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ГИДРОФОБИЗАЦИЯ ЧАСТИЦ КРЕМНЕЗЕМА РАЗЛИЧНЫМИ КАТИОННЫМИ ПОВЕРХНОСТНО-АКТИВНЫМИ ВЕЩЕСТВАМИ

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Частицы кремнезема радиусом 3-7 нм (людокс и аэросил) и 270 нм (синтезированные методом Стобера), модифицированные цетилтриметиламмония бромидом (CTAB) и гексиламином, применялись для стабилизации эмульсий. Гистерезисные углы θ избирательного смачивания частиц измеряли методом сидячей капли на вертикальной поверхности или методом вытягивания шара, используя стеклянную подложку, модифицированную контактной коагуляцией кремнезема. Краевой угол на границе водная фаза - предельный углеводород (октан, декан) достигал значений θ_{rec} = 53±2° и θ_{adv} = 116±4° (угол оттекания и натекания воды, соответственно) при увеличении исходной концентрации длинноцепочечного CTAB до $(1,4–9,5)\cdot 10^{-2}$ ммоль на 1 г кремнезема. При дальнейшем увеличении концентрации формировался второй переориентированный слой, что понижало краевой угол. Соответственно с применением CTAB, были получены только прямые эмульсии при объемной доле фазы масла $\O_{oil} = 0,5$. Количество короткоцепочечного гексиламина, необходимое для начала стабилизации эмульсий, оказалось на 2-3 порядка больше количества CTAB. С помощью гексиламина удалось увеличить краевой угол до значений $\theta_{rec} = \theta_{adv}$ = 163±12° при концентрации 7-21 ммоль/г. Это объясняется тем, что для гексиламина не характерно мицеллообразование и формирование переориентированных слоев. Вероятно, адсорбция гексиламина возможна не только на диссоциированных силанольных группах ≡Si–OH, но и на силоксановых группах ≡Si–O–Si≡, что и позволяет сделать поверхность кремнезема супергидрофобной. С измеренными краевыми углами коррелировала область устойчивых прямых и обратных эмульсий.

Ключевые слова: кремнезем, эмульсии, смачивание, краевой угол

HYDROPHOBIZATION OF SILICA PARTICLES WITH VARIOUS CATIONIC SURFACTANTS

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Silica particles with a radius of 3-7 nm (Ludox and Aerosil) and 270 nm (synthesized by the Stöber method), modified with cetyltrimethylammonium bromide (CTAB) and hexylamine, were used to stabilize emulsions. The hysteresis angles θ of the particle selective wetting were measured by the sessile droplet method on the vertical surface or by the pulling a ball method at using a glass substrate modified by contact coagulation of silica. The contact angle at the boundary between the aqueous phase and the saturated hydrocarbon (octane, decane) reached the values $\theta_{rec} = 53 \pm 2$ ° and $\theta_{adv} = 116 \pm 4$ ° (the aqueous phase receding and advancing angle, respectively) with an increase in the initial concentration of long-chain CTAB to $(1.4–9.5)\cdot 10^{-2}$ mmol/g of silica. With a further increase in CTAB concentration, a second reoriented layer was formed, which lowered the contact angle. Accordingly, using CTAB, only oil-in-water emulsions were obtained with the oil phase volume fraction $Ø_{oil} = 0.5$. The amount of short-chain hexylamine required to start stabilizing the emulsions turned out to be 2-3 orders of magnitude higher than the amount of CTAB. At using hexylamine, it was possible to increase the contact angle up to the values $\theta_{rec} \approx \theta_{adv} = 163 \pm 12$ ° at a concentration of 7-21 mmol/g. This is due to the fact that hexylamine is not characterized by formation of micelle or reoriented layers. Apparently, the adsorption of hexylamine is possible not only on dissociated silanol groups Si–OH, but also on siloxane groups Si–O–Si≡, which makes it possible to make the silica surface superhydrophobic. The measured contact angles were correlated with the region of stable oil-in-water and water-in-oil emulsions.

