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Formation of water film from aqueous film forming foam drops on the surface of oil products

Evgeniy Degaev¹, Valeria Razvalyaeva and Svetlana Sabenina

Moscow State University of Civil Engineering, Yaroslavskoe shosse 26, Moscow, 129337, Russia

E-mail: ¹degaev@inbox.ru

Abstract. The article formulates the research problem as determining the speed of drops spreading on the surface of oil products by the direct measurements, for example, changes in the diameter of the drops in time. Experimentally studied the process of spreading droplets on the oil surface. The technology of quenching oil supply directed jets of water sprayed was has been proposed. It is shown that the nature of the mutual wetting aqueous solution and the hydrocarbon concentration varies with the blowing agent in aqueous solution. There are experiments for various hydrocarbons is used to identify the dependence of the spreading speed from the spreading coefficient. The solutions for which the value of the spreading coefficient is negative, and the surface tension is lower than heptane has, form a heptane droplets on the surface that have a shape close to spherical and float on the surface of the hydrocarbon. There is a dependence of the speed of drops spreading from the spreading coefficient. It was presented the theoretical values of speed of drops spreading that calculated by the formula and the experimental results. It's shown satisfactory correlation of calculated and experimental data. It is established that solutions with a positive value of spreading coefficient is able to spread over the surface of the hydrocarbon and the rate of their spreading is directly proportional to the spreading coefficient.

1. Introduction

Extinguishing fires of petroleum products during emergency spill at industrial facilities of capital construction, transport, gas stations and the destruction of oil tanks is most effective when using film-forming foamers. The main difference of film-forming foamers lies in an especially low interracial tension, the value of which is significantly lower than that of petroleum products. The film-forming ability of foamers is judged by the magnitude of the spreading coefficient of the aqueous-based solution over the hydrocarbon surface. If the value of the spreading coefficient is positive, spontaneous spreading of the solution droplets over the surface of the petroleum product should be expected. This proposition is based on the second law of thermodynamics, from which it follows that the process can occur spontaneously only when the free energy of the system decreases.

In connection with the discussion on the accuracy of methods for measuring the interfacial tension, the magnitude of which is comparable with the measurement error, the task is to determine the spreading rate by direct measurements, by directly measuring the change in the droplet diameter through time.



The purpose of this work is to study experimentally the spreading of water droplets over the surface of petroleum products. Petroleum products were gasoline, diesel fuel and heptane [1-5].

2. Materials and Methods

A binocular microscope was used to measure the droplet size. A drop of the test aqueous-based solution was applied with a needle to the surface of the hydrocarbon. The time of observation did not exceed 30 s. Due to the high measurement error the experiments were repeated many times.

Interracial and interfacial tensions were determined by the ring method. Figure 1 shows the isotherms of interracial and interfacial tensions, as well as the coefficient of spreading of the aqueous solution on hydrocarbon – f_σ .

The spreading coefficient of the aqueous-based solution on heptane – $f_{\sigma(01)}$ and of heptane on the solution – $f_{\sigma(10)}$ was calculated by the following relationships [1-2]:

$$f_{\sigma(01)} = \sigma_1 - (\sigma_{10} + \sigma_0) \quad (1)$$

$$f_{\sigma(10)} = \sigma_0 - (\sigma_{10} + \sigma_1) \quad (2)$$

where σ_0 - is the interracial tension of heptane, mN/m; σ_{10} - is interfacial tension at solution-heptane junction, mN/m; σ_1 - is the interracial tension of an aqueous-based at solution-air junction, mN/m.

Interracial tension of an aqueous-based at solution-air junction $\sigma_0 = 16...19$ mN/m.; interfacial tension $\sigma_{10} = 1.0...6.0$ mN/m. To ensure that the droplet spreads over hydrocarbons that have $\sigma_1 \cong 22$ mN/m, it is necessary to have an aqueous-based solution of $\sigma_0 \cong 16$ mN/m, and interfacial tension $\sigma_{10} = 2.5$ mN/m. In this case $f_\sigma \cong 2.0-3.0$ mN/m.

