

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## The Effect of Organic Liquids on the Stability of the Films and Foams Stabilized by Surfactants of Various Types.

Natalya G Vilkova<sup>1\*</sup>, and Svetlana I Mishina<sup>2</sup>.

<sup>1</sup>Penza State University of Architecture and Construction, Department of Physics and Chemistry, 28 GermanaTitovastr., Penza, Russia.

<sup>2</sup>Penza State University, Department of Chemistry and Theory and Methodology of Teaching Chemistry, 40 Krasnaya str., Penza, Russia.

### ABSTRACT

Petroleum products are one of the most common anthropogenic pollutants in water bodies. Flotation methods are widely used to purify water from such pollutants. The efficiency of the process is determined in much by the stability of the dispersed systems used for flotation. The purpose of the work is to investigate the effect of organic liquids on the stability of macroscopic foam films and foams stabilized by surfactants of various types. The following results were obtained. The stability of the isolated film decreased with an increase in its area. Films obtained from ionic and nonionic surfactants showed greater stability when in contact with hydrocarbon droplets compared to the interaction with drops of alcohol. Foam containing protein and surfactant in a certain ratio remains stable in the presence of diesel fuel in water and provides an efficient separation of organic liquid from the aqueous solution.

**Keywords:** foam, foam film, ionic surfactants, nonionic surfactants, diesel fuel, foam stability.

*\*Corresponding author*

## INTRODUCTION

Petroleum products are one of the most common anthropogenic pollutants in water bodies. Flotation methods are widely used to purify water from such pollutants [1-6]. The efficiency of the process is determined by the content of oil in the water, the stability of the dispersed systems formed, the properties of chemicals (surfactants, coagulants) that improve the quality of water treatment.

The stability of foams formed from aqueous solutions containing petroleum products when adding surfactant and dispersed gel particles to solutions was studied in [1]. Foam stability depended on the amount of surfactant, particle concentration, salt content, oil concentration, and gas-liquid ratio. The authors of this work consider the change in the value of the surface tension and viscosity of the solution as the reason for increasing the stability of foams. The method of aggregation of nanotubes at the oil / water interface aggregation (OWIA) was proposed in [2] to remove carbon nanotubes (CNT) from aqueous suspension. It is shown that the aggregation of CNT at the oil / water interface is possible at a certain pH of the water ( $1.8 \geq \text{pH} \geq 13.2$ ) or with the addition of a cationic surfactant cetyltrimethylammonium bromide, CTAB (0.075-1 mM). In the OWIA process, more than 99% of the carbon nanotubes were removed from the water, and the CNT residues in the water were less than 1 mg / l.

The flotation method was used to treat oil-in-water emulsions (O / W emulsions) obtained from synthetic oils by the addition of chemicals such as the cationic surfactant CTAB and coagulants. [3]. In the work [4] foam flotation, operating in continuous mode, was used for cleaning oily wastewater. A model emulsion (contaminating oil in water) and sodium dodecyl sulfate as a blowing agent were used. The effect of the electrolyte, the air flow rate, and the retention time of the hydraulic fluid on the productivity of the process, were studied.

The process of flotation separation of organic liquids strongly depends on the stability of the formed foam and foam films containing the organic phase [7]. The effect of organic substances on the foams stability is complex, and similar studies are usually conducted in the study and description of defoaming processes [8-10]. The review [8] gives an analysis of the mechanisms of the effect of an organic liquid on the stability of foams. The role of asymmetric foam films for the stability of these disperse systems is noted. These issues were also investigated in detail in firefighting [10]. It was found that the rate of destruction of aqueous films is determined by the intensity of diffusion penetration or extraction of alcohol from mixed organic fuels. With the accumulation of alcohol molecules at the water-organic interface, a layer consisting of a mixture of an aqueous solution and an alcohol is formed. The destruction of the insulating film is due to the desorption of the foaming agent molecules from the interphase boundary.

