Experimental and numerical study of gravitational sedimentation of the polydisperse water-in-oil emulsion

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Abstract. Experimental and numerical studies of the process of gravitational deposition of a polydisperse water-in-oil emulsion are carried out. The dynamics of emulsion deposition is determined based on the results of digital image processing. Histograms of the size distribution of emulsion droplets at different sampling depths during deposition are obtained. A comparative analysis of numerical and experimental data is performed.

1. Introduction
Most emulsions, which occur in nature, are polydisperse systems. Research in the field of emulsions has been constantly increasing in recent years, as evidenced by numerous publications [1, 2]. This huge interest is caused by widespread applications, for example, in food, pharmaceutical and cosmetic industries, oil refining, etc. [3–5]. For example, [6] provides an overview of recent research on the identification, characterization, and use of natural food emulsifiers, such as proteins, polysaccharides and phospholipids. Special attention is paid to the relationship between the structural properties of these emulsifiers and their ability to form and stabilize emulsions.

However, emulsions are non-equilibrium systems and can undergo a destructive process of coalescence, precipitation, and precipitation maturation. To make them kinetically stable, some emulsifiers, such as surfactants, polymers, and solids are always added. An important role of emulsifiers is to adsorb at the oil-water interface and reduce the interfacial tension.

Understanding the hydrodynamics of liquid droplets is a necessary condition for rationalizing the overall transfer processes and stability of emulsions. The stability of emulsions is affected by a large number of variables, and the rate of precipitation (or separation) of the dispersed phase under static conditions is a key parameter in determining the overall emulsion stability characteristics. Considerable efforts have been made to understand the hydrodynamic behavior of a single drop in Newtonian and non-Newtonian media [7–9]. Most of these studies focused on moving one drop into another immiscible liquid in the absence of surface tension effects. Although such idealized studies related to the hydrodynamic behavior of a single drop provide useful information about the physics of flow, many drops are often found in most practical applications [10].

The aim of the present work is a comprehensive (experimental and theoretical) study and establishment of the main regularities governing the process of gravitational sedimentation of polydisperse emulsions. The topicality of the work is due to the fact that one of the most important processes of oil preparation is the separation of oil emulsions (demulsification), which are characterized by a high degree of polydispersity. The obtained results can be used to determine the optimal parameters of gravitational precipitation and centrifugation of oil emulsions.
2. Emulsions preparation

The object of research in this work is a reverse water-in-oil emulsion. Medical paraffin oil was used as the dispersed phase \((\rho_f = 0.845 \text{ g/cm}^3, \mu_f = 71.5 \text{ mPa}s\) at a temperature of 23°C). The dispersion medium was distilled water (Milli Q). To obtain a stable emulsion, a non-ionic surfactant, sorbitan monooleate Span 80, was used. The manufacturing procedure was as follows: Span 80 was added to paraffin oil in the amount of 0.5% (by weight) and stirred for 5 minutes at a speed of 300 rpm using a top-drive agitator (ES 8300D, Ekros). After that, distilled water was added during mixing, the process of mixing water with oil lasted 5 minutes. An emulsion was obtained that satisfied the experimental method. During all the experiments, the separation of the emulsion into separate phases was not observed.

3. Experimental procedure

An experimental study of the process of gravitational sedimentation of the emulsion was carried out in a cylindrical test tube with a volume of 25 ml. The deposition process was recorded on a Canon EOS 1100 camera. Samples were taken from the test tube to obtain microphotographs during the process of settling the emulsion. Samples were taken at different heights from the surface of the bottom of the test tube. Studies to determine the size of emulsion droplets were carried out on an inverted Olympus IX71 microscope with subsequent image processing in the ImageJ program. Based on the results of digital image processing, histograms of the size distribution of emulsion droplets were obtained.

4. Numerical study of emulsion sedimentation

Mathematical modeling of the process of gravitational stratification of an emulsion with an initial concentration of C0 drops in a cylindrical test tube was performed. The gravity vector was directed downward. The problem was solved in a one-dimensional setting. The coordinate axis was directed along the gravity vector. It was believed that the processes of coalescence and crushing of droplets do not occur. Typically the mathematical model included averaged equations of conservation of mass and quantity of motion for the dispersed phase and the dispersion medium [11]. The system of equations is written in a single-fluid approximation, taking into account the forces under which the relative movement of the phases occurs and ignoring the macroscopic movement of the emulsion:

\[
\frac{\partial C}{\partial t} + \nabla (CU_d) = \nabla (D_{eff} \nabla C) \tag{1}
\]

\[
D_{eff} = \frac{kt^2}{6\mu_f r} \left( \frac{\mu_f + \rho_d}{2\mu_f + 3\mu_d} f(C) \left(1 - \frac{\rho_d C}{\rho}\right) \right) \tag{2}
\]

\[
U_d = \frac{2(\rho_d - \rho_f)r^2 g}{\mu_f} \frac{3\mu_f + 3\mu_d}{2\mu_f + 3\mu_d} f(C) \left(1 - \frac{\rho_d C}{\rho}\right) \tag{3}
\]

\[
f(C) = \left(1 - \frac{C}{C_{max}}\right)^\alpha \tag{4}
\]

\[
\rho = \rho_d C + \rho_f \left(1 - C\right) \tag{5}
\]

where \(C\) is the volume fraction of drops in the emulsion; \(T\) is the temperature of the emulsion; \(k\) is the Boltzmann constant; \(r\) is the average radius of the drops; \(g\) is the gravitational acceleration; \(D_{eff}\) is the effective diffusion coefficient; \(U_d\) is the velocity vector of the relative phase motion in the form of Rybczynski-Hadamard recorded taking into account the constrained deposition function; \(f(C)\) is the the constrained deposition function; \(C_{max}\) is the maximum packing density; \(\alpha\) is the empirical coefficient; \(\rho\) is the emulsion density; \(\mu_f, \mu_d\) is the coefficient of dynamic viscosity; indexes \(d\) and \(f\) are the parameters related to the droplet and the surrounding fluid, respectively.
All droplets will move at the same speed, proportional to the function of constrained deposition for the case of a monodisperse system. In this case, we are dealing with a polydisperse system with a certain average size of droplets, which can be calculated based on the distribution of droplets by size. The average drop radius was set as a function of the drop concentration.