Key words: silica, emulsions, wetting, contact angle

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INTRODUCTION

A special class of dispersed systems are systems with insoluble solid particles at the water/air or water/oil interface. These are emulsions stabilized by solid particles (oil in water – O/W, or water in oil – W/O) [1-3], foams and oil foams (oleofoams) [4-9], emulgels, and liquid marbles in the gas phase [10]. Silica, latexes, talc, organo-modified granules of starch, cellulose and many others, both synthetic and natural, are used as solid stabilizers. Solid-stabilized systems are used in the field of fine chemical catalysis; serve as a template for obtaining microspheres, microcapsules used for controlled targeted delivery of drugs; for the production of porous biomaterials serving as tissue frameworks, porous conductors, materials that respond to changes in environmental conditions [11-15]. Stabilization by solids includes the following mechanisms [4, 6, 16]: 1) the formation of a dense interfacial (adsorption) layer of particles on the surface of drops (or bubbles) at a high value of the wetting work of the particles; 2) capillary pressure in the solid-stabilized emulsion (or foam) films; 3) the formation of the branched network-structure in the continuous phase, including interphase layers of the particles. This work presents a comparison of the results of studying the modification of colloidal silica particles by the adsorption of various surfactant-modifiers in order to use the modified particles to stabilize emulsions.

EXPERIMENTAL PART

Colloidal silica (SiO_2) was used: aerosil A-200, A-380; Ludox-HS; S-3, prepared by hydrolysis of tetrapentyloxysilane in an alcoholic medium by Stöber method. The surface of the particles was modified with cetyltrimethylammonium bromide (CTAB, Merck) or hexylamine (Merck). The relative concentration of the surfactant-modifier was calculated by the formula:

$$n = C/m_{SiO_2},$$

where C is the initial molar concentration of the modifier; m_{SiO_2} – mass of the solid particles. Emulsions were obtained by shaking the aqueous phase with modified silica and a hydrocarbon phase (*n*-octane, *n*-decane (99%, Acros Organics)) at oil volume fraction of $Ø_{oil} = 0.5$. The emulsion was left for storage and determination of type and stability in a test tube with a ground-in lid at room temperature 25±2 °C. An emulsion was considered aggregatively stable (with respect to coalescence) if it did not release a dispersed phase within a week. As a rule, such an emulsion remained aggregatively stable for a long time (more than a year). An emulsion was considered kinetically stable (with respect to droplet sedimentation) if it did not release either a dispersed phase or a dispersion medium within a week. In this case, the type of emulsion (O/W or W/O) was determined by mixing with a drop of water.

The contact angles of the aqueous phase receding θ_{rec} and advancing θ_{adv} were determined by the sessile drop method on a vertical surface [17] or by the pulling a ball method [18]. Methods for measuring the contact angle θ directly on colloidal particles (for example, the method of wetting heat [19]) are not applicable for particles modified by adsorption from solution. Therefore, in this work, we used the macroscopic glass surface modified by contact coagulation of silica particles together with a surfactant-modifier. The dependence of the angle θ on the solid curvature is manifested for particles of several nm [20]. Only Ludox-HS particle size was within these limits: R = 7.5 nm (radius of aggregates R_{agr} = 30 nm). Aerosil particles were aggregated upto R_{agr} = 100 nm. The aggregate size was determined using a KFK-3 photocolorimeter.