The destruction of foams containing organic liquids can be caused by the following reasons:

1. the formation in the foam channels of a mixture of organic liquid with a solution (in the case, for example, of ethyl alcohol);
2. coagulation of drops of emulsified organic liquid in the Plateau border;
3. desorption of surfactant stabilizer molecules from the surface of foam films;
4. formation of unstable foam films containing drops of the organic phase.

Various methods are used to assess the defoaming ability of substances: observation of the behavior of a model foam film (usually macroscopic) when an antifoamant drops are applied to it; observation of the behavior of the foam after the introduction of antifoam (the lifetime of the foam layer), monitoring the nature of the destruction of dynamic foam.

The purpose of the work is to investigate the effect of organic liquids on the stability of macroscopic foam films and foams stabilized by surfactants of various types.

**MATERIALS AND METHODS OF RESEARCH**

**Materials**

Gelatin used technical, anionic surfactants: sodium dodecyl sulfate (DDSNa), sodium dodecylbenzenesulfonate (DDBSNa), nonionic surfactant-Triton-X100, technical diesel fuel (DT), density 0.788 g / ml

**Methods of research**

To form the film, round frames of diameter  $d = 0.4\text{ cm}$ ,  $0.7\text{ cm}$ ,  $1\text{ cm}$ , made of copper wire were used. The frames were immersed in a foaming agent solution and a drop of DT was applied from the syringe. The lifetime of the macroscopic foam films with the applied organic liquid was measured.

The comparative stability of foams containing an organic phase was determined from the lifetime of a foam column of a certain height under the action of an applied pressure drop [11-13]. To produce the foam, a POR-40 generator 3.5 cm high and a 4.5 cm diameter porous filter was used. The test solution was poured into the cell (the liquid volume was  $2.25\text{ cm}^3$ ). Under the filter, a reduced (compared to atmospheric) pressure equal to 1-1.5 kPa was created. The time of complete destruction of the foam column, 1-2 cm in height, was fixed. It was also observed for layer destruction of the foam pillar.

**RESULTS AND DISCUSSION**

As noted earlier, to obtain quantitative characteristics of defoaming ability, a direct or indirect determination of the decrease in foam stability (lifetime) or a decrease in its volume under the influence of a certain amount of defoamer is used. These characteristics are obtained most often based on the average lifetime of the foam or the relative (as compared with foam without additives) lifetime of the foam in the presence of antifoam. In this study, the time for the complete destruction of the foam column ( $H = 1-2\text{ cm}$ ), obtained from various foaming agents, with the addition of organic matter and without it under the action of an applied pressure drop, was recorded.

Correlation between the stability of foams and foam films with the use of the Foam Pressure Drop Technique method was considered in [11, 13]. The stability of a foam film as an element of the foam structure can determine the stability of the foam as a whole. However, there is no one-to-one correspondence between the stability of foams and films. In particular, the destruction of foam from a solution of a nonionic surfactant, Triton X-100, occurs at a lower ( $P_o = 7\text{ kPa}$ ) capillary pressure in the Plateau border (compared to a film breaking pressure of 100 kPa) [11]. A similar pattern is noted in the study of films and foams obtained from a solution of  $2 \cdot 10^{-4}\text{ mol / dm}^3$  NP-20 +  $0.2\text{ mol / dm}^3$  NaCl. The maximum capillary pressure in the foam was  $2 \cdot 10^4\text{ Pa}$ , the insulated films were destroyed at a pressure of  $10^5\text{ Pa}$ . At the same pressure, foams and foam films obtained from a solution of the lysozyme protein in the presence of an electrolyte were destroyed.

Stability of macroscopic foam films of different area, obtained from solutions of ionic surfactants (sodium dodecylbenzenesulfonate DDBSNa, sodium dodecyl sulfate DDSNa) and nonionic surfactant (Triton X-100) in interaction with organic substances is shown in Table 1.

