

DOI:10.29013/EJHSS-25-3-9-14



# THE INFLUENCE OF SURFACTANTS ON CLEANING HARD SURFACES FROM OIL CONTAMINANTS

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Cite: Stanislav D., Maryaskin Y.B., Maslak H.S. (2025). The Influence of Surfactants on Cleaning Hard Surfaces From Oil Contaminants. European Journal of Technical and Natural Sciences 2025, No 3. https://doi.org/10.29013/EJHSS-25-3-9-14

### **Abstract**

The factors influencing the cleaning of hard surfaces from oil spills are considered. The role of surfactants in this process is highlighted.

**Keywords:** degree of surface cleaning, interfacial tension, contact angle, overcoming cohesive interactions

# Introduction

Oil spills on hard surfaces present significant challenges in both environmental management and industrial cleaning processes. Effective removal of oil contaminants is critical to maintaining operational efficiency, safety, and environmental standards. Among the numerous strategies available, the use of aqueous surfactant solutions has emerged as a versatile and effective method for cleaning oil-contaminated surfaces.

Surfactants, with their amphiphilic nature, reduce interfacial tension and promote the detachment of oil from substrates. However, their performance depends on a complex interplay of thermodynamic and kinetic factors, including adsorption at phase boundaries, micelle formation, and the disruption of cohesive forces within the oil layer.

Understanding these interactions is essential to optimize cleaning efficiency and select appropriate surfactant formulations for specific applications.

This study investigates the role of various surfactants in the degreasing process, focusing on their interfacial properties and cleaning capabilities. By analyzing the influence of surfactant adsorption and micellar activity at critical phase boundaries, this work aims to provide insights into the mechanisms that govern oil removal. Additionally, the effects of external factors such as temperature, mixing, and energy inputs are considered to highlight potential pathways for enhancing cleaning performance.

It is well known that aqueous solutions of surface-active substances (surfactants) are used in various technological processes. Consider, for example, the use of such solutions for cleaning hard surfaces from oil stains.

In aqueous solutions of surfactants, at a sufficiently high concentration, a certain part of the surface-active particles participates in two processes: it is adsorbed at the interface between the solution and air and forms micelles in the main phase.

When an oiled substrate is immersed in such a solution, new phase boundaries are

formed: oil-solution, substrate-solution, substrate-oil, at which adsorption of surfactants is also possible. Such a change in the initial state in turn causes the formation of new micellar structures in the solution.

Several compounds were selected as the surface-active additives to be investigated, the composition of which is shown in Table 1.

Chemical composition of the compounds used (Abramzon A. A., 1979).

**Table 1.** Chemical composition of the compounds used

Name	Chemical formula		
Sintanol DS-10	$C_n H_{2n+1} O(C_2 H_4 O)_m$ ; n=10-18, m=8-10		
OS-20	$C_n H_{2n+1} O(C_2 H_4 O)_m$ ; n=14-18, m=20		
Sulfonol NP-3	$C_n H_{2n+1} C_6 H_4 SO_3 Na; n=10-12$		
Dispersing agent NF	NaO <sub>3</sub> SC <sub>10</sub> H <sub>6</sub> CH <sub>2</sub> C <sub>10</sub> H <sub>6</sub> SO <sub>3</sub> Na		
" Volgonate "	$(C_n H_{2n+1} C_m H_{2m+1}) CHSO_3 Na; n+m=11-17$		
Tetrabutylammonium iodide	$(C_4H_9)_4NI$		

Figure 1.

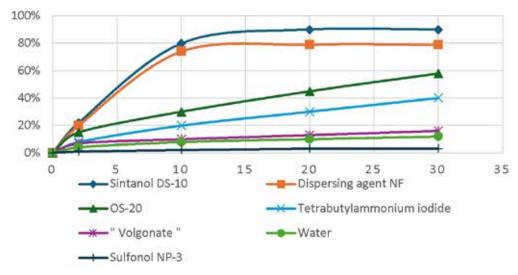


Figure 1 shows the dependence of the degree of cleaning of steel samples on the duration of degreasing in aqueous solutions of selected components, measured according to the method described in (Maryaskin Yu. B., Danilov F. I., Loshkarev M. A., 1981). It can be seen from the data that these compounds have different abilities to remove impurities. The highest degree of cleaning is achieved in a solution of Sintanol DS-10, the lowest – in solutions of anion-active components – "Volgonat" and Sulfonol NP-3.

According to the thermodynamics of the cleaning process, this takes place at the three-phase interface substrate – oil – solution.

The change in the free surface energy of this interface when the contamination is torn off  $(\Delta G)$  is the same (Friedrichsberg D. A., 1984):

$$\Delta G = (\gamma_{s/s} + \gamma_{o/s} - \gamma_{s/o})S, \qquad (1)$$
 where  $\gamma_{s/s}, \gamma_{o/s}, \gamma_{s/o}$  – are the interfacial tensions at the substrate – solution, oil – solution and substrate – oil interfaces; S – is the surface area of the contaminant-free substrate.

