The separation of oil emulsions is an important step in the purification of crude oil from water, mineral salts, and various associated contaminants, asphaltene-resinous substances, and paraffin contained in the oil. In the formation and stabilization of oil emulsions in the form of colloidal particles in the oil, insoluble dispersed solids also have a high effect. Examples of such substances are microcrystals of solid paraffins, asphaltenes, ferrous sulfides, and other mechanical mixtures. These substances form a strong mechanical barrier on small water droplets distributed in the oil phase, which prevents the separation of water. In this work, the effect of various compounds in the oil on the separation of oil emulsions was studied in detail, a suitable model was proposed, and information was provided on promising methods for the separation of oil emulsions.

**Keywords:** oil emulsions, asphaltene, resin, separation oil emulsions, water-in-oil, oil-in-water.


**Introduction**

One ton of any oil extracted from the surface, regardless of the depth and location of extraction, contains 50–100 m³ of gas, 200–300 kg of water, 10–15 kg of mineral salts, and mechanical mixtures. Various systems are used in the fields to separate water from oil. Pressure systems are used in new oil fields. In this system, the crude oil from the well is fed to an individual metering device. Here, the gas is separated from the liquid products, and the amount of products purchased is determined. The separated gas is re-mixed with oil and water and fed to the separator at the pumping station for redistribution of gas from oil [1]. The separated gas is transported to gas refineries, and partially degassed oil is transported to an oil refinery. The second and third separation of gas from oil, as well as the purification of oil from water and salts, are carried out at the oil refining plant. The separated gas is processed here, and the water is returned to the oil fields after purification. The purified oil is transferred to special tanks to determine its quantity and quality [2]. If the oil does not meet the quality standard, it is recycled. Even after several stages of oil separation, C₁–C₄ gaseous hydrocarbons remain in a certain amount of dissolved form. These gases, as well as light fractions, can be separated from the oil during storage and transfer from one tank to another, which in turn leads to losses, environmental pollution and ecological imbalance. Therefore, in most fields, oil is stabilized by rectification. The content of C₁–C₄ gas hydrocarbons in stabilized oils is up to 1%, and in non-stabilized oils, the content of these gases is 2–3%. Water is freely soluble in oil and is in the form of an emulsion. Free water is separated in sediments in oil fields, as mentioned earlier. Dissolved and dispersed water does not separate from oil by itself. The amount of dissolved water depends on the chemical composition and temperature of the oil [3]. Aromatic-based oils contain more dissolved water. This is because aromatic hydrocarbons are 24 times more hygroscopic than other classes of hydrocarbons. However, as the temperature increases, the solubility of water in all three classes of hydrocarbons increases. As the temperature decreases, there may be water dissolved in the oil, which separates in the form of dispersions (small particles) to form an oil-water emulsion. These emulsions are usually very durable and do not break down for a long time, even a few months. The structural and mechanical stability of emulsion systems is associated with the formation of
adsorbed layers on the surface of oil and water. They consist of asphaltenes, paraffins, mineral salts, and solids, ie surfactants [4]. The durability of oil and water emulsions is influenced by several factors, including some substances (emulsifiers) in the oil. Many compounds in oil belong to the class of surfactants (naphthenic acids and their salts, resinous compounds).

In addition to surfactants, highly insoluble dispersed solids in the form of colloidal particles in oil have a high effect on the formation and stabilization of oil emulsions. Examples of such substances are microcrystals of paraffins, asphaltenes, ferrous sulfides, and other mechanical mixtures. These substances form a strong mechanical barrier on small water droplets distributed in the oil phase, which prevents the separation of water [5].

The durability of the oil–water emulsion is also affected by the composition of the oil fraction and the concentration of salts in the water. The higher the amount of light fractions in the oil, the lower the durability of the oil–water emulsion. This is due to the large difference between this fraction and the specific gravity of water. Oil and water emulsions formed in high-viscosity oils are very durable [6]. This is because in high-viscosity systems, the ability of water particles to meet each other to form large water droplets is reduced. Unlike crude oil, petroleum products contain very little water, both dissolved and emulsified. When the amount of water in oil and oil products exceeds the standard (0.3%), adverse events such as explosion due to pressure generated in oil refineries, corrosion of metal surfaces, the formation of cracks on the inner surfaces of pipes and equipment, and the resulting deterioration of heat transfer, etc. can give. Therefore, the quality and quantity of water in oil and oil products must be determined before processing.

