

Properties of Foams Stabilized by Hydrophobized Silica Particles

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Abstract

The stability of foams stabilized by modified silica particles has been studied. Stable foams are formed from suspensions of Ludox and Aerosil at a relative degree of hydrophobization (n_g) of the surface of silica particles from 1.4 to 2.4 and, respectively, the water receding angle $\theta_w = 32^\circ - 45^\circ$. Stable foams are not formed when the degree of hydrophobization of the silica surface is $n_g \leq 0.25$ and $\theta_w \leq 19^\circ$. At the same mass contents of the solid phase in the initial suspensions and the relative degrees of its hydrophobization, the most stable foams and foam films are obtained from Aerosil suspensions. The process of aggregation of silica particles in the initial suspensions affects the stability of the resulting foams and films.

Keywords: foams, foam films, silica particles, stability.

INTRODUCTION

It is known, that emulsions stabilized with solid particles were intensively studied. The possibility of obtaining foams that contain solid modified particles as stabilizers was considered in [1-5]. An important role in the study of the stability of these disperse systems was played by the study of the adsorption layers of particles, the degree of their aggregation [6-8], and also the decrease in the interfacial (water-gas or water-oil) surface energy as a result of the release of hydrophobized particles to the interface. It was shown earlier that the presence of solid particles at the phase interface leads to a reduction in the excess of free interfacial energy and, consequently, interfacial tension at the liquid/ liquid [9, 10] and liquid/ gas interfaces [11-13]. An analysis of the effect of solid hydrophobized particles on the interfacial tension at various interfaces (water/ oil, water/ gas) was carried out in [12, 13]. It was shown that adsorption of solid particles (varying degrees of hydrophobicity) leads to a significant decrease in the interfacial tension of water/ oil and relatively a small decrease in the surface tension of water/ gas. Dependences of the relative decrease in the interfacial energy on the contact angle $\Delta\sigma/\sigma$ (Θ_w) have peaks that correspond to the angles $\Theta_w = 45^\circ$ for the water / gas surface and $\Theta_w = 30^\circ - 40^\circ$ for the oil/ water surface [13]. It is interesting to note that the value of the relative interfacial energy at the oil-water interface is always greater than the relative interfacial energy at the water-gas interface, and high values of the contact angle

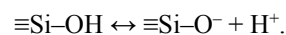
of the solid surface of silica (up to 180°) were reached only at the water-oil interface. It is well known that silica particles dispersed in water can aggregate due to silanol bonds. Particle aggregates (with a high concentration of solid phase) can form a spatial grid that will affect the stability of the resulting foams. Although shear stresses in silica suspension have been measured in [14], their variation with the degree of hydrophobization of the surface of solid particles and the relationship with the stability of foams have not been studied. It is known that the properties of foams (lifetime of the foam layer, syneresis) are largely determined by the properties of the foam films that form the dispersed system. Foam films are models that in some cases allow describing and predicting the stability of a dispersed system as a whole.

The purpose of this work is the effect of the concentration of hexylamine on the degree of hydrophobicity of silica particles in the initial suspensions and the properties of foams and foam films.

MATERIALS AND METHODS

1. Materials

To stabilize foams used: a) Aerosil -380 (silica with a specific surface of 380 ± 30 m²/g and an average primary particle radius of 7 nm); b) Ludox brand Ludox HS-40 (sol silica with a mass content of solid phase 40%). To modify the silica surface, hexylamine (Merck chad) was used. It is known that silanol $\equiv\text{Si-OH}$ and siloxane $\equiv\text{Si-O-Si}\equiv$ groups are present on the surface of silica (SiO_2). The hydrophilicity of the silica surface is associated with a high content of silanol groups, which dissociate according to the equation:



To obtain stable foams, the particles are to some extent hydrophobized. Hexylamine ($\text{C}_6\text{H}_{15}\text{N}$) - short-chain surfactant, which practically does not have foaming capacity (the height of the layer of foam obtained from a solution of hexylamine with a concentration of 10-30 mmol/l, does not exceed one centimeter, and the lifetime is 1-2 minutes). When dissolved in water, this substance dissociates to form positively charged surface-active ions, which are adsorbed on the silica surface and lead to hydrophobization of the solid surface.