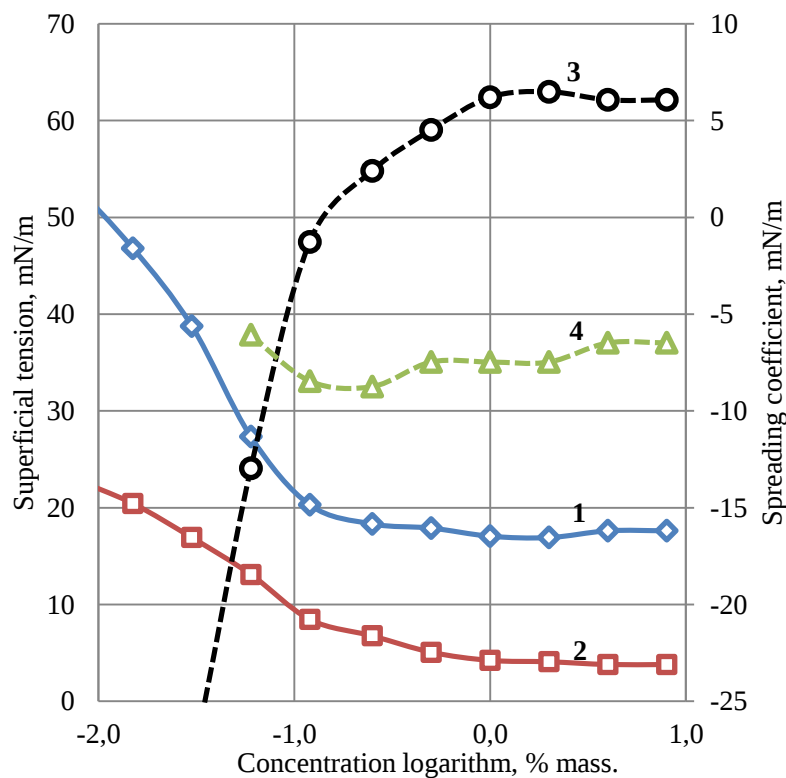


Figure 1. Isotherms of interracial (1) and interfacial (2) tensions, as well as the coefficient of spreading of the aqueous solution (3) on hydrocarbon - diesel fuel and hydrocarbon on aqueous solution (4)

Such low values of interracial tension can only be obtained with the help of fluorine-containing surface-active substances (SAS). The special structure of these molecules makes it possible to weaken the interaction of water molecules in the surface layer so that its value decreases from 72 to 15-18 mN/m. It should be noted that the interracial tension of aqueous-based solutions of conventional hydrocarbon foamers is 28-35 mN/m.

The peculiarity of these substances is the provision to the aqueous-based solution of inertness to the action of hydrocarbons with which the fluorine-containing SAS solutions do not mix and dissolve. Foam, obtained from film-forming foamers, can be applied to the burning surface of the petroleum product from a long distance [6-11].

3. Results and Discussion

Taking into account the special properties of aqueous-based solutions of film-forming foamers, a technology for extinguishing petroleum products by applying aqueous-based solutions as directed sprayed water jets was proposed. Studies on extinguishing hydrocarbons by sprayed water were carried out in Refs.

When the droplet of a sprayed solution of fluorine-containing SAS hits the hydrocarbon surface, a contact profile is formed at the interface of the immiscible liquid phases. The profile of the contact line depends on the nature of the mutual wetting of the aqueous-based solution and the hydrocarbon. Judging by the results shown in Figure 1, the nature of mutual wetting of the aqueous-based solution and the hydrocarbon - diesel fuel varies with increasing concentration of the foamer in the aqueous-based solution. Up to concentrations equal to 0.01% by mass.

The coefficient of spreading of fuel on the solution is greater than of solution on hydrocarbon, i.e. in the system, preferential wetting by hydrocarbon is observed, therefore a drop of solution, falling on the surface of the petroleum product, immediately immersed into a flammable liquid. At a concentration of more than 0.01% by weight, the spreading coefficient of the solution over the hydrocarbon becomes larger than that of hydrocarbon on the solution. In this situation, a drop of solution will keep buoyancy on the diesel fuel, but it is not capable of spreading.

When the concentration of the foamer is more than 0.25% by weight, the spreading coefficient of the solution over the hydrocarbon becomes positive, so a drop of solution, after hitting the surface, will begin to spread over the surface. The spreading speed depends, first, on the magnitude of the driving force - surface pressure, concentrated along the perimeter of spreading, and viscosity. The value of the surface pressure is determined by the spreading coefficient.

Figure 2 shows the results of experiments carried out with solutions of the foamer Storm F. Solutions having a positive spreading coefficient of 2.5 mN/m and 6.5 mN/m were used. Figures 2-4 show the experimental spreading measurements. The results of the measurements show that the higher the spreading coefficient, the faster the solution droplet spreads over the hydrocarbon [12-16].

