OF COMPLEX EMULSIFIER

Purpose. Justification of complex emulsifier from the standpoint of physical and chemical properties of stabilized system.

Methodology. The surface tension was determined by stalagmometric method at the interface of liquid-liquid and parameter calculation of adsorption layers were determined by methods of Gibbs and Langmuir.

Findings. It was studied the behavior of molecules mono- and diesters of oleic acid and mono- and diesters of stearic acid in a mixture of polyethylene glycol 400 at phase interface of oil-water in the production of cosmetic emulsions. The use of 0,5% by weight. high-dispersive powder of glauconite, which concentrates at interfaces with formation of a strong spatial coagulation structure for stability of dispersed system.

Originality. It was proved the increasing of stabilization properties of surfactants mixture via intermolecular interactions at interface with the formation of dense packing of molecules.

Practical value. It was established the lower limit of complex emulsifier concentration to reduce the cost of cosmetic products.

Keywords: cosmetic emulsion, glauconite, emulsifier, PEG-400 Stearate, PEG-400 Oleate.

Introduction. Important component of cosmetic emulsions are emulsifiers - compounds that provide a stable of emulsion. A wide range of surfactants for creating the emulsion system leads to finding emulsifiers with several benefits and additional features: moisturizing, reparative, protective, compensatory, and other nutrients.

In domestic cosmetic production there are the most popular of mono- and diglycerides of fatty acids (E471), glycerol esters, fatty and organic acids (E 472), lecithin, phosphatides (E 322), ammonium salts phosphatidic acid (E 442), polysorbate, Tween (E 432 ... E 436), sorbitan esters, Spenn (E 491... E 496), ethers together esterified polyglycerol and ricin acid (E 473), sodium stearoillaktaty (E 481), potassium stearoillaktaty (E 482). The main requirement for emulsifier is the ability to emulsify a wide range of emollients to facilitate the selection of other prescription ingredients in developing cosmetics.

There are a number of surface-active agents (surfactants) different classes of approximately equal emulsifying ability. However, while their choosing physical and chemical properties of the whole system and the scope of the emulsion should be taken into account. Thus, in the acidic medium cationic emulsifiers are used, and anionic emulsifiers are in alkaline medium. If the polar phase has a significant amount of salt, it is preferable to use nonionic emulsifiers as in pH oscillations [1]. The main criteria for the selection of emulsifiers for cosmetic emulsions model include purity and properties of individual compounds, as well as their availability and the use of a real cosmetic products.

Setting objectives. We have checked stabilization feature of the mixture of PEG-400 stearate (according to TU 22942814.007-2000) with PEG-400 oleate (according to TU 942814.006-2000 22) that are compatible with many kinds of cosmetic raw materials, stearin, spermaceti/spermaceti oil, waxes and others. Despite the fact that these surfactants are compounds that are produced on an industrial scale, their colloid-chemical characteristics are absent in literature. Knowledge of these characteristics is necessary for evidence-based approach when developing recipes based on them, as

appropriate turns their experimental determination. We have investigated the possibility of minimizing the emulsifier content in the composition of the emulsion by introducing a system of high glauconite powder. Glauconite (Eng. Glauconite) is natural disperse clay mineral structure of layered aluminosilicate radial circuits [2, 3]. The purpose of the research is studying of complex emulsifier, setting the lower limit of concentration for reducing the cost of finished cosmetic products.

Research results. It's known that for stabilizing emulsions we can use a mixture of surfactants. Typically, the ability to adjust the properties of emulsions, in particular, increase their resistance in this case is much wider compared with individual surfactants. This is inter-molecularly (associate) the interaction of surfactants on the interfacial boundaries to form a denser and more orderly packing of molecules on the surface [4]. The most effective stabilizers are blended mixture of ionic and non-ionic surfactants, often-used mixtures of anionic and nonionic surfactants [5].

