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PICKERING EMULSIONS STABILIZED WITH KAOLIN PARTICLES

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Abstract: *Emulsions stabilized with kaolin clay particles with a size of 23,80 μm were obtained. The concentration of kaolin particles in water suspension varied from 0,5 to 3 wt.%. It was shown that it is possible to obtain stable emulsions in the presence of natural origin particles, namely kaolinite clay, free from surfactants. The stability of the emulsions was increased with an increase of the concentration of kaolin microparticles.*

Keywords: *Pickering emulsions; inorganic particles; kaolin; clay, direct emulsions.*

INTRODUCTION

Emulsions stabilized by solid particles are called as Pickering emulsions. This type of emulsion is named after S. W. Pickering, who first described it. He showed that solid-particle-stabilized emulsions are more stable than surfactant-based emulsions. Although Pickering emulsions had certain advantages over surfactant-based emulsions, they were ignored for a long period. Pickering emulsions contain solid particles at the interface between the two liquid phases, which serve as stabilizing agents. While for the stabilization of traditional emulsions, low - and high-molecular surfactants (surfactants) are used [1].

Every year there is an increasing interest in Pickering emulsions due to their wide range of applications in food, pharmaceuticals and cosmetics. The demand for conventional emulsions is falling, as toxicity is the main problem when using surfactant-stabilized emulsions. An important advantage of Pickering emulsions is low cost and environmental friendliness when using natural clays and other biocompatible materials [2, 3].

Pickering emulsions, unlike traditional emulsions, can maintain their stability for several months or even years. Pickering emulsions and conventional emulsions have similarities and differences. The high stability of emulsions stabilized with solid particles has a great advantage in terms of shelf life [4].

Various colloidal particles, including inorganic and polymer colloids, such as silicon dioxide [5], polymer latex [6], magnetic particles [7], graphene [8], polymethylmethacrylate particles [9], nanoparticles of metals and metal compounds [10 -12] and natural clay particles [13] have been successfully used to produce Pickering emulsions. Clay particles are among the most readily available and easy to modify materials.

Kaolin clays were used to stabilize the Pickering emulsion, since Kazakhstan contains 19 % of the total balance reserves of kaolin in the CIS countries [14].

The aim of this work was to study the possibility of obtaining stable Pickering emulsions due to kaolinite clay microparticles spontaneous adsorption at the oil/water interface. The study of emulsions stabilized by clay particles is interesting for the development of stable oil-in-water emulsions without additional surfactants or surface treatment [15], since the studies were conducted mainly using modified clays.

EXPERIMENTAL PART



In this work, kaolin particles ("Chempack", Russia), distilled water, hexane (chemically pure) (Alita, Russia) as a dispersed medium were used to produce emulsions. In the work, the reagents were not subjected to additional purification.

The particle size of kaolin clay was determined using a laser particle size analyzer Partica LA-960, HORIBA by dynamic light scattering. The dynamic light scattering method allows to estimate the size and dispersion of particles. For measurement carrying out an optically transparent 1 cm polymethylmethacrylate cell was filled with 1 ml of particle dispersion. The sample was placed in the cuvette section of the analyzer, the cuvette was covered with a thermally insulating cover, and the measurement procedure was started in manual mode. The measurements were carried out at 25 °C. The readings were taken three times. For further analysis, the average result was taken.

Aqueous clay suspensions with different concentrations (C=0,5%, 1%, 2%, 3%) was used to prepare Pickering emulsions. The aqueous suspension was mixed with hexane using an Ultra Turrax IKA T10 homogenizer (Germany) (mixing speed 4000 rpm) for 10 minutes.

To determine the stability of emulsions, the separation time of the dispersed phase H, % was measured using the following formulas:

$$H = \frac{V \cdot 100}{V_1}, \% \quad (1),$$

where V – volume of released water, ml
V₁ – total volume of emulsion, ml.

To find the life time A, min, of an emulsion, the dependence H, % on the time is constructed. Extrapolating the initial straight part of the curve to the ordinate at H=100%, the point found in the abscissa will be taken as a lifetime of the emulsion.

RESULTS AND DISCUSSION

Kaolin clay particles were used to produce Pickering emulsions. The sizes of clay particles were previously determined by the method of dynamic light scattering. Figure 1 shows the differential distribution curve of kaolin particles. The data show that the average kaolin particle size is 23,80 μm.