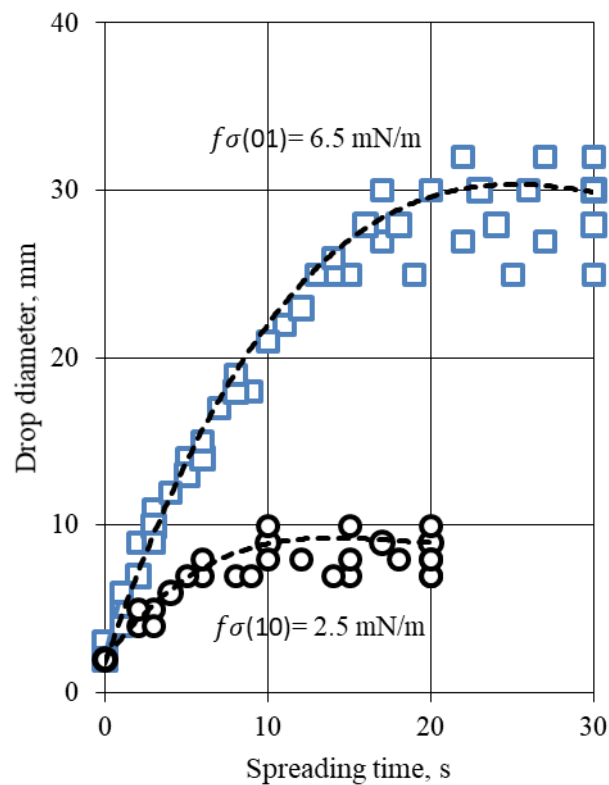


Figure 2. Spreading of a drop of Storm F foamer solution with different spreading coefficient over the surface of diesel fuel

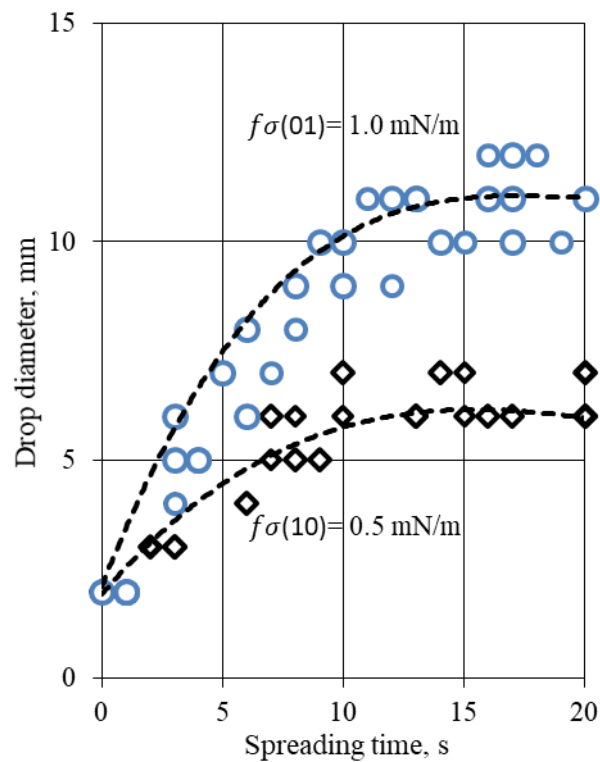


Figure 3. Spreading of a drop of Storm F foamer solution with different spreading coefficient over the surface of gasoline