Additives manufacturers in supporting documentation declare the sharp increase in the stability of emulsions joint application stearate and PEG-400 oleate, but did not cite any quantitative guidance. We built mathematical dependence compatible emulsifiers influence in the process of obtaining an emulsion. Experimental samples emulsions prepared using the following technologies: pre-weighed vegetable oil, emulsifier and water heated in a water bath to the temperature 80-90°C. To the fat phase water was added at a ratio of fat and water phase and 30:70 emulsified using laboratory homogenizer (1500 rev/min.) until smooth. Determination of the colloidal stability of the samples was performed after 24 hours after complete cooling and structuring system. As the variable factors were taken: the content of PEG-400 stearate x_1 content oleate PEG-400 x_2 . Response function y_1 chosen colloidal stability of the emulsion.

Table 1.

Plan of experiment

| № | X_0 | Content of PEG-400 stearate, x_1 | | Content oleate PEG-400, x_2 | | Stability of emulsion, y_1 |
|---|-------|------------------------------------|---------|-------------------------------|---------|------------------------------|
| | | conditions | g/100 g | conditions | g/100 g | % |
| 1 | +1 | +1 | 1,5 | +1 | 0,75 | 100 |
| 2 | +1 | -1 | 1,0 | +1 | 0,75 | 42 |
| 3 | +1 | +1 | 1,5 | -1 | 0,25 | 38 |
| 4 | +1 | -1 | 1,0 | -1 | 0,25 | 66 |

The main level for factor x_1 is 1,0g/100 g, the range of variation of 0,5; basic level for factor x_1 , 5 g/100 g range of variation of 0,25. The resulting dimensionless regression equation takes the form:

$$Y_1 = 84,27 - 16,03x_1 + 4,23x_2 - 3,54x_2x_3$$

Checking the criterion of Fisher at significance level $\alpha = 0,05$ showed that the resulting equation is adequate experiment. Fig. 1 shows one of the surfaces obtained depending colloidal stability of emulsion from the joint presence of emulsifiers.

We can conclude the feasibility of using PEG-400 stearate as emulsifier systems for oil / water together with PEG-400 oleate in an amount of 1.5% at a ratio of 2:1 to 3: 1. Thus, the combined use of stearate and PEG-400 oleate together can reduce the emulsifier content of 3% to 1.5% to give satisfactory emulsion stability. Revealed that a further increase in the content of

surfactants in the composition of the emulsion does not result in significant improvement emulsifying, action shows no significant effect on the behavior of the system. Therefore, it is disadvantageous from an economic point of view.

The phenomenon of synergy that occurs in mixtures of surfactants, taken in the ratio of 2: 1 to 3: 1, can be explained partly anionic character PEG-400 stearate, interacting with the nonionic PEG-400 oleate. The observed synergistic effects demonstrated by studies [6], which found that the mixture ionogenic of surfactants (sodium alkyl benzene sulphonate) and nonionic of surfactants (proksanol-228) more surface-active than each of the studied surfactants. Also in [7] that the introduction of ancillary of surfactants accompanied by an increase adsorption of primary of surfactants and decrease interfacial tension.

In the study published works about stabilizing emulsions there was found an opportunity to improve the structure of the emulsion cosmetic product through the use of fine powders of minerals. The first publications explaining the mechanism of action of stabilizing powders appeared about 15 years ago, mainly foreign sources [8-18]. The mechanism of stabilizing powders action due to the formation of high structural and mechanical barrier resulting adhesive interactions powder to the surface of the emulsion dispersed phase. Powder particles concentrated at the interface boundaries and form a very solid coagulation spatial structure that stabilizes the dispersed system. Powders of hydrophilic surface (clay, silica) direct stabilize emulsions; hydrophobic powders (soot, water repelling agent Aeros, cellulose) are able to stabilize inverse emulsions [19-20]. To stabilize cosmetic emulsions used bentonite in an amount of 1...2% [21].

In this respect, the use of glauconite powder of high interest to change the surface tension at the interface of emulsion, which determines the structure of the emulsion cosmetic product. Clay minerals glauconite has the unique properties compared with other clay minerals:

- 1) dispersed particles are spherical shape of glauconite and virtually no swell in aqueous solutions;
- 2) the active exchange of potassium cations;
- 3) high physical and chemical activity that characterized the exchange and adsorption capacity;
- 4) the ability of unauthorized isothermal restore the structure in time, that is manifestation of self-organization;
- 5) the ability to regenerate [2, 22].