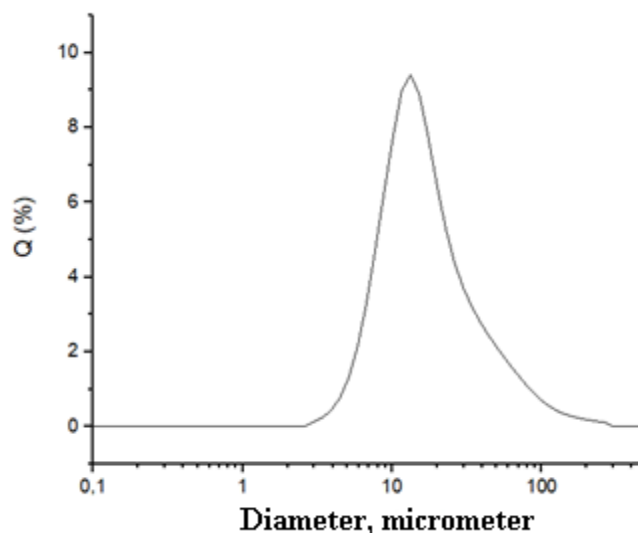


Fig. 1. Differential distribution curve of kaolin suspension particles



The effect of the concentration on the stability of the Pickering emulsion with different concentrations of clay suspension from 0,5 to 3% was investigated. It was found that the higher the kaolin particles concentration in water, the more stability of the emulsions.

Figure 2 – 3 shows the dependences of the separated dispersed phase H, %, on the observation time at different clay concentrations and ratios (water/oil). It was found that at the ratios of 2:8 and 3:7 (water/oil), the emulsion behaves steadily and H, % takes the lowest values, does not exceed 10% at a clay concentration of 2%. At a ratio of 9: 1 (water/oil), the emulsion quickly delaminates and H reaches 90% at C=3%, while at C=2%, H has the lowest value with about 57%.

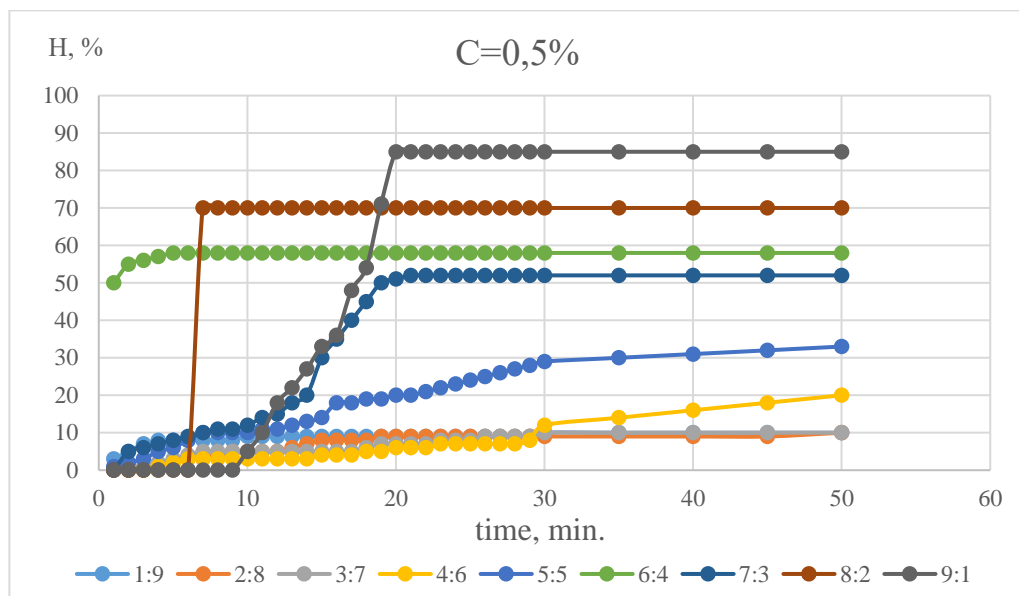


Fig. 2 Dependence of the dispersed phase volume H, % of time separated from the emulsion at the concentration of kaolinite clay particles C=0,5%