RESULTS AND DISCUSSION

The silica surface contains silanol ≡Si–OH and siloxane ≡Si–O–Si≡ groups. Fig. 1 shows the values of the contact angles of selective wetting of silica as the result of the adsorption of long-chain surfactants on dissociated silanol groups *≡Si–O*$^{-}$: CTAB – obtained in our work (the method of submerged ball), as well as octadecylammonium chloride (ODAC, the method of a pressed drop) from Ref. [18]. Long-chain surfactants at high concentrations tend to form spherical and lamellar micelles. Therefore, with an increase in the concentration of the surfactant modifier, the contact angles of the aqueous phase receding θ_{rec} and advancing θ_{adv} increased up to the maximum values $\theta_{rec} = 53 \pm 2°$ and $\theta_{adv} = 116 \pm 4°$ (CTAB) и $\theta_{rec} = 57 \pm 9°$, $\theta_{adv} = 116 \pm 14°$ (ODAC) at a concentration of (2-5)$\cdot 10^{-4}$ mol/L, approaching the critical micelle concentration: CMC(CTAB) = (8-9)$\cdot 10^{-4}$ mol/L, CMC (ODAC) = $3\cdot 10^{-4}$ mol/L. With a further increase concentration, long-chain surfactants form a second reoriented adsorption layer [21], and the contact angles decrease (Fig. 1B). At all concentrations of the modifier, starting from 10^{-5}-10^{-6} mol/L CTAB (θ_{rec} = 10–20° and θ_{adv} = 78–85°), modified silica particles provided stabilization of O/W emulsions (Table 1). W/O emulsions were obtained only in the case of the predominant oil volume fraction $\varnothing_{oil}$ = 0.7-0.8.

By modifying silica with a short-chain surfactant – hexylamine – contact angles were achieved up to 140-155 ° at C_{SiO_2}= 1% and 160-180° at C_{SiO_2}= 5%, corresponding to a superhydrophobic surface (Fig. 2, the method of a sessile drop on a vertical surface). Higher hydrophobization degree is explained by micelle formation is not typical for short-chain hexylamine. Therefore, with the concentration increase, hexylamine does not form a second adsorption layer, but it is incorporated into the first one due to the adsorption on siloxane groups ≡Si–O–Si ≡ on the silica surface due to hydrogen bonds or van der Waals interactions.

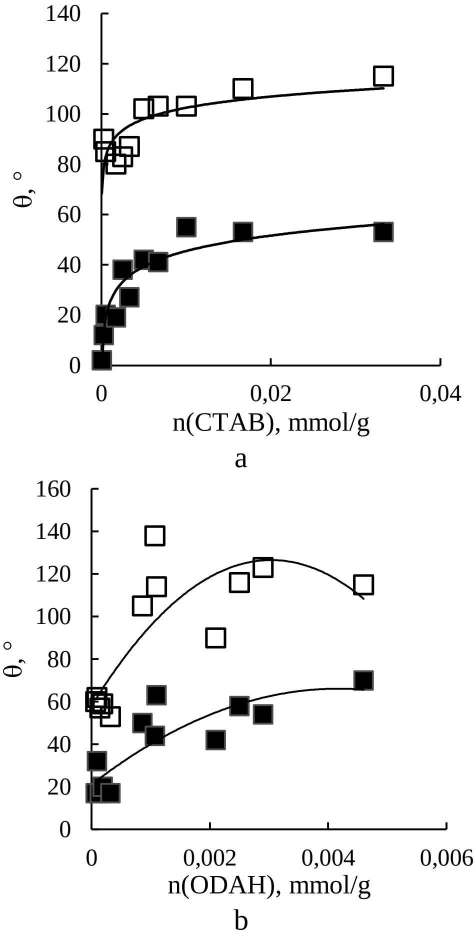

Fig. 1. The contact angles of aqueous phase receding (dark symbols) and advancing (open symbols) at the boundary with a hydrocarbon, depending on the concentration of the long-chain modifier: (A) CTAB + 0.5-3% silica, octane or decane; (B) ODAC + 14% glass particle suspension

Рис. 1. Краевые углы оттекания (темные символы) и натекания (светлые символы) водной фазы на границе с углеводородом в зависимости от концентрации длинноцепочечного модификатора: (A) CTAB + 0.5-3% кремнезем|, октан или декан; (B) ОДАХ + 14% суспензия частиц стекла