According to (1), spontaneous detachment of impurities is possible under the condition  $\Delta G < 0$ ,  $\gamma_{s/s} + \gamma_{o/s} < \gamma_{s/o}$ . Therefore, effective detergents should ad-

Therefore, effective detergents should adsorb at the interfaces between oil – solution and between substrate – solution (and thus reduce the interfacial tension at these inter-

faces) and not reduce the excess surface energy at the interface between substrate – oil.

Let us now consider the behavior of the compounds used at the specified phase boundaries.

Figure 2.

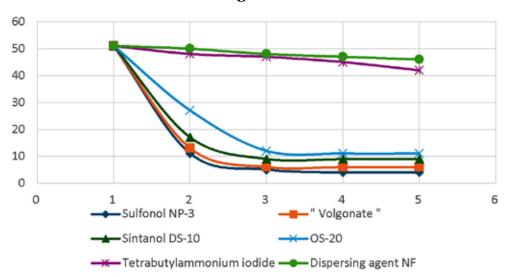


Figure 2 shows the dependence of the value of  $g_{o/s}$  on the concentration of surfactants in the water, measured by the stalagmometric method. The data presented show that the greatest reduction of this value is achieved in solutions of "Volgonat" and Sulfonol NP-3. At the same time, these solutions do not have the ability to remove impurities from the steel surface. Solutions with Dispersing agent NF and Tetrabutylammonium iodide contribute to partial cleaning of the substrate, practically without reducing the value of  $\gamma_{o/s}$ . Molecular surfactants, Sintanol DS-10 and OS-20, reduce the value of  $\gamma_{o/s}$  less than solutions of " Volgonat " and Sulfonol NP-3, remove impurities much more effectively than the latter.

When studying the effect of surfactants on the state of the metal-oil interface, oil-soluble compounds, pentadecanoic acid and pentadecyl alcohol were used in addition to the above-mentioned components. Weighed quantities of these substances were added to a model oil (decane). A drop of water was applied to the surface of the substrate, the sample was immersed in a glass cell filled with a model impurity and the contact angles of wetting  $(\theta)$  in the system steel – water – decane were measured.

The data presented in Table 2 show that sulfonol NP-3 and "Volgonat" as well as oil-soluble substances – pentadecyl alcohol and pentadecanoic acid – are adsorbed at the steel-oil interface (which makes it difficult to fulfill the condition  $\gamma_{s/s} + \gamma_{o/s} < \gamma_{s/o}$ ). This is probably the reason for the low ability of these surfactants to clean the metal surface. At the same time, Sintanol DS-10, Dispersing agent NF and Tetrabutylammonium iodide have practically no influence on the condition of this interface.

**Table 2.** Values of wetting contact angles at the steel-water-decane three-phase interface

surfactants	$\theta$ , $^{o}$
_	66.6
" Volgonate "	106
Sulfonol NP-3	112
Pentadecanoic acid	132
Pentadecyl alcohol	115
Tetrabutylammonium iodide	69.2

surfactants	θ,º		
Sintanol DS-10	67.5		
Dispersing agent NF	66.7		

The investigation of the influence of the adsorption of surfactants on the state of the metal-solution interface was carried out by measuring the contact angle of wetting in the steel-solution-air system.

From Young's equation (Frolov Yu.G., 1989):

 $\sigma_{\rm a/s}{\rm Cos}\theta = \gamma_{\rm s/a} - \gamma_{\rm s/s}$ , (2) where  $\sigma_{\rm a/s}$  is the surface tension at the air-solution interface;  $\gamma_{\rm s/a}$  and  $\gamma_{\rm s/s}$  are the interfacial tensions at the substrate-air and substrate-solution interfaces, respectively;  $\theta$  – is the contact angle.

Considering that in the case of water and surfactant solution, the interfacial tension at the substrate-air interface has the same value:

 $\sigma_{a/s}^{1} Cosq^{1} - \sigma_{a/s}^{0} Cos \ \theta^{\,0} = -\Delta \gamma_{s/s}, \qquad (3)$  where the subscript "1" denotes the corresponding parameters of the surfactant solutions and the subscript "0" denotes the parameters of the background solution (water),  $\Delta \ \gamma_{s/s}$  is the change in interfacial tension at the substrate-solution interface during surfactant adsorption.

The results obtained are summarized in Table 3.

<b>Table 3.</b> The influence of surfactant adsorption on the
state of the interface between steel – solution

surfactants	$\sigma_{_{\rm B/p}}^{}*10^3, { m N/m}$	θ	$-\Delta \gamma_{s/s}^* 10^3$ , N/m
_	72.75	79.2	0
Tetrabutylammonium iodized	67.2	70.5	8.8
Synthanol DS-10	29	16	14.3
Sulfonol NP-3	32.5	27	15.4
Dispersing agent NF	72.75	59.6	23.2

The data presented shows that all surfactants used are capable of being absorbed at the interface between substrate-solution. At the same time, the greatest contribution to reducing the excess energy of the surface layer was achieved when using the Dispersing agent NF.