**Table 1: Stability of foam films obtained from solutions of various surfactants when interacting with diesel fuel and ethanol.**

The composition of the initial solution	The organic phase	The area of the frame, $\text{cm}^2$	The lifetime and the nature of the destruction
$10^{-3}\text{ mol / l Triton X-100} + 0,4\text{ mol / l NaCl}$	Diesel fuel	0,385	From 1.5 hours to 24 hours
$2,46 \cdot 10^{-4}\text{ mol / l DDBSNa} + 0,1\text{ mol / l NaCl}$	Diesel fuel	0,385	1 hour 10 minutes
$10^{-3}\text{ Triton X-100} + 0,4\text{ mol / l NaCl}$	Ethanol	0,126	18 minutes

2,4610 <sup>-4</sup> mol/l DDBSNa + 0,1 mol / l NaCl	Ethanol	0,126	13 minutes
10 <sup>-3</sup> mol / l Triton X-100 + 0,4 mol / l NaCl	Ethanol	0,385	Destroy instantly
2,4610 <sup>-4</sup> mol / l DDBSNa + 0,1 mol / l NaCl	Ethanol	0,385	Destroy instantly
5·10 <sup>-4</sup> mol/l DDSNa + 0,02% gelatin	Diesel fuel	0,385	24 hour
5·10 <sup>-4</sup> mol/l DDSNa + 0,02% gelatin	Diesel fuel	0,785	1,5 hour

Table 1 shows the lifetime of foam films obtained from solutions of nonionic and ionic surfactants. The stability of the insulated film decreased with an increase in its area. Films obtained from ionic and nonionic surfactants showed greater stability when in contact with hydrocarbon droplets compared to the interaction with drops of alcohol.

It was also established that the stability of the films increased with a decrease in the diameter of the foam film (Table 1). In particular, the lifetime of films with an area of 0.785 cm<sup>2</sup> obtained from solutions of Triton X-100 + 0.4 mol / l NaCl varied from 5 seconds up to 60 minutes. Films of the same area from a solution of DDBSNa + 0.1 mol/l NaCl were destroyed in 5 seconds. The lifetime of films stabilized by ionic and nonionic surfactants increased with decreasing the film area to 0.385 cm<sup>2</sup> and exceeded 60 minutes. It should be noted that stable films (when they were in contact with diesel fuel) were obtained from a solution of ionic surfactant sodium dodecylsulfate and gelatin. In particular, macroscopic films obtained from an aqueous solution of 5·10<sup>-4</sup> mol / l DDSNa + 0.02% gelatin, with an area of 0.385 and 0.785 cm<sup>2</sup> (Table 1) were stable for 24 and 1 hours, respectively. It will be shown below that the foams stabilized by ionic surfactant and gelatin show considerable stability, and their use is promising in the processes of removing diesel fuel from aqueous solutions.

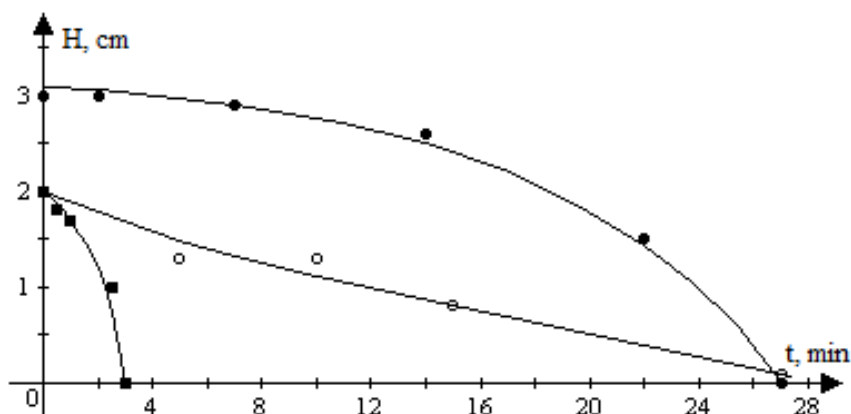
Films of area 0.126 cm<sup>2</sup>, obtained from solutions of 10<sup>-3</sup> mol / l Triton X-100 + 0.4 mol/l NaCl and 2.46·10<sup>-4</sup> mol/l DDBSNa + 0.1 mol / l NaCl, were relatively stable. Their lifetime on contact with ethyl alcohol was 18 and 13 minutes, respectively. Films of a larger area (0.785-0.385 cm<sup>2</sup>) obtained from solutions of these foaming agents were destroyed instantaneously when an ethanol droplet was deposited on their surface.