Table 1

Stabilizing effect of CTAB-modified silica on emulsion

***Таблица 1.* Стабилизирующее действие CTAB-модифицированного кремнезема на эмульсии**

C_{SiO_2}, %	n(CTAB), mmol/g	
	O/W	W/O
0,5 A-200	> $1.1\cdot 10^{-3}$	> (4–9.5)$\cdot 10^{-2}$
2 Ludox	> $5\cdot 10^{-3}$	–
3 S-3	> $1\cdot 10^{-3}$	> $1.4\cdot 10^{-2}$

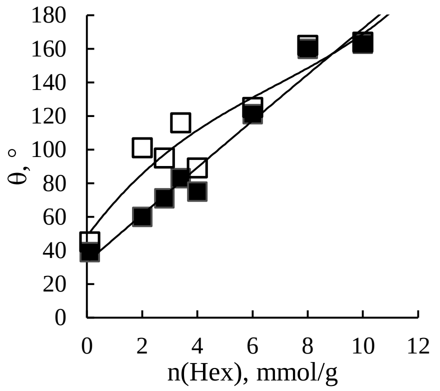

Fig. 2. The contact angles of selective wetting (aqueous phase/decane) of hexylamine-modified 5% aerosil A-380: aqueous phase receding (dark symbols) and advancing angles (open symbols)

Рис. 2. Краевые углы избирательного смачивания (вода/декан) 5% аэросила А-380, модифицированного гексиламином: углы оттекания (темные символы) и натекания (светлые символы)

In accordance with the measured contact angles, stable emulsions of both types (Table 2) were obtained from the complex of Aerosil with hexylamine. The beginning of stabilization of O/W emulsions was found for θ_{rec} = 25-30° и θ_{adv} = 55° (C_{SiO_2}= 1%), θ_{rec} = 39° и θ_{adv} = 45° (C_{SiO_2}= 5%). The transition from O/W emulsions to W/O emulsions was observed with an increase in the hexylamine concentration from 0.10 to 0.14 mol/L (at C_{SiO_2}= 1%) and from 0.14 to 0.20 mol/L (at C_{SiO_2}= 5%). Moreover, the modification of SiO_2 with hexylamine, in contrast to long-chain CTAB and ODAC, achieved such the hydrophobization degree, when even the W/O emulsions became unstable. The upper limit of stability of the emulsions corresponded to the contact angle θ_{rec} = 160°and θ_{adv} = 162° at C_{SiO_2} = 5%.

Table 2

Stabilizing effect of hexylamine-modified silica on emulsion

Таблица 2. **Стабилизирующее действие кремнезема, модифицированного гексиламином, на эмульсии**

C_{SiO_2}, %	n(Hex), mmol/g	
	O/W	W/O
1	2-12	12-21
3	0.3-6	6-13
5	0.1-3.5	3.5-10
7	0.04-3.5	3.5-7

Comparison of the concentrations of hexylamine and silica in the same dimension (as a volume fraction in the aqueous phase) showed that stable W/O emulsions were formed only if the volume fraction of hexylamine exceeded the volume fraction of the solid phase by at least 1.5-3 times [22]. Thus, at high concentrations of hexylamine, a hybrid particle is formed in which the core is a silica aggregate and the shell is hexylamine. The attachment of just such hybrid particles at the water-oil interface promotes the formation of oil droplets in water.

CONCLUSIONS

The amount of short-chain hexylamine required to modify silica to form emulsions is 2-3 orders of magnitude higher than the amount of long-chain surfactants. The W/O emulsion was formed only under the condition that the volume fraction of hexylamine exceeded the volume fraction of the solid particles.