In this paper, a relative value $n_g = C_H/C_s$ was used to estimate the degree of hydrophobicity of the silica surface, where C_H is the concentration of the surfactant in the initial suspension (mmol/l), C_s is the solid content (g/l). The degree of hydrophobicity n_g is calculated in mmol/g.

2. Research Methods

1) Preparation of foam

The foam was obtained by mixing a certain sample of Aerosila-380 with a certain volume of distilled water. Hexylamine was added dropwise to the resulting suspension and whipped until a foam formed. Similarly, a modifier was added dropwise to a determined volume of the LudoxHS-40 sol and whipped until a foam formed.

2) Definition of the boundary angles

a) The method of the pressed gas bubble

For particles of micron (and smaller) size, there is no method for determining the actual water receding angle (θ_w). So usually such angles are measured on a macroscopic surface of the same or similar chemical composition.

In our work, the contact angle was determined by the method of pressing a gas bubble against a modified plate, which is created in a quartz cuvette. Using a syringe, the gas bubble is placed on a solid, water-repellent glass surface. A magnified microscope image of the web camera is transferred to the computer. The resulting photos are processed graphically or using a specially designed program.

b) Measurement of the edge angles on the surface of the glass sphere

A similar measurement method was used earlier to measure the edge angles at the oil / water interface [9, 13].

The angle θ was determined at the receding of the aqueous phase (the water receding angle θ_w) by the method of a glass sphere hydrophobized together with the silica. For silica modified with cationic surfactants, a method was used to directly measure the edge angles (the water receding angle θ_w) on the surface of a glass ball (radius $R = 4.90-0.025$ mm), modified together with silica particles. In this case, the glass ball is drawn or immersed in the aqueous phase. The procedure for drawing the glass bowl to the water/ gas interface is shown in Fig. 1. The glass bowl fixed to the rigid frame is placed in a cuvette with the test suspension mounted on a table with a screw-type lifting device.

After 30 minutes, slowly lower the table with the cuvette until the tip of the ball touches the surface of the water / air, which at the same time spontaneously bends. Then again pull the ball, observing the catheter KM-6, until the surface is leveled (Figure 1). The height of the h-segment in the air is determined using a cathetometer with an accuracy of 0.01 mm. The cosine of the corner angle is calculated by the formula:

$$\cos\theta = \frac{R - h'}{R}$$

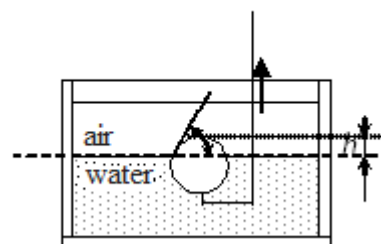


Figure 1. Scheme of measurement of the angle: 1 – glass ball fixed to the wire frame, h' – height of the ball segment in the air

3) Determination of the stability of foams under the influence of applied pressure drops (Foam Pressure Drop Technique [15]). The foam was placed on a porous ceramic filter impregnated with a foaming agent solution, and the foam sample was covered with a glass plate (Figure 2).

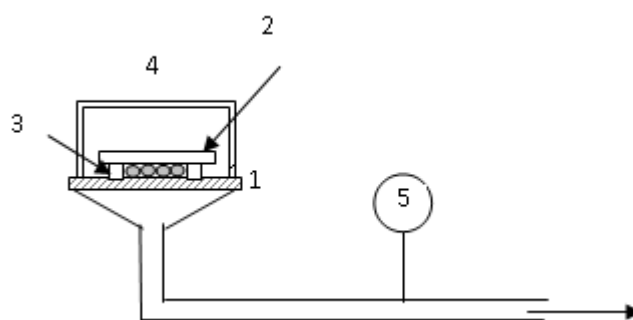


Figure 2. Schematic of the device for studying the stability of foam due to the applied differential pressure: 1 – glass filter; 2 – slide; 3 – glass plates that regulate the thickness of the foam layer; 4 – a glass with a flat bottom; 5 – manometer.