A different character of the destruction of foams stabilized by ionic and nonionic surfactants under the influence of applied pressure drops was established earlier. The foams stabilized by ionic surfactants are the most stable. The lifetime of the foam (height 2 cm) obtained from the DDSNa solution was 1.5 hours at a temperature of 25°C and an applied pressure drop of 10 kPa. The lifetimes of the foam layers obtained from DDBSNa, two and one centimeter in height, were 180 and 100 minutes, respectively (with a pressure drop of 2 kPa). In this study, a significant decrease in the lifetime of the foam stabilized by DDBSNa and Triton X-100 was observed when even small amounts of diesel fuel were added to the initial solution.

A change in the height of a foam layer (initial height 1 cm), obtained from Triton-X-100 + 0.4 mol/l NaCl + 24 mg/l diesel fuel under the action of an applied pressure drop equal to 1 kPa was studied.

It was found that 85% of the foam layer was destroyed within three minutes, even with a small (24 mg/l) content of diesel fuel in the initial solution at 26.4°C. In the absence of an organic liquid, as noted earlier, the lifetime was one hour at such same pressure drop and temperature.

Figure 1 shows the change in the height of a column of foam obtained from a solution of Triton X-100 + 0.4 mol / l NaCl, without the addition of diesel fuel (curve with point ●) and its additive (curve with point ■). As can be seen from the figure 1, the addition of even small amounts of diesel fuel results in a complete destruction of the foam column 2 cm high for 3 minutes. Earlier it was shown that under the influence of applied pressure drops, it is possible to achieve maximum capillary pressures of 7-8 kPa in foam stabilized by Triton-100. It is interesting to note that in the presence of an organic liquid, the equilibrium capillary pressure is not established even for small values of the applied pressure drops. In particular, at a diesel fuel concentration of 24 mg / l and an applied pressure drop of 1000 Pa, an avalanche-like destruction of the foam from the Triton X-100 solution was observed even when the capillary pressure reached 350-400 Pa.



**Fig 1: Kinetics of foam destruction.**

- –  $10^{-3}$  mol/l Triton X-100 + 0,4 mol/l NaCl + 24 mg/l diesel fuel,  $\Delta P=1$  kPa,  $H=2$  cm;
- –  $2 \cdot 10^{-3}$  mol/l DDSNa + 0,01% gelatin + 312 mg/l diesel fuel;
- –  $10^{-3}$  Triton X-100 + 0,4 mol/l NaCl,  $\Delta P=1$  kPa

A comparison of the stability of a foam obtained from an ionic surfactant DDBSNa with and without an organic phase was carried out. As noted earlier, the lifetimes of foam layers of 2 and 1 cm in height obtained from DDBSNa were 180 and 100 minutes, respectively (at  $\Delta P = 2$  kPa). At diesel fuel concentrations of 25 and 150 mg / l, the lifetime was 800 and 200 seconds, respectively (at  $\Delta P = 1$  kPa), and the expansion ratio in such foams did not exceed 35. Thus, diesel fuel additives (24 mg / l and more) to a solution of a nonionic surfactant Triton X-100 and ionic surfactant DDBSNa in all the investigated cases were defoaming action.