The volume content of droplets was equal to $C_0$ at the initial time, and the condition for no flow was set at all borders, $\nabla C = 0$.

5. Results
An experiment on the settling of a polydisperse emulsion in a cylindrical vessel was performed. The process of deposition of the emulsion was recorded by a camera with a frame rate of 5 minutes. Samples were taken from the vessel at various levels from the bottom of the vessel during the settling process. The sampling scheme and photos of subsidence are shown in figure 1.

![Figure 1. Selection diagram (left) and characteristic photos of the time-dependent settling of the emulsion (right) 1 – 0 min; 2 – 55 min; 3 – 110 min; 4 – 165 min; 5 – 220 min.](image)

A tablet consisting of 44 frames was built based on digital image processing. The areas in the middle of each image were selected to combine the frames into a panoramic image (figure 2).

![Figure 2. Panoramic tablet of the dynamics of subsidence at different times.](image)
The dependence of the intensity of light passing through the emulsion at different heights was constructed (figure 3) based on the obtained image. The graphs of light intensity over time were approximated by the dependence $I=I_0+(1-e^{-x/\tau})$, where $\tau$ is the relaxation time of the light intensity, on the basis of which we can talk about the characteristic times of redistribution of emulsion drops at different heights.

Figure 3. The dependence of the intensity of light passing through the emulsion at different heights.

Figure 3 shows that the intensity of transmitted light at the level of 0 mm rapidly decreases and reaches a plateau in 5 minutes. This means that large drops of the emulsion quickly settle on the bottom of the flask, where the concentration of drops is maximum. With increasing sampling height, the intensity of transmitted light gradually increases and tends to a value of 0.7, which corresponds to a concentration of drops equal to 0.1%.

Figure 4. The dependence of the light intensity relaxation time on distance.

Figure 4 shows the dependence of $\tau$ on distance. It can be seen that the redistribution of drops occurs quickly, within 5 minutes at the bottom of the test tube. With increasing sampling height, the relaxation time of light intensity decreases.
Figure 5. Drop size distribution functions built at different heights.

Histograms of the size distribution of emulsion droplets were obtained based on digital image processing. The histograms were approximated by the Log-normal distribution function, which satisfactorily describes the distribution of particle frequencies by their sizes during random splitting. The average droplet size of the original emulsion was 35 μm, μ=3.37, and σ=0.608. Figure 5 shows the functions that were used to approximate experimental data at different sampling heights. It is seen that with an increase in the sampling height, the average size and spread of the drops decreases. At the height h=20.5 mm the average droplet size was <d>=10.14 μm (μ=2.20, σ=0.474), h=41 mm – <d>=5.085 μm (μ=1.584, σ=0.288), h=61.5 mm – <d>=5.60 μm (μ=1.652, σ=0.374), h=82 mm – <d>=5.63 μm (μ=1.64, σ=0.403).

The average droplet size determined at different heights was compared with the values of light intensities (Figure 3) and the dependence of the average droplet size on the intensity value (volume fraction of drops) was constructed. The resulting dependence closes the system of equations of the mathematical model. Figure 6 shows the simulation results in the form of curves for the distribution of the volume fraction of droplets along the height of the flask.

Figure 6. The distribution of the volume fraction of droplets in the emulsion by height at different points in time: 1 – 10 min; 2 – 30 min; 3 – 50 min.
The average size of drops varies from 1 to 150 μm depending on the volume fraction of drops in the emulsion. The figure shows that over time, the volume fraction of drops in the upper part decreases, and in the lower part it increases. In this case, the rate of precipitation of drops decreases over time in accordance with the change in the average size of the drops. This results in an almost linear distribution of the emulsion droplets along with the height. The drops continue to settle, but at a rate significantly lower than the initial one. The results obtained are in qualitative agreement with the results of experimental studies (figure 2), where an almost linear distribution of light intensity over height was observed.

Conclusions
An experimental study of the dynamics of emulsion deposition in a flask has been conducted. Characteristic times of the emulsion redistribution along the sampling height have been obtained based on the dependence of the intensity of light passing through the sample. The minimum relaxation time was 5 minutes at the bottom of the vessel. The dependence of the time of redistribution of the emulsion in the range of 20-80 mm varied within 20-40 min. Histograms of droplet size distribution have been constructed based on the results of digital image processing selections. The average droplet size is found to shift to the region of low diameters, while there is a decrease in the spread of the average droplet size. Numerical simulation of the deposition process of drops of a polydisperse system has been performed based on the constructed dependence of the average size of drops on the intensity value. The mathematical model has been constructed in a single-fluid approximation. A qualitative agreement of the simulation results with experimental data, and an almost linear distribution of emulsion droplets along the height have been obtained. The results can be used to describe the dynamics of convective flows in emulsion media, as well as in modeling the constrained deposition of a disperse system.

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