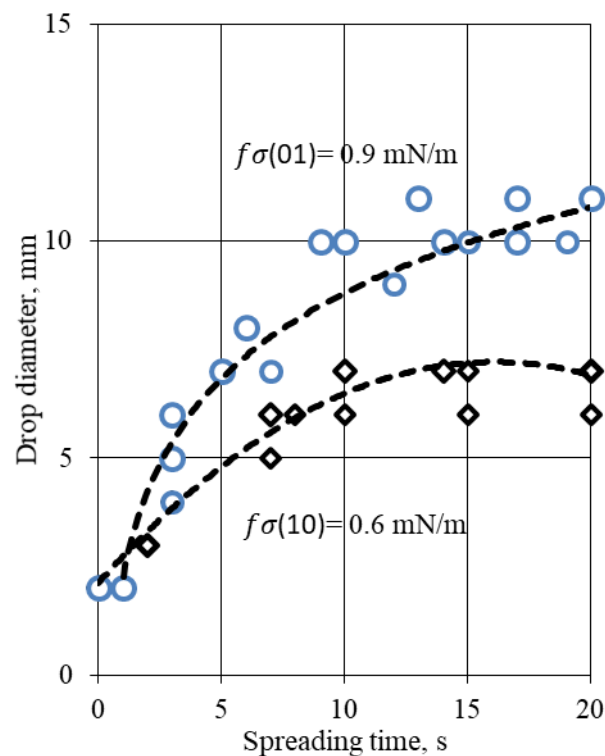


Figure 4. Spreading of a drop of Storm F foamer solution with different spreading coefficient over the surface of heptane

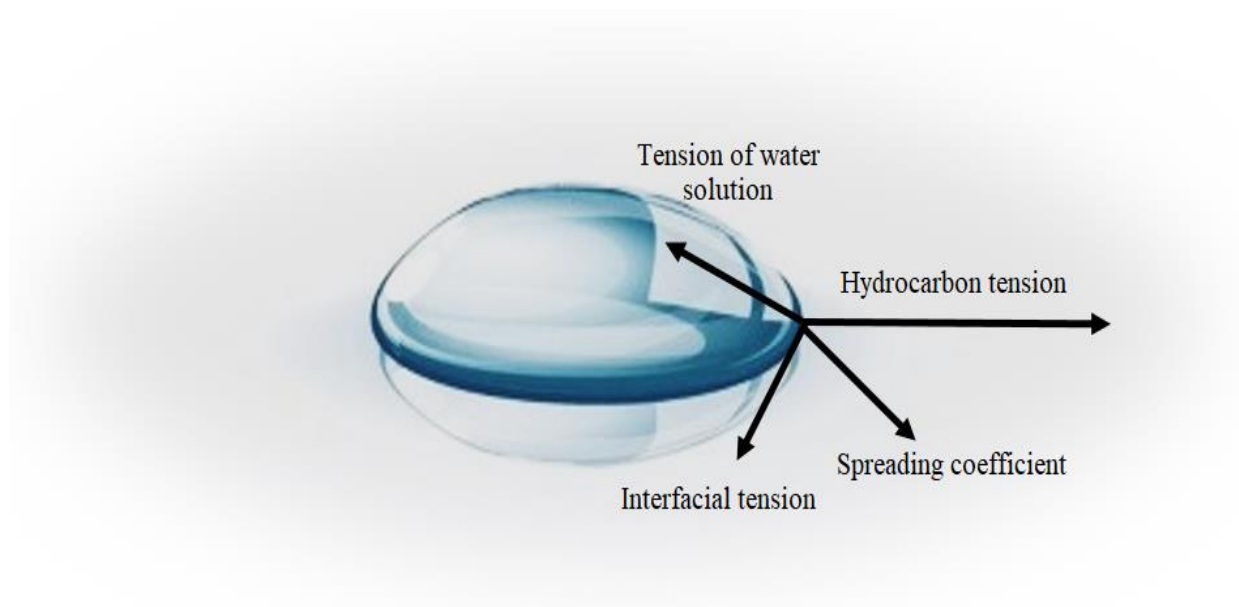


Figure 5. Scheme of the distribution of interracial tension forces at the junction of solution droplet of and a hydrocarbon (analysis of the process of spreading an aqueous-based solution over the surface of diesel fuel)

Let us estimate the rate of solution spreading on the surface of hydrocarbons. To do this, we use the following model, represented schematically in Figure 5.

The theoretical aspect of oil droplets spreading on the surface of water is considered in the work of Shuleikin. Based on the consideration of the driving force concentrated along the line of contact between the two liquids, he proposed a formula for calculating the rate of spreading a drop of liquid over a liquid backing:

$$U = 2.1 \cdot \sqrt[3]{\frac{f_{\sigma}^2}{\eta \rho R \left(\ln \frac{R}{R_0} \right)^2}} \quad (3)$$

The formula relates the surface pressure to the physical parameters of the backing fluid. The value of the surface pressure, numerically equal to the spreading coefficient (f_{σ}) is a maximum of 2.0 mN/m for heptane and gasoline and 8 mN/m for diesel fuel. Hydrocarbon viscosities η are 0.4 Pa·s for heptane, 0.5 Pa·s for gasoline and 1.5 Pa·s for diesel fuel; average density $\rho = 1000 \text{ kg/m}^3$; the initial radius of the drop is $R_0 = 1 \cdot 10^{-3} \text{ m}$; $R = 1 \cdot 10^{-2} \text{ m}$.