ЛИТЕРАТУРА

1. **Aveyard R., Binks B.P., Clint J.** Emulsions stabilized by solely colloidal particles. *Adv. Colloid Interface Sci.* 2003. V. 100-102. P. 503-546. DOI: 10.1016/S0001-8686(02)00069-6.
2. **Dickinson E.** Use of nanoparticles and microparticles in the formation and stabilization of food emulsions. *Trends Food Sci. Technol.* 2012. V. 24. P. 4–12. DOI: 10.1016/J.TIFS.2011.09.006.
3. **Koroleva M., Bidanov D., Yurtov E.** Emulsions stabilized with mixed SiO_2 and Fe_3O_4 nanoparticles: mechanisms of stabilization and long-term stability. *Phys. Chem. Chem. Phys.* 2019. V. 21. P. 1536–1545. DOI: 10.1039/c8cp05292a.
4. **Horozov T.S.** Foams and foam films stabilised by solid particles. *Curr. Opin. Colloid Interf. Sci.* 2008. V. 13. N 3. P. 134-140. DOI: 10.1016/j.cocis.2007.11.009.
5. **Studart A.R., Nelson A., Iwanovsky B., Kotyrba M., Kündig A.A., Dalla Torre F.H., Gonzenbach U.T., Gauckler L.J., Löffler J.F.** Metallic foams from nanoparticle-stabilized wet foams and emulsions. *J. Mater. Chem.* 2010. V. 22. P. 820-823. DOI: 10.1039/C1JM14353K.
6. **Kruglyakov P.M., Elaneva S.I., Vilkova N.G.** About mechanism of foam stabilization by solid particles. *Adv. Colloid Interf. Sci.* 2011. V. 165. P. 108-116. DOI: 10.1016/j.cis.2011.02.003.

REFERENCES

1. **Aveyard R., Binks B.P., Clint J.** Emulsions stabilized by solely colloidal particles. *Adv. Colloid Interface Sci.* 2003. V. 100-102. P. 503-546. DOI: 10.1016/S0001-8686(02)00069-6.
2. **Dickinson E.** Use of nanoparticles and microparticles in the formation and stabilization of food emulsions. *Trends Food Sci. Technol.* 2012. V. 24. P. 4–12. DOI: 10.1016/J.TIFS.2011.09.006.
3. **Koroleva M., Bidanov D., Yurtov E.** Emulsions stabilized with mixed SiO_2 and Fe_3O_4 nanoparticles: mechanisms of stabilization and long-term stability. *Phys. Chem. Chem. Phys.* 2019. V. 21. P. 1536–1545. DOI: 10.1039/c8cp05292a.
4. **Horozov T.S.** Foams and foam films stabilised by solid particles. *Curr. Opin. Colloid Interf. Sci.* 2008. V. 13. N 3. P. 134-140. DOI: 10.1016/j.cocis.2007.11.009.
5. **Studart A.R., Nelson A., Iwanovsky B., Kotyrba M., Kündig A.A., Dalla Torre F.H., Gonzenbach U.T., Gauckler L.J., Löffler J.F.** Metallic foams from nanoparticle-stabilized wet foams and emulsions. *J. Mater. Chem.* 2010. V. 22. P. 820-823. DOI: 10.1039/C1JM14353K.
6. **Kruglyakov P.M., Elaneva S.I., Vilkova N.G.** About mechanism of foam stabilization by solid particles. *Adv. Colloid Interf. Sci.* 2011. V. 165. P. 108-116. DOI: 10.1016/j.cis.2011.02.003.