The research was conducted on the verge of an oil-water adsorption because it is on this verge plays a major role in stabilizing the fat globules in emulsion systems. For the experiment, prepare a series of solutions with different concentration of the surfactants in sunflower oil. Used a mixture of PEG-400 stearate of PEG-400 oleate in the ratio of 2:1 and 3: 1. Fig. 1 shows the interfacial tension isotherms emulsifier mixture containing powder glauconite from 0,1 to 3,0%.

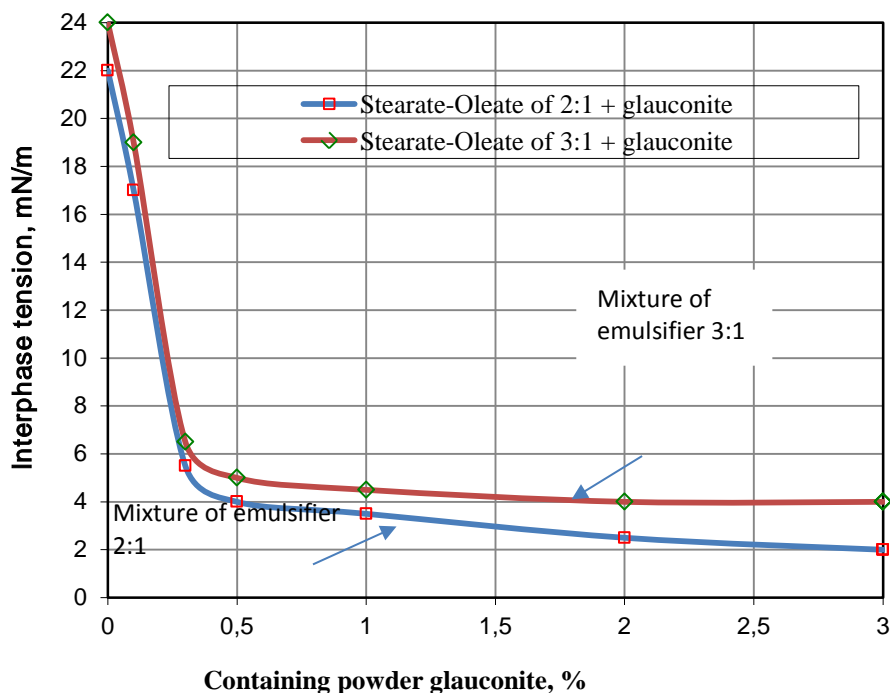


Fig. 1. Isotherms of surface tension emulsifier blends with glauconite powder at the interface of liquid-liquid

Figure 1 presents the surface tension isotherm for a mixture of stearate and PEG-400 oleate in the ratio of 2:1 and 3:1, with the addition of fine powder glauconite introduced in an amount of 0.1, 0.3, 0.5, 1.0, 2.0, 3.0. As shown in the figure, the introduction of glauconite in an amount of 0.1 to 0.5% effectively reduces the surface tension of both the ratio of 2:1, and to 3:1. However, a mixture of emulsifiers 2:1 is more effective compared with a ratio of 3:1, which can be seen on location isotherms in the figure. Moreover, the introduction of 0.5% of glauconite in most environments emulsion reduces surface tension, showing a great surface activity, due to its better adsorption at liquid-liquid boundaries. Glauconite additives Efficiency 1,0, 2,0 and 3,0% lower compared to that probably explains a powder on the surface of emulsion droplets so that most of the surface is a dispersion medium. To ensure the stability of the emulsion should be dense surface coverage drops powder. Obviously, if the degree of wetting powder stabilizer medium and dispersed phase varies greatly, the entire powder volume will be in the phase that wets it well and will not stabilize [23, 24]. This is probably observed in excess of the optimal concentration of powder more than 0,5%.

Mathematical treatment received isotherms of surface tension makes it possible to apply the fundamental equation of Gibbs and build Gibbs isotherm adsorption. To calculate the parameters of the initial adsorption layer treated area isotherms (for concentrations of 0,5 g/100 g), as the processing isotherms after entering the plateau (after reaching the critical micelle concentration) is not correct. The study of these characteristics is important for selection of the most effective stabilizer that can emulsify system with a defined content of fat phase and get songs from a certain distribution of drops in size, which in turn will determine a number of consumer characteristics, among them easy distribution in the skin, absorption, etc.