Several filters with a pore diameter of 1.4 to 20 μm were used. The space under the filter was connected to a container with a reduced (compared to atmospheric) pressure. The magnitude of the applied pressure drop ΔP was equal to:

$$\Delta P = P_1 - P_2,$$

where P_1 is the air pressure under the filter; P_2 is the pressure above the filter (and over the foam, respectively) equal to atmospheric pressure.

The applied pressure difference ΔP was measured with a U-shaped water gauge or a vacuum manometer. To protect against evaporation, the foam was covered with a glass beaker with a flat bottom. With the help of a microscope, the coalescence of foam bubbles was controlled. To measure the stability, the percent (D, %) of the destruction of a certain area of the foam layer was used for 30 minutes or a foam column of a certain height.

Figure 3 shows the dependence of the water receding angle θ_w from the degree of hydrophobicity of the surface, which was determined by the methods of a gas bubble (Ludox) pressed

against a hydrophobized plate and by a glass sphere (Aerosil) at the water-gas interface.

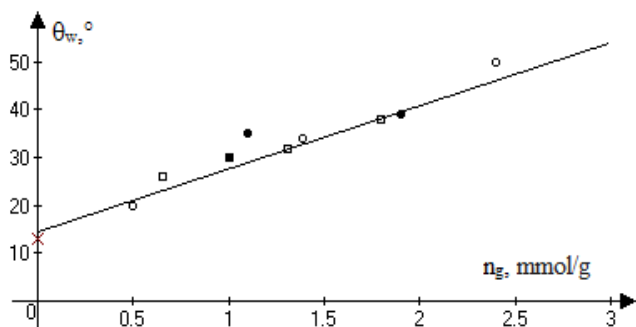


Figure 3. Dependence of the water receding angle θ_w on the degree of modification with hexylamine hard surface: ■ – 0.5% LudoxHS-40; □ – 2% LudoxHS-40; ● – 1% Aerosil-380; ○ – 2% Aerosil-380; × - without modifier [6, 7]

In the absence of a modifier (most hydrophilic silica particles), the contact angle is 13° [6, 7].

As can be seen from the figure above, with an increase in the degree of hydrophobization of the surface of silica Aerosil-380 and Ludox-HS-40 to 2.5, the value of the contact angle does not exceed 50° . A further increase in the concentration of hexylamine in the initial suspension did not lead to a significant change in the contact angle. In particular, for $n_g = 8.6$ the contact angle is $\theta_w = 52^\circ$. The change in the rheological properties of the initial suspensions as the degree of hydrophobicity of the silica surface increases is shown in Fig. 4.

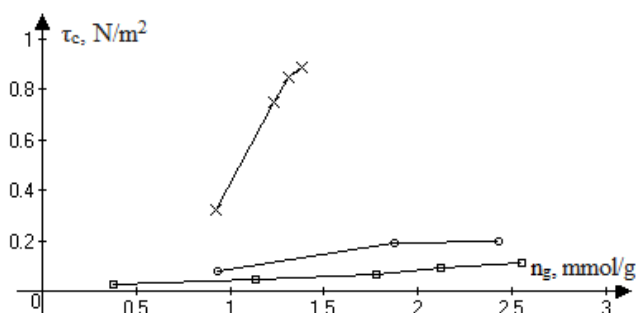


Figure 4. Dependence of the shear stress on the degree of surface modification silica: □ – 2% Ludox HS-40; ○ – 2% Aerosil-380; × – 4% Aerosil-380

As can be seen from the figure, in all the suspensions studied, the shear stress increases with increasing hexylamine concentration and, correspondingly, with an increase in the degree of hydrophobization of the solid surface. At the same concentration of the solid phase (2%) and degree of hydrophobization of the solid surface $n_g = 2.4$, the shear stresses in suspensions of Aerosil and Ludox were equal to 0.2 and 0.1 N/m^2 , respectively. An increase in the concentration of the solid phase of silica leads to an increase in the value of the shear stress even at a lower degree of hydrophobization of