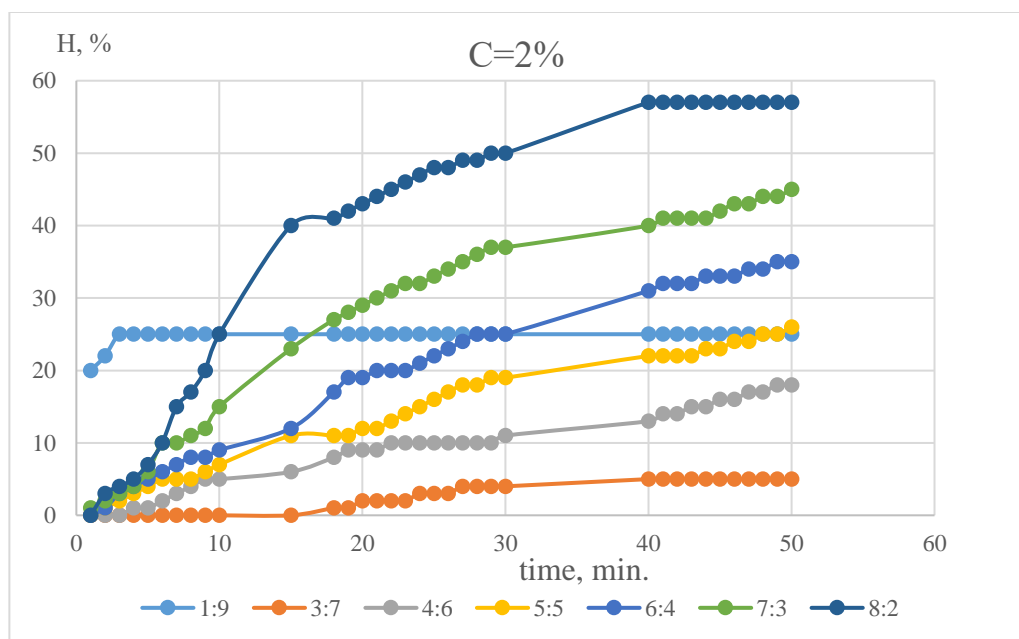


Fig. 3. Dependence of the dispersed phase volume H, % of time separated from the emulsion at the concentration of kaolinite clay particles C=2%



Table 1 shows the effect of the concentration of kaolin clay particles on the emulsion lifetime A (min.) at different water/oil ratios. It was found that the most optimal concentration for obtaining stable emulsions is 2%.

Table 1. Effect of the concentration on the emulsion lifetime A (min.) at different water/oil ratios.

Concentration, %	The ratio of water/oil								
	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
	The life time of the emulsion, min. (A)								
0,5	680	380	520	400	100	50	37	10	23
1	0	104	135	350	150	70	60	50	0
2	5,5	1560	450	122,5	150	107	62	360	0
3	5,1	1440	880	650	220	100	80	20	8

Pickering emulsions stabilization mechanism assumes that solid particles are adsorbed at the oil-water interface to form a monolayer of particles acting as a rigid film and providing a mechanical barrier against the droplet coalescence [16,17].

The emulsions obtained at this concentration at a ratio of 2:8 and 3:7 retain their stability for a long time (the observation time is more than 5 months), which confirms the possibility of obtaining emulsions in the presence of kaolin particles and the prospects of their use for obtaining stable emulsions based on non-toxic microparticles of natural origin, suitable for use in medicine and cosmetics industry.

CONCLUSION

It was established that direct stable Pickering emulsions can be obtained on the basis of kaolin particles. At C=2% of aqueous suspension of particles and a ratio of 2:8 and 3:7, stable emulsions were obtained that remain stable for more than 5 months without phase separation. The effect of the concentration on the stability of the emulsion was studied. It was found that the higher the concentration of kaolin particles in water, the more stable the emulsion. The most optimal concentration for obtaining stable emulsions is 2%. The results obtained in this work can be used to create microcapsules of various types based on emulsions stabilized by kaolin particles.

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ЖАУЖАПЫРАҚ ӨСІМДІГІНІҢ УЛЬТРАДЫБЫСТЫ ЭКСТРАКТЫ НЕГІЗІНДЕ ЭМУЛЬСИЯЛЫҚ ТҮРДЕГІ ЕМДІК – КОСМЕТИКАЛЫҚ ЖАҚПАМАЙ ӘЗІРЛЕУ ТЕХНОЛОГИЯСЫ

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Аннотация: Отандық өсімдік шикізаты негізінде қабынуға қарсы және антиоксидантты қасиетке ие майлы-сулы түрдегі емдік-косметикалық жақпамай әзірлеу технологиясы және оның құрамын талдау.

Түйін сөздер: Фитотерапия, биологиялық белсенді заттар, дәрілік өсімдік, жаужапырақ, экстракт, лимон гүлі, эмульсия, эфир майлары, жақпамай, ультрадыбыс, сулы фаза, майлы фаза.

Қазіргі уақытта фитотерапияға қызығушылық артты. Дәрілік өсімдіктер емдік қосылыстардың бірегей көзі - адам ағзасының әртүрлі ауруларын алдын алу үшін де, емдеу үшін де қолданылатын биологиялық белсенді заттар (ББЗ) болып табылады. Ал,



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