Water in oil

It is known that the presence of water in oil and oil products, regardless of their form, is considered an unpleasant situation. When the oil contains water at the time of use, it affects its physical properties and does not give the correct results. During the dehydration of oil, first of all, depending on the form and amount of water in it, one of the existing methods is used. When the oil sample taken for the study contains a large amount of water, most of it remains in the separator funnel, and the rest is separated by incinerated CaCl₂. Dehydration of heavy oils is carried out by heating in a flask equipped with a counter-cooler. In recent years, autoclaves have become more widely used to disperse oil emulsions. The oil sample is gradually heated in an autoclave at a pressure of 1 MPa and a temperature of 200–220°C. Under selected conditions, the oil-water emulsion decomposes. Demulsifiers are not used in the dehydration of oil samples taken for research purposes. This is because a small amount of demulsifiers may remain in the oil during the process, which may affect the results of the study [7].

Under the influence of temperature, the paraffin crystals surrounding the water droplets in the oil emulsion melt, and the protective film weakens. At the same time, the solubility of naphthenic acids and resinous compounds in the oil improves. In all cases, favorable conditions for water precipitation. Alternating current is widely used in the oil industry to separate water from oil. The high-voltage alternating current emitted from the system charges the water molecules with a reverse electric current. As the direction of the electric current changes, so does the direction of the water molecules. In this case, the spherical shape of the water droplets changes and falls into an elongated shape. As a result, the water droplets start to dance, meet each other and create conditions for the emulsion to disintegrate. The higher the power of the alternating current, the higher the rate of decomposition of the emulsion [8].

Salts in oil

Salts enter the oil mainly in the form of dissolved in mineral waters. In the process of dehydration of oils, most of the salts are released along with water. The amount of salts in mineral waters varies widely. The amount of salts in mineral waters varies widely. Mineral waters contain more Ca²⁺, Mg²⁺, Na⁺, K⁺-cations and Cl⁻, SO₄²⁻, HCO₃⁻, CO₃⁻-anions, while other ions are less. If the amount of salts in the oil exceeds the state standards, as a result of the corrosion process and the formation of sedi-
ments of these salts, technological equipment and devices can be damaged in a short time. Therefore, the amount of salts in refined oils is strictly controlled.

Existing chemical and physical methods are used to determine the amount of salts in oil and oil products. The chemical method – is based on the titration of chlorides in oil and oil products by indicator or potentiometric method to remove them from the oil with water. In both cases, titration is carried out with silver nitrate in accordance with state standards. Recently, conductometric and atomic adsorption methods have been widely used. The conductometric method is based on the measurement of electrical conductivity with both constant and variable currents. The atomic adsorption method is widely used in laboratory studies to determine the amount of salts in oil [9].

**Mechanical mixtures in oil and oil products**

When mechanical impurities remain in the oil, accurate results are not obtained when determining its molecular weight, density, coking, amount of sulfur, nitrogen, micronutrients, and resin-asphalt compounds. Therefore, before the oil is analyzed, its mechanical impurities (sand, suspension salts, clay minerals, metal oxides) must be separated by precipitation or filtration.

Mechanical mixtures are included in the composition of petroleum products during oil refining. Products of corrosion in pipes and equipment during processing, catalyst dust, particles of used clays and mineral salts are included in the composition of petroleum products as a mechanical mixture. Prior to the initial refining of the oil, the mechanical impurities in the oil must be removed. Otherwise, mechanical mixtures will settle on the surface of the furnace and heating pipes, sharply reducing the heat transfer coefficient and therefore increasing fuel consumption. The presence of mechanical compounds in petroleum products is more dangerous. Thus, mechanical contaminants in fuels can clog the pores of fuel lines and filters. Mechanical impurities in lubricating oils can cause scratches on friction surfaces and block the oil passages leading to friction surfaces.

In addition to the above-mentioned compounds, one of the compounds that affect oil emulsions is heavy asphalt-resin compounds.

**Influence of asphaltene-resinous substances**

According to various researchers, the most widely accepted definition for asphaltenes is their solubility, stating that asphaltenes are not soluble in aliphatic hydrocarbons such as n-heptane or n-pentane, but are soluble in aromatic hydrocarbons such as toluene [10–24]. According to another view, asphaltenes represent insoluble precipitates obtained from petroleum solutions in low molecular weight alkanes such as pentane, hexane and heptane [25].

Changes in temperature, pressure and chemical composition can cause asphaltenes to precipitate from crude oil. Subsequent precipitation and asphaltenes can cause various problems at all stages of production, such as transportation and refining, as well as loss of equipment efficiency during crude oil production.