7. **Вилкова Н.Г., Мишина С.И., Депутатов Е.Д.** Свойства пен, содержащих гидрофобизированный диоксид титана. *Изв. вузов. Химия и хим. технология.* 2020. Т .63. Вып. 3. С. 23-29. DOI: 10.6060/ivkkt.20206303.6126.
8. **Вилкова Н.Г., Мишина С.И., Дорчина О.В.** Устойчивость пен, содержащих дизельное топливо. *Изв. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 6. С. 48-53. DOI: 10.6060/tcct.20186106.5361.
9. **Saha S., Saint-Michel B., Leynes V., Binks B.P., Garbin V.** Stability of bubbles in wax-based oleofoams: decoupling the effects of bulk oleogel rheology and interfacial rheology. *Rheologica Acta.* 2020. V. 59. P. 255-266. DOI: 10.1007/s00397-020-01192-x.
10. **McHale G., Newton M.I.** Liquid marbles: principles and applications. *Soft Matter.* 2011. V. 7. P. 5473-5481. DOI: 10.1039/C1SM05066D.
11. **Tseng W.J., Kao W.-H.** Preparation of electrically conductive calcium phosphate composite foams by particle-stabilized emulsion route. *Ceramics*. 2018. N 1. P. 319–328. DOI: 10.3390/ceramics1020025.
12. **Yang Y., Fang Z., Chen X., Zhang W., Xie Y., Chen Y., Liu Z., Yuan W.** An overview of Pickering emulsions: solid-particle materials, classification, morphology, and applications. *Front. Pharmacol*. 2017. V. 8. Art. 287. DOI: 10.3389/fphar.2017.00287.
13. **Rodriguez A.M.B., Binks B.P.** Capsules from Pickering emulsions template. *Curr. Opin. Colloid Interface Sci.* 2019. V. 44. P. 107-129. DOI: 10.1016/j.cocis.2019.09.006.
14. **Матера А., Длуска Э., Марковска-Радомская А., Тудек Б., Кочиский К.** Поверхностно функционализированная эмульсия для селективного транспорта лекарственных средств. *Изв. вузов. Химия и хим. технология.* 2019. Т. 62. Вып. 8. С. 113-119. DOI: 10.6060/ivkkt.20196208.5925.
15. **Simonenko E.P., Simonenko N.P., Nikolaev,V.A.** Sol–Gel Synthesis of Functionally Graded SiC–TiC Ceramic Material. *Russ. J. Inorg. Chem.* 2019. V. 64. P. 1456–1463. DOI: 10.1134/S0036023619110202.
16. **Вилкова Н.Г., Нуштаева А.В.** Пены и эмульсии, стабилизированные твердыми частицами: механизмы стабилизации. *Изв. вузов. Поволжск. регион. Ест. науки.* 2017. № 4(20). С. 74-85. DOI: 10.21685/2307-9150-2017-4-6.
17. **Nushtaeva A.V.** Contact angles of selective wetting of hexylamine- modified silica surface. *Colloids Surf. A: Physicochem. Eng. Asp.* 2014. V. 451. P. 101-106. DOI: 10.1016/j.colsurfa.2014.03.050.
18. **Kruglyakov P.M.** Hydrophile-lipophile balance of surfactants and solid particles. Amsterdam: Elsevier. 2000.
19. **Нуштаева А.В.** Стабилизация эмульсий микрочастицами талька. *Коллоид. журн.* 2019. Т. 81. № 4. С. 487-492. DOI: 10.1134/S0023291219040104.
20. **Drelich G.W., Boinovich L., Chibowski E., Volpe C.D., Holysz L., Marmur A., Siboni S.** Contact angles: history of over 200 years of open questions. *Surf. Inn*. 2020. V. 8(1-2). P. 3-27. DOI: 10.1680/jsuin.19.00007.
21. **Churaev N.V., Sobolev V.D.** Physical chemistry of wetting phenomena. In: Colloid Stability: The role of surface forces Part II. Ed. by T.F. Tadros. Weinheim: Wiley-VCH Verlag GmbH and Co. KGaA. 2007. P. 127-152.
22. **Nushtaeva A.V.** Stabilization of water-in-oil emulsions with complex of silica particles and hexylamine. *Nanosystems: Physics, Chemistry, Mathematics.* 2015. V. 6. P. 726-732. DOI: 10.17586/2220-8054-2015-6-5-726-732.