the surface. In particular, the shear stress in Aerosil suspensions at a solid phase content of 4% was $0.9 N/m^2$ at $n_g = 1.45$. We note that the process of aggregation of silica particles in the initial suspensions proceeds to varying degrees as the degree of their hydrophobicity increases. According to the sedimentation analysis, the particle sizes in the aerosil suspension always exceeded the particle sizes in the Ludox suspension at the same mass content of the solid phase in the initial suspension. For example, in suspensions of 2% Ludox HS-40 + 40 mmol/l hexylamine, the average radius of aggregated particles was $8.5 \mu m$. The average radius of aggregates in a suspension with a mass concentration of 2% Aerosil increases to $65 \mu m$ with an increase in the concentration of hexylamine to 40 mmol/l. Although the stability of all the investigated foams increases with an increase in the degree of hydrophobicity of the particles and correlates with an increase in the shear stress, the nature of their fracture and the lifetime are determined by the value of the contact angle of the particles in the initial suspension and the degree of their aggregation. As can be seen from Table 1, the most stable foams are obtained from Aerosil suspensions.

Table 1. Dependence of foam stability 1-2 cm in height from the degree of hydrophobization of a solid surface

Concentration of solid phase in the initial suspension	n_g , mmol/g	ΔP , kPa	D, %	t, min
20% Ludox HS-40	0,055	1	100	10
20% Ludox HS-40	0,61	4	5	65
2% Ludox HS-40	0,55	5	100	15
4% Aerosil-380	0,25	3	13	30
6% Aerosil-380	1,73	3	1	30
2% Aerosil-380	2,4	3	5	30

At $n_g = 1.73$ and 2.4, and corresponding increase in the contact angle of Aerosil wetting from 35 to 45 degrees, no more than 5% of the foam layer is destroyed within 30 minutes under the effect of an applied pressure drop of 3 kPa. Earlier it was noted that the contact angle of solid particles $\theta_w = 45^\circ$ corresponds to the maximum energy reduction at the water/ gas interface due to the adsorption of hydrophobized silica. However, the stability of foams obtained from Aerosil suspensions decreases with further increase in the relative degree of hydrophobization of the solid surface (more than 2.5) and exceeding (more than 50°) the wetting contact angle. A possible reason for the decrease in the stability of foams is a significant (up to $100 \mu m$) aggregation of particles in the initial suspension and weak fixation of such large particles at the interface. A similar phenomenon was observed in [14]: when the concentration of valeric acid was increased above 40 mM, the foaming capacity decreased, correlating with an increase in the viscosity of the suspensions. Foams derived from Ludox suspensions are less stable than those obtained from Aerosil suspensions (Table 1). The destruction of the froth layer (by nature and speed) is similar to foams stabilized

by nonionic surfactants. Suspensions containing Ludox, as shown earlier, are characterized by small (with a radius of no more than 5 μm) aggregate sizes in the initial suspension, even at the contact angles of particles $\theta_w = 40^\circ$. As can be seen from Table 1, the lifetime of the foam obtained from a Ludox slurry with a mass solids content of 20% and the degree of hydrophobization of the surface ($n_g = 0.055$) until its complete failure was 10 minutes (with an applied drop of pressure of 1 kPa). Note that with a less (2%) content of the solid phase in the initial suspension and the same degree of hydrophobization of the solid surface, the lifetime of the foam is also small and amounts to several minutes. The increase in the relative degree of hydrophobization of the solid surface of the Ludox to 0.55 and 0.61 ($\theta = 20^\circ$ and 22°), although it increases the stability of the obtained foams, but affects the properties and the nature of their destruction, depending on the concentration of the stabilizer particles. In particular, from a sol of 2% Ludox + 10 mmol / l hexylamine, foams with a volume fraction of a liquid of less than 0.01 can be obtained [16]. Such foams are completely layer-by-layer destroyed under the action of even a small applied pressure drop. Foams made from a sol with a high solids content (20% Ludox) and the same wetting edge of solids are destroyed intensively during the first five minutes (65% of the height of the column, Table 1). However, the concentration of particles of the solid phase during the destruction of the foam and the observed gelling process can be one of the reasons for the increased stability of the remaining layer. It should be noted that a small concentration of solid stabilizer particles in the initial suspension, even with a significant degree of hydrophobization corresponding to the edge angle of 50° , does not provide a stable foam (78% of foam from the Ludox slurry with a 0.5% solid phase content is rapidly destroyed within 5 minutes). Figure 6 shows the change in the lifetime of a foam layer from a suspension of 20% Ludox HS-40, depending on the degree of hydrophobization of the solid surface.