Dispersion of asphaltenes is mainly related to resins. Resin molecules play the role of surfactants in stabilizing colloidal particles of asphaltenes in oil. There are various theories about the collapse of asphaltenes, and one of the most widely accepted ideas is the collapse of asphaltenes after the melting of resins [26].

Asphaltene and resins are the main constituents of crude oil, and these compounds combine with adsorption on other organic and inorganic solids to form an emulsion stabilizing layer in the oil-water bond, thus contributing to the formation of dense emulsions that are difficult to process [27–29]. Many researchers believe that emulsification is mainly due to asphalt and resin compounds [30–33].

According to several researchers, the stability of asphaltenes in oil depends on the ratio of resin/asphaltene in the oil. Unlike asphaltenes, resins are soluble in alkanes (n-heptane, n-pentane) [34].

Asphaltenes are observed to establish rigid, cross-linked, elastic films which act as vital agents in balancing out water-in crude oil emulsions. The asphaltene films are found to be intensely adsorbed proposing that asphaltene are solidly tied down to the interfacial film and to
each other, possibly through numerous inter-
molecular interactions [35].

The mechanism of formation of the ad-
sorption layer on the surface goes through
the following stages:

a) Transfer of the diffusion mass of asphal-
tene from the volume of oil to the surface of water
droplets. At the unit time, at small values of Re =
\( \frac{\mu \sigma r}{\nu_c} \ll 1 \), the mass flow to the surface of a mov-
ing droplet is expressed as follows [36]:

\[
I = \sqrt{\frac{\pi}{6}} \frac{D}{a_r \eta_C + \eta_d} \Delta C \frac{a_r}{\sqrt{\gamma}}
\]  

(1)

Here, \( \Delta C = C_0 - C_S \) and \( C_0, C_S \) are the composition of asphaltenes and resins in vol-
ume and surface, respectively. Assume that the change in the mass of the adsorbed layer is
determined by \( \frac{dm}{dt} = I \), then we get \( m - m_0 = \tau I \) (\( \tau \) – retention time and \( m_0 \) is the initial mass of
the adsorbed layer taken equal to zero). Then, taking into account the insignificance of the ex-
pansion conditions of \( m = \frac{1}{6} \pi \rho_a (a_r + 2\Delta)^3 - \frac{1}{6} \pi \rho_a a_r^3 \) and 2\(^{nd} \), 3\(^{rd} \) degree smallness (\( \frac{\Delta}{a_r} \ll 1 \)),
we obtain that \( m \approx \pi \rho_a a_r^3 \frac{\Delta}{a_r} = I \tau \). Taking into
account expression (1), the thickness of the adsorbed
layer is determined as follows

\[
\frac{\Delta}{a_r} \approx \frac{1}{\sqrt{6\pi}} \left[ \frac{1}{Pe} + \frac{1}{Sh} \right] \frac{1}{\sqrt{\gamma}} \frac{\Delta C}{\rho_a} \frac{1}{\eta_d} \frac{1}{\eta_C}
\]  

(2)

where, \( \gamma = \frac{\eta_d}{\eta_C} \), \( Pe = \frac{U \sigma r}{\rho a} \), \( Sh = \frac{U \tau}{\sigma r} \), \( \eta_d, \eta_C \) are the surface tensions of the adsorbed layer.

b) Adsorption of the substance on the sur-
face of the droplets.

c) Desorption and destruction of the ad-
sorption layer in the presence of surfactants

\[
\Gamma = \frac{K C_0}{1 + K_0 C_0} (3)
\]

Where, \( \alpha, \beta \) are temperature-dependent
variables, \( K = \beta / \alpha \), \( K_0 = \beta / \alpha \Gamma_\infty \), \( \nu \in \Gamma_\infty \) is the
maximum saturation degrees of the droplet sur-
face.

**Formation of oil emulsions**

Emulsions are defined as a system of het-

erogeneous liquids consisting of immiscible li-

uids, where one liquid exists in the form of drop-
lets in another. Emulsions differ in the amount of
liquid dispersed in the other. The emulsion con-

sists mainly of two phases: a continuous phase in
which the droplets are dispersed (external) and a
dispersed phase in which they are dispersed (in-

ternal or continuous).