The relationship between adsorption Γ , kmol/m^2 surface tension σ , N/m , and the concentration of dissolved substances adsorbed C , kmol/m^3 expressed by the equation Gibbs adsorption isotherm:

$$\Gamma = - \left(\frac{c}{RT} \right) \frac{d\sigma}{dc}$$

The knowledge of the adsorption maximum values (Fig. 3) allows determining the thickness of the adsorbed layer (δ) interfaces on the verge of an oil-water:

$$\delta = \frac{\Gamma_{\infty} \cdot M}{\rho},$$

M – molar mass of surfactants, kg/mol ,

ρ – density surfactants, kg/m^3 ,

Γ_{∞} – limiting the concentration of the substance adsorbed per 1 m^2 of the interface, the maximum adsorption, mol/m^2 .

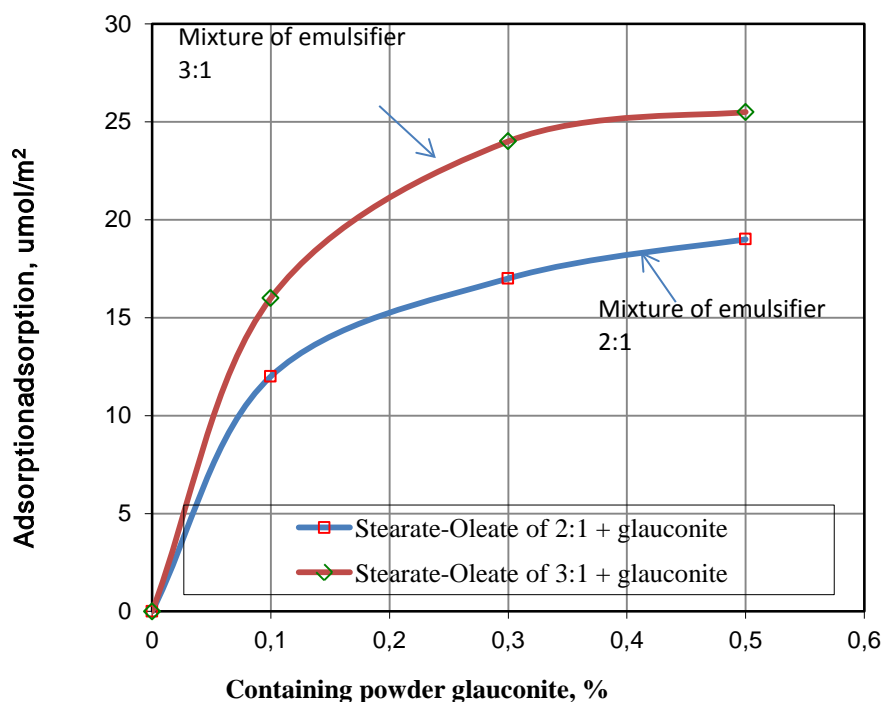


Fig. 2. The surface tension isotherm in coordinates Gibbs

Since the accumulation of surfactants in the interface is only possible to a certain value, the value of adsorption Γ_{∞} calculated from Langmuir equation:

$$\Gamma = \Gamma_{\infty} \frac{bC}{1+bC},$$

b – adsorption equilibrium constant, equal to the rate constants of processes of adsorption and desorption, $B = \frac{1}{\Gamma_{\infty} \cdot K}$.

Langmuir adsorption isotherm lead to the appearance of the line:

$$\frac{C}{\Gamma} = \frac{1}{\Gamma_{\infty} \cdot b} + \frac{1}{\Gamma_{\infty}} \cdot C.$$