The stability of foams obtained from a solution of a nonionic surfactant depended on the concentration of ethyl alcohol in the initial solution. At an ethanol concentration of 78.9 mg / l, the foam stability to failure was 13 minutes. 38 seconds. In this case, foams of high expansion ratio ( $n = 300$ ) are formed. Increasing the alcohol concentration to 23670 mg / l dramatically reduces the foam life time to 8 s. It is known that the desistance of foam formation occurs when the concentration of ethyl alcohol is equal to 25%. The rapid destruction of foams stabilized by the ionic surfactant DDBSNa in the presence of diesel fuel was shown earlier.

It is interesting to note that some of the foams obtained from aqueous solutions of ionic surfactants and protein, taken in certain ratios, remain stable in the presence of diesel fuel. In particular, with a periodic foaming regime, foams from a solution of  $2 \cdot 10^{-3}$  mol / l DDSNa + 0.1% gelatin are most resistant (in 27 minutes 95% of the foam layer is destroyed, under the action of an applied pressure drop  $\Delta P = 2$  kPa). Foams obtained from solutions of  $5 \cdot 10^{-4}$  mol / l DDSNa + 0.02% gelatin and  $2 \cdot 10^{-3}$  mol / l DDSNa + 0.01% gelatin are less stable: more than 90% of the foam column is destroyed in 5 and 13 minutes, respectively.

It was established earlier that under the influence of applied pressure drops it is possible to form foams of high expansion ratio ( $n = 1000$  and more). For example, the expansion ratio of the foam 2 cm in height obtained from a solution of DDSNa + 0.4 mol / l is equal to 1050 at an applied pressure drop  $\Delta P = 1$  kPa.

The presence of an organic phase slows the process of syneresis even under the action of applied pressure drops. It was noted that the expansion ratio of the foams from DDBSNa did not exceed 35 at the time of its destruction. The maximum expansion ratio in the foam from the solution  $2 \cdot 10^{-3}$  mol / l DDSNa + 0.1% gelatin and  $5 \cdot 10^{-4}$  mol / l DDSNa + 0.02% gelatin was 180 and 110, respectively.

Further studies were aimed at extraction the dissolved diesel fuel with foam containing gelatin and sodium dodecylsulfate. To the water containing a certain amount of surfactants and gelatins, diesel fuel was added and its amount was determined on the fluorite ( $C_{in}$ ). Table 2 shows the decrease in the concentration of dissolved diesel fuel in the initial solution after the organic phase has been removed by foam. It was found that when using the initial solution of the composition  $5 \cdot 10^{-4}$  mol / l DDSNa + 0.02% gelatin and  $C_{gelatin}/$

Csurfactant ratio equal 1.38, the organic matter in the initial solution was reduced by 86.6%. As was shown in [14, 15], the gelatin/ surfactant ratio in the initial solution determines the composition and structure of adsorption layers and affects the properties of the disperse system. Foam concentration of gelatin from its aqueous solution with sodium dodecylsulfate was studied in [16]. In this paper, it is shown that the stability of the foam at a  $C_{\text{gelatin}}/C_{\text{surfactant}}$  ratio equal 1.74 is retained even in the presence of organic matter. Therefore, a noticeable reduction in the concentration of diesel fuel was observed when using a solution of the composition:  $2 \cdot 10^{-3} \text{ mol / l DDSNa} + 0.1\% \text{ gelatin}$ .

**Table 2: Change in the concentration of dissolved diesel fuel using foams of different composition (initial concentration of organic liquid is 320 mg / l).**

The content of DDSNa in the initial solution	The content of gelatin in the initial solution	Reduction of the organic liquid concentration in the initial solution
$5 \cdot 10^{-4} \text{ mol/l}$	0,02%	86,6%
$2 \cdot 10^{-3} \text{ mol/l}$	0,01%	90,9%
$2 \cdot 10^{-3} \text{ mol/l}$	0,10 %	91,3%

### CONCLUSION

The stability of the isolated film decreased with an increase in its area. Films obtained from ionic and nonionic surfactants showed greater stability when in contact with hydrocarbon droplets compared to the interaction with drops of alcohol. Foam containing protein and surfactant in a certain ratio, remain stable in the presence of diesel fuel in water and provides an efficient separation of organic liquid from the aqueous solution.