7. **Vilkova N.G., Mishina S.I., Deputatov E.D.** Foams stabilization by hydrophobized oxides of various chemical nature. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* [ChemChemTech]. 2020. V. 63. N 3. P. 23-29. DOI: 10.6060/ivkkt.20206303.6126.
8. **Vilkova N.G., Mishina S.I., Dorchina O.V.** Stability of foams containing diesel fuel. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* [ChemChemTech]. 2018. V. 61. N 6. P. 48-53 (in Russian). DOI: 10.6060/tcct.20186106.5361.
9. **Saha S., Saint-Michel B., Leynes V., Binks B.P., Garbin V.** Stability of bubbles in wax-based oleofoams: decoupling the effects of bulk oleogel rheology and interfacial rheology. *Rheologica Acta.* 2020. V. 59. P. 255-266. DOI: 10.1007/s00397-020-01192-x.
10. **McHale G., Newton M.I.** Liquid marbles: principles and applications. *Soft Matter.* 2011. V. 7. P. 5473-5481. DOI: 10.1039/C1SM05066D.
11. **Tseng W.J., Kao W.-H.** Preparation of electrically conductive calcium phosphate composite foams by particle-stabilized emulsion route. *Ceramics*. 2018. N 1. P. 319–328. DOI: 10.3390/ceramics1020025.
12. **Yang Y., Fang Z., Chen X., Zhang W., Xie Y., Chen Y., Liu Z., Yuan W.** An overview of Pickering emulsions: solid-particle materials, classification, morphology, and applications. *Front. Pharmacol*. 2017. V. 8. Art. 287. DOI: 10.3389/fphar.2017.00287.
13. **Rodriguez A.M.B., Binks B.P.** Capsules from Pickering emulsions template. *Curr. Opin. Colloid Interface Sci.* 2019. V. 44. P. 107-129. DOI: 10.1016/j.cocis.2019.09.006.
14. **Metera A., Dłuska E., Markowska-Radomska A., Tudek B., Kosicki K.** Surface functionalized emulsion for selective drugs transport. *Izv. Vyssh. Uchebn.Zaved. Khim. Khim. Tekhnol.* [ChemChemTech]. 2019. V. 62. N 8. P. 113-119. DOI: 10.6060/ivkkt.20196208.5925.
15. **Simonenko E.P., Simonenko N.P., Nikolaev,V.A.** Sol–Gel Synthesis of Functionally Graded SiC–TiC Ceramic Material. *Russ. J. Inorg. Chem.* 2019. V. 64. P. 1456–1463. DOI: 10.1134/S0036023619110202.
16. **Vilkova N.G., Nushtaeva A.V.** Foams and Emulsions Stabilized by Solids: Stabilization Mechanisms. *Izv. Vyssh. Uchebn. Zaved. Povolzhsk. region. Est. nauki.* 2017. N 4(20). P. 74-85. DOI: 10.21685/2307-9150-2017-4-6.
17. **Nushtaeva A.V.** Contact angles of selective wetting of hexylamine- modified silica surface. *Colloids Surf. A: Physicochem. Eng. Asp.* 2014. V. 451. P. 101-106. DOI: 10.1016/j.colsurfa.2014.03.050.
18. **Kruglyakov P.M.** Hydrophile-lipophile balance of surfactants and solid particles. Amsterdam: Elsevier. 2000.
19. **Nushtaeva A.V.** Stabilization of emulsions with talc microparticles. *Kolloid. Zhurn.* 2019. V. 81. N 4. P. 487-492 (in Russian). DOI: 10.1134/S0023291219040104.
20. **Drelich G.W., Boinovich L., Chibowski E., Volpe C.D., Holysz L., Marmur A., Siboni S.** Contact angles: history of over 200 years of open questions. *Surf. Inn.* 2020. V. 8(1-2). P. 3-27. DOI: 10.1680/jsuin.19.00007.
21. **Churaev N.V., Sobolev V.D.** Physical chemistry of wetting phenomena. In: Colloid Stability: The role of surface forces Part II. Ed. by T.F. Tadros. Weinheim: Wiley-VCH Verlag GmbH and Co. KGaA. 2007. P. 127-152.
22. **Nushtaeva A.V.** Stabilization of water-in-oil emulsions with complex of silica particles and hexylamine. *Nanosystems: Physics, Chemistry, Mathematics.* 2015. V. 6. P. 726-732. DOI: 10.17586/2220-8054-2015-6-5-726-732.

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