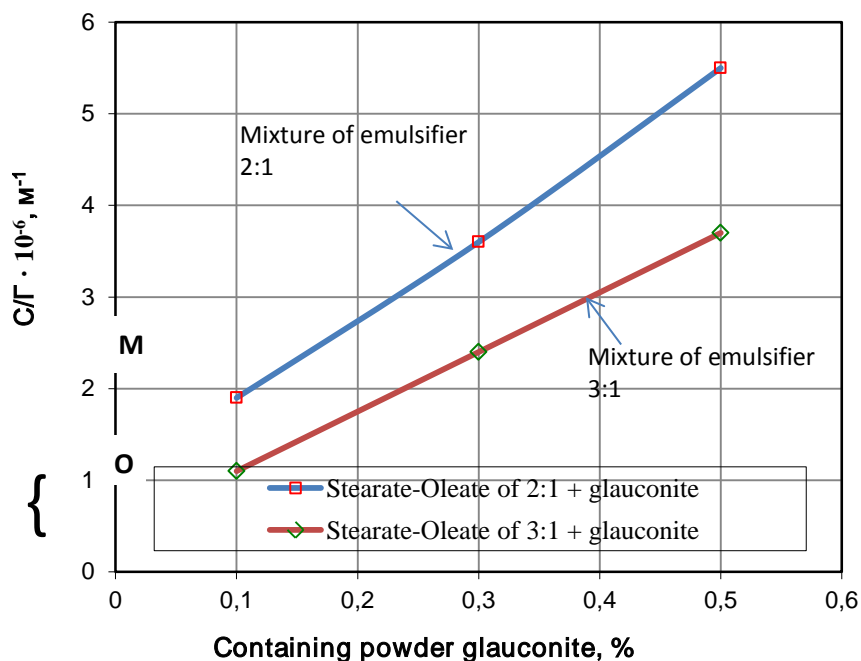


Fig. 3. Adsorption isotherm in coordinates Langmuir

The value of monolayer adsorption Γ_{∞} finds a cotangent ratio adjacent cathetus to the opposite cathetus: $tg \alpha = \frac{1}{\Gamma_{\infty}} \circ ctg \alpha = \Gamma_{\infty} r$.

The constant adsorption of equilibrium is due to the length of the segment OM on the chart:

$$b = \frac{1}{\Gamma_{\infty}} \cdot OM$$

For more information on colloidal chemical behavior of surfactant mixture at the interface oil-water boundaries can give constant $K = 1/C$. This constant, as constant adsorption equilibrium can indirectly characterize molecular interactions in mixed adsorption layers.

The parameters for each adsorption layers of surfactant mixtures with different content of glauconite are summarized in Table 2.

Table 2

The values of adsorption layers of powder mixtures emulsifier glauconite on the verge of liquid-liquid phase

| Emulsifiers, powder of high content of glauconite, % | Interphase tension, σ , mN/m | Constant of adsorption equilibrium b | Limiting adsorption, Γ_{∞} , $\mu\text{mol}/\text{m}^2$ | Thickness of adsorbed layer, δ , Nm |
|------------------------------------------------------|-------------------------------------|--------------------------------------|---------------------------------------------------------------------|--------------------------------------------|
| Stearate-oleate 2:1, | | | 4,5 | 9,5 |
| 0,1 | 17,0 | 28 | | |
| 0,3 | 5,5 | 124 | | |
| 0,5 | 4,0 | 344 | | |
| Stearate-oleate 3:1, | | | 2,0 | 5,4 |
| 0,1 | 19,0 | 12 | | |
| 0,3 | 6,5 | 89 | | |
| 0,5 | 5,0 | 218 | | |

Analysis of the data presented in the table shows that a mixture of stearate oleate in the ratio 2:1 tightly adsorbed on the verge of an oil-water because the value of its marginal adsorption higher

(4,5 vs. 2,0 $\mu\text{mol}/\text{m}^2$). The thickness of the adsorbed layer of both compounds is high enough, probably due to the formation of glauconite additional structures. Adsorption layers of surfactant in the ratio of 3:1 over dilution, since the thickness of the adsorbed layer less than in surfactants in the ratio 2:1. Increase of stearate in a mixture of emulsifiers weakens the interaction and interfacial layer thickness is reduced from 9,5 to 5,4 Nm. Comparing the adsorption equilibrium constants shows that it corresponds to the maximum content of glauconite powder 0,5% in the mixture of emulsifiers, taken in the ratio 2:1.

Conclusions. Thus, to stabilize the emulsion cosmetic emulsifier selected following composition: a mixture of stearate and PEG-400 oleate in the ratio 2:2 with a highly dispersed powder of glauconite 0.5%. The composition of complex emulsifier allows not only provide 100% emulsion stability, but also its long life without the use of additional stabilizers.