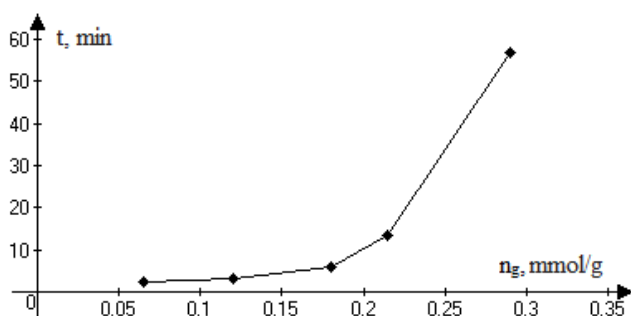


Figure 5. Dependence of the lifetime of the foam layer (2-3 mm in height), obtained from a suspension of 20% LudoxHS-40 + hexylamine, on the degree of modification of the solid surface with hexylamine

As can be seen from the figure above, the lifetime of such a foam (before its complete destruction) increases at n_g more than 0.2 and is 57 minutes at a degree of hydrophobization of the surface of 0.3. It was shown in [11] that the degree of hydrophobization of the solid surface of Ludox particles is less than 0.2 corresponds to the formation of unstable isolated

foam films with a thickness of 8-10 μm of the presumably bilayer structure and unstable foam: the lifetime of 1 cm of foam until it is completely destroyed from 5 to 20 minutes. It has also been established that the formation of a stable foam film from a Ludox sol with a mass solids content of 20% occurs at a degree of hydrophobization of a solid surface of 0.28 mmol/g. Such films had a thickness of 24.5 μm and were partially destroyed (20% of the area for 30 minutes, the rest of the film existed for several hours, their stability correlated with the formation of stable foams.

It should be noted that films from Aerosil suspensions were more stable than films obtained from Ludox sol, with the same mass content of solid particles in the initial suspension and the same degrees of hydrophobization of their surfaces. In particular, the thicknesses of films obtained from Aerosil and Ludox sols (with their mass content in the initial suspension of 2% and $n_g \approx 2.3$) were 132 and 8.9 μm . Such films could remain stable for 190 and 70 minutes, respectively. We also note that stable films of these silica suspensions are not formed with a small content of the solid phase (less than 1%), even with a significant value of the relative degree of hydrophobization of the surface of the silica particles ($n_g = 5$ mmol/g). In particular, films with an Aerosil content of 0.5% even with a relative degree of hydrophobization of the surface $n_g = 5$ were completely destroyed (burst), similar to films obtained from Ludox sols. Of 4 and 6% Aerosil suspensions (at $n_g = 1.4$ and 1.17), very stable films were obtained, with a thickness of 155 and 199 μm . Such films were not destroyed for an unlimited time, gradually turning into solid plates. Probably, in such films, the dispersion medium, together with the adsorption layers, is a hard gel. Obviously, when the film is in contact with air, a rapid gel formation of the dispersion medium occurs, as a result of which the mobility of the water layer in the gravitational field is lost, and thinning of such a film is possible only when a pressure drop is applied.

We also note that at the above degrees of hydrophobization of the aerosol, stable foams are formed. Within 30 minutes, under the applied differential pressure ($\Delta P = 3$ kPa), no more than 1% of the foam layer obtained from Aerosil with a mass solids content of 6% and a degree of hydrophobization of $n_g = 1.73$ is destroyed.

CONCLUSIONS

1. Stable foams are formed from silica suspensions when the relative degree of hydrophobization of the particle surface varies from 1.4 to 2.4, which corresponds to a change in the contact angles of solid particles from 32° to 45° degrees and correlates with a marked decrease in the relative interfacial energy at the water/ gas.
2. The low degree of hydrophobization of the particle surface ($n_g \leq 0.25$, $\theta \leq 19^\circ$) does not lead to the formation of stable foams, even with a significant (20%) solids content in the initial suspension.
3. When the degree of hydrophobization of a solid surface $n_g = 0.55 - 0.61$ ($\theta \approx 20 - 22^\circ$) is reached, foams are formed according to the nature of failure and stability,

like foams obtained from nonionic surfactants: low stability under the action of applied pressure drops and complete destruction of the foam.