### REFERENCES

- [1] Zhao, G., Dai, C., Wen, D., & Fang, J. (2016). Stability mechanism of a novel three-Phase foam by adding dispersed particle gel. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, 497, 214–224.
- [2] Lili, G., Huayi, Y., Hua, Z., Xuhui, M., Fuxing, G., & Dihua, W. (2014). Separation of dispersed carbon nanotubes from water: Effect of pH and surfactants on the aggregation at oil / water interface. *Separation and Purification Technology*, 129(29), 113-120.
- [3] Simjoo, M., Rezaei, M. T., Andrianov, A., & Zitha, P. L. J. (2014). Foam stability in the presence of oil: effect of surfactant concentration and oil type. *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, 438, 148-158.
- [4] Karhu, M., Leiviskä, T., & Tanskanen, J. (2014). Enhanced DAF in breaking up oil-in-water emulsions. *Separation and Purification Technology*, 122, 231-241.
- [5] Apichay, B., Orathai, P., Suchaya, N., Jittipan, C., & Sumaeth, C. (2013). Cutting oil removal by continuous froth flotation with packing media under low interfacial tension conditions. *Separation and Purification Technology*, 107(2), 118-128.
- [6] Suzuki, Y. (2005). Removal of Emulsified Oil from Water by Coagulation and Foam Separation. *Separation Science and Technology*, 40(16), 3407-3418.
- [7] Vilko, N. G. (2016). Effect of the properties of foams and foam films on the flotation release of an organic liquid. *Izvestiyavuzov. Povolghskii region. Estestvennienauki*, 2, 30-38.
- [8] Kruglyakov, P. M. (1994). Mechanisms of defoaming action. *Uspehiihimii*, 63(6), 493–505.
- [9] Pletnev, M. U., Vlasenko, I. G., Ivanova, N. B., & Koghanov, B. P. (1983). To the problem of contact interaction of water foams with polar organic liquids. *Colloid Journal*, 35(5), 930-935.
- [10] Sharovarnikov A. F., Molcanov V. P., Voevoda S. S., & Sharovarnikov, S. A. (2002). *Extinguishing fires of oil and oil products*, 370-373.
- [11] Exerowa D., & Kruglyakov, P. M. (1998). *Foam and foam films. Theory, experiment, application*. Elsevier: Amsterdam.
- [12] Vilko, N.G., Kruglyakov, P.M., & Malkov, V.D. (1992). Investigation of foam destruction in the centrifugal field. *Mendeleev Communication*, 4, 149-150.
- [13] Vilko, N.G., & Mishina, S.I. (2018). Properties of foams stabilized by hydrophobized silica particles. *International Journal of Applied Engineering Research*, 3, 1763-1767.



- [14] Vustnek, R., Castro, L., &Krechmar, G. (1985). Investigation of the surface properties of gelatin adsorption layers with surfactant additives at the air-solution interface. *Colloid Journal*,37(3), 462-470.
- [15] Izmailova, V. N., Derkach, S. R., Zotova, K. V., &Danilova, R. G. (1993). The influence of hydrocarbon and fluoride surfactants on the properties of gelatin in the volume of the aqueous phase and on the boundary with air. *Colloid Journal*,55(3), 54-90.
- [16] Vilko, N. G., Khaskova, T. N., &Kruglyakov, P. M. (1995). Foaming concentration of gelatine from it's solution containing sodium dodecyl sulfate. *Colloid Journal*,57(6), 741-744.