References

1. Laplante, Serge. Effect of pH, ionic strength, and composition on emulsion stabilizing properties of chitosan in a model system containing whey protein isolate / Serge Laplante, Sylvie L. Turgeon, Paul Paquin // *Food Hydrocolloids*. – 2005. - №19. – P. 721–729.
2. Kotelnikov D.D. Clay minerals of sedimentary rocks / D.D. Kotelnikov, A.I. Konyukhov. – Moscow: Nedra, 1986. – 247 p.
3. Kukovsky E.G. Features of the structure and physicochemical properties of clay minerals / E.G.Kukovsky – K. : Naukova Dumka, 1966. – 128 p.
4. Soboleva O.A. Mixed micelle and sorption yersandn on ionic surfactant with cationic (monomericanddimeric) / O. A. Sobolev, M. V. Krivobokova // *Vestnik Mosk. Univ.* – 2004 – “Chemistry” Series 2. – T. 45. – № 5. – P. 344–349.
5. Ariyaprakai, Suwimon. Solubilization in monodisperse emulsions / Suwimon Ariyaprakai, Stephanie R. Dungan // *Journal of Colloidand Interface Science*. – 2007. – № 314. – P. 673–682.
6. Peregudova L.I. Colloid-chemical propertiesofthemixtureofsurfactants / L.I.Peregudova, N.B.Uriev // *ColloidJournal*. – 1984. – T. 46. – №6. – P. 1166 – 1171.
7. Mukhtarov S.E. Dispersion and aggregate stability of cosmetic emulsions stabilized with stearate soaps. Diss. Candidate Chem. Sciences. M., 2003. – 153 p.
8. Binks B.P. Particlesas Surfactants – Similarities and Differences / B.P. Binks // *Colloid Interface Sci.* – 2002. –№ 7. – P. 21–41.
9. Aveyard R. Emulsions stabilised solely by colloidal particles / R. Aveyard, B.P. Binks, J.H. Clint // *Colloid Interface Sci.* – 2003. – № 100. – P. 503–546.
10. Murray B.S. Foam stability: proteins and nanoparticles / B.S. Murray, R. Ettelaie // *Colloid Interface Sci.* – 2002. – № 9. – P. 314–320.
11. Binks B.P. pH-responsive aqueous foams stabilized by ionizable latex particles / B.P. Binks, R. Murakami, S.P. Armes and all. // *Langmuir*. – 2007. – № 23. – P. 8691–8694.
12. Binks B.P. Double inversion of emulsions by using nanoparticles and di-chain surfactant / B.P. Binks, J. Rodrigues // *A. Angew. Chem., Int. Ed.* – 2007 – № 46. – P. 5389–5392.
- 13 Melle S. Pickering emulsions with controllable stability / S. Melle, M. Lask, G.G. Fuller // *Langmuir*. – 2005. – № 21. – P. 2158–2162.
14. Xu H. Shape and buckling transitions in solid-stabilized drops / H. Xu, S. Melle, K. Golemanov, G.G. Fuller // *Langmuir*. – 2005. – № 21. – P. 10016–10020.
15. Subramaniam A. B. Microstructure, morphology and lifetime of armored bubbles exposed to surfactants / A.B. Subramaniam, C. Mejean, M.bkarian, H.A. Stone // *Langmuir*. – 2006. – № 22. – P. 5986–5990.