Comparative graphs of theoretical calculations and experimental studies are constructed (Figure 6) using the formula (2) and the results of the experiments. In this case, a satisfactory correlation between the calculation results and the experiment is observed [1-3].

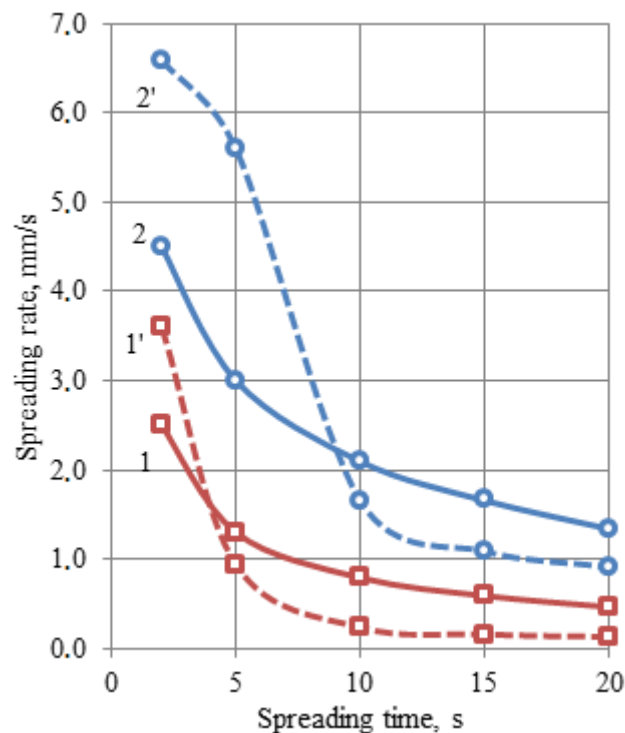


Figure 6. Experimentally obtained and calculated by the Shuleikin's formula results of droplets spreading study with a positive spreading coefficient over the surface of diesel fuel

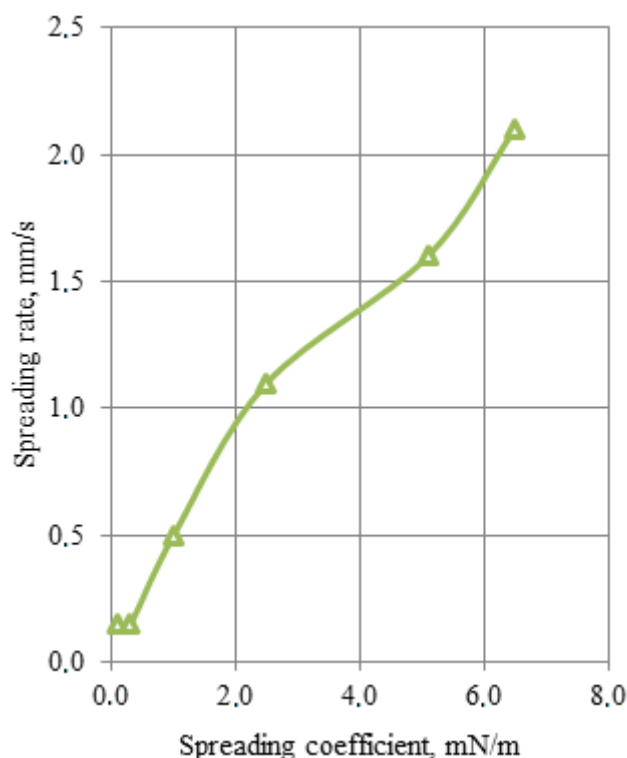


Figure 7. The final dependence of the droplets spreading rate of film-forming solutions on the value of the spreading on hydrocarbon coefficient

4. Conclusions

The results of the experiments were used to determine the dependence of the spreading rate on the spreading coefficient, using the results obtained with various hydrocarbons.

Solutions for which the spreading coefficient is negative, but the interracial tension is lower than that of heptane, form droplets on the heptane surface that are close in shape to spherical, which float on the hydrocarbon surface.

Experimental studies have shown that solutions having a positive spreading coefficient spread over the surface of hydrocarbons, but the spreading rate is the higher, the larger is the spreading coefficient.

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