4. Aggregation of Aerosil particles in the initial suspensions as the degree of their hydrophobization increases leads to the formation of more stable foams and foam films as compared to those obtained from the Ludox sols.

REFERENCES

- [1] Gonzenbach U.T., Studart R.R., Tervoort E. et.al., 2006, "Stabilization of foams with inorganic colloidal particles", *Langmuir*, 22, pp. 10983-10988.
- [2] Alargova R.G., Warhadpande D.S., Paunov V.N. et.al., 2004, "Foam superstabilization by polimer microrods", *Langmuir*, 20, pp. 10371-10374.
- [3] Velikov K.P., Velev O.D., 2007, *Colloid Stability and Application in Pharmacy* (Ed. Th.F.Tadros). Wiley-VCH Verlag GmbH and Co. KgaA, k3.
- [4] Dickinson E., Etteiaie R., Kostakis T. et.al., "Factors Controlling the Formation and Stability of Air Bubbles Stabilized by Partially Hydrophobic Silica Nanoparticles", 2004, *Langmuir*, 20, pp. 8517-8525.
- [5] Hassander H., Johansson B., Törnell B., 1989, "The mechanism of emulsion stabilization by small silica (Ludox) particles", *Colloids and Surfaces*, 40, pp. 93-105.
- [6] Binks B.P., Lumsdon S.O., 2000, "Influence of Particle Wettability on the Type and Stability of Surfactant-Free Emulsions", *Langmuir*, 16, pp. 8622-8631.
- [7] T.S.Horozov T.S., Binks B.B., Aveyard R., 2006, "Effect of particle hydrophobicity on the formation and collapse of fumed silica particle monolayers at the oil-water interface", *Colloids and surface A: Physicochem. Eng. Aspects*, 282-283, pp. 377-386.
- [8] Menon V.B., Wasan D.T., 1988, "Characterization of oil-water interfaces containing finely divided solids with applications to the coalescence of water-in-oil Emulsions: A review", *Colloids and Surfaces*, 29, pp. 7-27.
- [9] Nushtaeva A.V., P.M. Kruglyakov P.M., 2004, "Investigation of model emulsion films stabilized by solid particlesthickness of films, their stability, and interfacial tension", *Colloid J.*, 66(4), pp. 456-465).
- [10] Kruglyakov P.M., Elaneva S.I., Vilкова N.G. et.al., 2011, "About mechanism of foam stabilization by solid particlkes", *Advances in Colloid and Interface Science*, 165, pp. 108-116.
- [11] Vilкова N.G.,Elaneva S.I.,Kruglyakov P.M. et.al., 2011, "Foam films from hehylamine stabilized by the silica particles", *Mendelev comm.*, 21, pp. 344-345.
- [12] Vilкова N.G., Nushtaeva A.V., 2013, "Influence of hydrophobized solid particles on the reduction of interfacial tension", *Mendelev comm.*, 23, pp. 155-156.
- [13] Vilкова N.G., Nushtaeva A.V., 2013, "Vliyanie ponigheniya meghfaznogo natyagheniya na svoistva pen i emulsii stabilizirovanih tverdimi chasticami", *Izvestiya vuzov. Povolghskii region*, 1, pp.127-134.
- [14] Gonzenbach U.T., Studart R.R., Tervoort E. et.al., 2006, "Ultrastable particle-stabilised foams", *Angew. Chem. Int. Ed. Engl.*, 43, pp. 3526-3530.
- [15] Exerowa D., Kruglyakov P.M., 1998, *Foam and foam folms*. Elsevier, Amsterdam.
- [16] Vilкова N.G., Elaneva S.I., 2013, "Vliyanie gidrofobnosti chastic kremnezema na ustoichivost pen i pennih plenok", *Izvestiyavishshih uchebnihi zavedenii. Himiya I himicheskaya tehnologiya* (Russian Journal of Chemistry and Chemical Technology), 56(9), pp. 62-66.