16. Subramaniam A. B. Controlled assembly of jammed colloidal shells on fluid droplets / A.B. Subramaniam, M. Abkarian, H. Stone // *Nat. Mater.* – 2005 – № 4. – P. 553–556.
17. Studart A. R. Materials from foams and emulsions stabilized by colloidal particles / A.R. Studart, U.T. Gonzenbach, I. Akartuna and all. // *J. Mater. Chem.* – 2007. – № 17. – P. 3283–3289.
18. Hunter T. N. The role of particles in stabilizing foams and emulsions / T.N. Hunter, R.J. Pugh, G.V. Franks, G. J. Jameson // *Advances in Colloid and Interface Science.* – 2008. – № 137. – P. 57–81.
19. Wege, Hartmut A. Long-Term Stabilization of Foams and Emulsions with In-Situ Formed Microparticles from Hydrophobic Cellulose / Hartmut A. Wege, Sejong Kim, Vesselin N. Paunov and all. // *Langmuir.* – 2008. – № 24 (17). – P. 9245–9253.
20. Wenbin Sun. Oil-in-water emulsions stabilized by hydrophobically modified hydroxyethyl cellulose: Adsorption and thickening effect / Wenbin Sun, Dejun Sun, Yunping Wei and all // *Journal of Colloid and Interface Science.* – 2007. – № 311. – P. 228–236.
21. A. Margolina. *Newcosmetology. Volume 1* / A. Margolina, E. Hernandez. – М.: “Firm Clavel”, 2005. – 424 p.
22. Osipov V.I. Microstructure of argillaceous rocks / V.I. Osipov, V.N. Sokolov, N.A. Romyantsev. – М.: Nedra, 1989. – 211 p.
23. Bulavchenko A.I. Surface for cesand boundary layers of liquids / A.I. Bulavchenko, P.M. Kruglyakov, V.P. Belosudov – М.: Nauka, 1983. – 229 p.
24. Great Encyclopedia of oil and gas. Portal of scientific and technical information “Electronic Library” Oil and Gas” [Electronic resource]. – Access: <http://www.ngpedia.ru/id474619p1.html>. – Name from the screen.

ИССЛЕДОВАНИЕ СИНЕРГЕТИЧЕСКИХ ЭФФЕКТОВ В СИСТЕМЕ КОМПЛЕКСНОГО ЭМУЛЬГАТОРА

МАНК В.В., ПОЛОНСЬКА Т.А.

Национальный университет пищевых технологий

Цель. Обоснование состава комплексного эмульгатора с позиции физико-химических свойств стабилизированной системы.

Методика. Поверхностное натяжение на границе жидкость-жидкость определяли сталагмометрическим методом, расчет параметров адсорбционных слоёв – методами Гиббса и Ленгмюра.

Результаты. Изучено поведение молекул моно- и диэфиров олеиновой кислоты и моно- и диэфиров стеариновой кислоты в смеси с полиэтиленгликолем-400 на границе раздела фаз масло-вода при производстве косметических эмульсий. Предложено использование 0,5% масс. высокодисперсного порошка глауконита, который концентрируется на межфазной границе с образованием прочной пространственной коагуляционной структуры для стойкости дисперсной системы.

Научная новизна. Доказано повышение стабилизационных свойств смеси ПАВ путем межмолекулярного взаимодействия на межфазной границе с образованием плотной упаковки молекул.

Практическая значимость. Установлен нижний предел концентрации комплексного эмульгатора для снижения себестоимости косметических изделий.

Ключевые слова: косметическая эмульсия, глауконит, эмульгатор, стеарат ПЭГ-400, олеат ПЭГ-400.

ДОСЛІДЖЕННЯ СИНЕРГІТИЧНИХ ЕФЕКТІВ В СИСТЕМІ КОМПЛЕКСНОГО ЕМУЛЬГАТОРА

МАНК В.В., ПОЛОНСЬКА Т.А.

Національний університет харчових технологій

Мета. Обґрунтування складу комплексного емульгатора з позиції фізико-хімічних властивостей стабілізованої системи.

Методики. Поверхневий натяг на межі рідина-рідина визначали сталагмометричним методом, розрахунок параметрів адсорбційних шарів методами Гіббса та Ленгмюра

Результати. Вивчено поведінку молекул моно- і диефірів олеїнової кислоти та моно- і диефірів стеаринової кислоти у суміші з поліетиленгліколем-400 на межі поділу фаз олія-вода при виробництві косметичних емульсій. Запропоновано використання 0,5%мас. високодисперсного порошку глауконіту, що концентрується на міжфазній межі з утворенням міцної просторової коагуляційної структури для стійкості дисперсної системи.

Наукова новизна. Доведено підвищення стабілізаційної властивості суміші ПАР через міжмолекулярну взаємодію на міжфазній межі з утворенням щільної упаковки молекул.

Практична значимість. Встановлено нижню межу концентрації комплексного емульгатора для зниження собівартості косметичних виробів.

Ключові слова: косметична емульсія, глауконіт, емульгатор, стеарат ПЕГ-400, олеат ПЕГ-400.