Summarizing the results, we note the following:

- the highest degree of steel cleaning is achieved in an aqueous solution of Sintanol DS-10, a surface-active additive adsorbed at the substrate-solution and oil-solution interfaces without affecting the energy state of the substrate-oil interface. In this case, the thermodynamic condition for carrying out the purification process is best fulfilled (see analysis of equation 1).
- the low degree of purification in solutions of Sulfonol NP-3 and "Volgonat" is since these components can be absorbed at the substrate-oil interface, fixing the oil on the surface to be purified.

a medium degree of purification obtained with tetrabutylammonium solutions iodide and Dispersing agent NF, organic components that only have adsorption activity at the substrate-solution interface.

In addition to the listed thermodynamic laws, other factors influencing the washing process should also be considered.

The layer of impurities covering the treated surface is a barrier that prevents the fulfillment of the thermodynamic conditions required for the cleaning of the substrate. Therefore, the oil layer must be destroyed in the cleaning process. According to equation (4), the work required to overcome the cohesive forces between the impurity molecules  $(W_k)$  depends on the value of the interfacial tension at the interface between the oil – solution (Frolov Yu.G., 1989):

$$W_k = 2\gamma_{o/s}. (4)$$

From this point of view, the least work to destroy the oil layer should be done in the case of Sulfonol NP-3 and "Volgonat", whose solutions have considerable surface activity at this phase boundary (see Fig. 2). At the same time, as already mentioned, these solutions have a low washing capacity. At the same time, the surface-inactive Dispersing agent NF and tetrabutylammonium iodide ensure a noticeable cleaning of the substrate, which is not possible without destroying the oil layer.

As already mentioned, two processes take place simultaneously in aqueous solutions of surfactants: the adsorption of surface-active components on the surface and the formation of micelles in the main phase. It was suggested in (Maryaskin Y. B., Derman S. E., 2018) that at concentrations well above the critical micelle concentration (which is the case for detergent solutions), the presence of many micelles can influence the phase of delivery of the surfactant to the phase boundary. This is likely to affect the speed of movement of the surfactant to the interphase surface and consequently its kinetic energy.

At the same time, the energy reserve of the surfactant molecules, together with their ability to reduce the interfacial tension, can influence the destruction of the oil layer and thus ultimately the cleaning ability. This is shown in (Maryaskin Y. Derman S., 2021) using the example of two surfactants with similar adsorption properties but different energy reserves.

It is likely that in solutions of Dispersing agent NF and Tetrabutylammonium iodide, in which no micellar structures are present, the rate of release of molecules to the surface is high enough to ensure partial destruction of the oil barrier and contact of the components of the cleaning solution with the surface of the substrate.

It is also possible that the reserve of kinetic energy of the components influences the change in the shape of the oil droplet, i.e. the value of the contact angle.

It should be noted that an increase in the energy reserve of the particles of the cleaning solution can be achieved by external influences, e.g. by increasing the temperature, mixing the solution, using ultrasonic and electrochemical cleaning methods.

Other factors that determine the quality and speed of the cleaning process are the influence of inorganic salts, the type of impurities and the substrate to be cleaned.

#### Conclusion

This study provides a comprehensive examination of the role of surfactants in cleaning hard surfaces from oil contamination. Key findings underscore the significance of interfacial tension and adsorption dynamics in determining the efficacy of various surfactant solutions. Among the compounds tested, Sintanol DS-10 demonstrated the highest cleaning efficiency due to its balanced adsorption behavior at oil-solution and substrate-solution interfaces, fulfilling the necessary thermodynamic conditions for effective oil removal. Conversely, solutions of Sulfonol NP-3 and "Volgonat" exhibited lower cleaning capacities, attributed to their tendency to adsorb at the substrate-oil interface, thereby stabilizing the oil layer.

The results also highlight the importance of kinetic and energy considerations in the cleaning process. Surfactants like Dispersing agent NF and Tetrabutylammonium iodide, despite limited micellar activity, showed moderate cleaning potential through mechanisms involving rapid adsorption and partial oil layer disruption. These insights emphasize the interplay between thermodynamic and kinetic factors in optimizing cleaning formulations.

Future investigations will explore the influence of external factors, such as temperature, mixing, and the presence of inorganic salts, to further enhance the efficiency and versatility of surfactant-based cleaning systems. By addressing these variables, this research aims to advance practical solutions for industrial and environmental applications.

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submitted 16.04.2025; accepted for publication 30.04.2025; published 26.06.2025 © Stanislav D., Maryaskin Y.B., Maslak H.S. Contact: stanislav.derman@gmail.com