In order to choose the right method of oil

purification (demulsification) of oil, it is im-

portant to know the mechanism of formation of
the emulsion and its properties. The formation of
the emulsion begins when the oil moves from the
formation to the wellhead and continues during the
subsequent movement in the field communica-
tions. That is, the emulsion is formed in places
where there is a continuous mixing of oil and
water. The intensity of emulsion formation in a

well depends on the method of oil extraction,
which in turn depends on the nature of the field,
its service life and the physical and chemical
properties of the oil itself. Three conditions are
required for the formation of an emulsion: 1) immiscibility between the liquids of the emul-
sion, 2) shaking to distribute one liquid to anot-

other, 3) the presence of emulsifying substances
(surfactants) [37].

Emulsions are divided into two types ac-


cording to the nature of the external en-

vironment and the internal phase: oil in water (n / s)
and water in oil (s / n) (Figure 1). The type of
emulsions formed depends mainly on the vol-

ume ratio of the two phases; The largest volume of
the liquid forming the emulsion is considered to be the external phase. In practice, water-type
emulsions are often (95%) found in water and
oil. Compared to oil-water emulsions, there is a
third type of emulsions - water-type emulsions
in water–oil. In addition to the ratio of phases,
emulsifiers, in other words, substances that
 promote the formation of emulsions, have a
great influence on the formation of oil and wa-
ter emulsions. They reduce the surface tension
at the phase separation boundary and create a
solid adsorption coating around the inner phase
particles. Water-soluble emulsifiers help to
form oil–water emulsions. Such hydrophilic
(well soaked in water) emulsifiers include alkali-line soaps, gelatin, starch, etc.

Surfactants have hydrophilic and hydrophobic areas to enter the oil-water field and stabilize emulsions. If the concentration of particles and surfactants is high enough, then the combination of water droplets is prevented and stable emulsions are formed.

Figure 3 shows the stabilization of one drop of water in the oil-resistant phase in the presence of a surfactant [38].

Accumulation of asphaltenes on the surface results in the formation of a hard, solid layer. According to the researcher, asphaltenes, when adsorbed in the water/oil phase, form a layer with high elasticity [40].

The condition of asphaltenes in crude oil also affects the stabilizing properties of emulsions. Stabilizes emulsions when asphaltenes are in colloidal form. There is strong evidence that the properties of stabilizers increase significantly during oil precipitation.

The schematic diagram shown in Figure 4 shows a water droplet stabilized with asphaltenes and paraffin crystals. The figure shows an unstable region with the formation of an incomplete barrier.

A number of studies demonstrate the importance of asphaltenes, resins and paraffins present in crude oil in stabilizing water/oil emulsions.
Some authors claim that asphaltenes stabilize the emulsion by creating hydrogen bonds between asphaltenes and water molecules [41–43].

Some researchers have suggested that asphaltenes stabilize water/oil emulsions in two stages [44]. First, disk-like asphaltene molecules bind to interfacially active particles. They then combine with physical interactions to form a network after adsorption in the water/oil field.

The destruction of the structural structure of oil emulsions is possible by performing the following operations in sequence:
- Combination of individual drops;
- Destruction of shield covers;
- Combining water particles into droplets;
- Droplets combine to form a large mass of water and settle at the bottom of the device.

Separation of oil emulsions

Thermal purification of oil from water — the essence of oil refining is gravitational deposition. Two types of sedimentation — periodic and continuous — are applied and carried out with appropriate sediments [45].

Thermal purification of oil from water — one of the main modern methods of purification of oil from water is the thermal (or thermal) method, the essence of which is that the oil is heated before settling. The viscosity of the shielding layer on the surface of water particles decreases with increasing temperature, and the strength of the coating decreases, making it easier for water droplets to coalesce. In addition, a decrease in viscosity with increasing temperature increases the rate at which particles fall during precipitation. Thermal dewatering of oil is rarely used as a separate method. In most cases, this method is used as part of more complex methods, such as thermochemical cleaning, electric treatment and other combined cleaning methods [46].

Chemical purification of oil from water-based on the separation of oil emulsions with the help of chemical reagents in the oil industry — the method of oil refining is widely used. The effectiveness of dry cleaning depends on the type of reagent used. A demulsifier-reagent is added to the cleaning emulsion, mixed with it, and then water is separated from the oil by precipitation. There are three ways to chemically purify oil from water:
- Water treatment is based on oil wells (in-well emulsion), in which the reagent is added to the emulsion directly in the well;
- Water treatment is carried out in the oil collection pipelines (road emulsion), where the reagent is emulsified at the beginning of the oil collection collector;
- Demulsification and oil purification are performed directly in the settling tanks. In this case, the precipitator is added to the filled emulsion to the tank.

The first two methods have advantages and are considered more energy.

Electric purification of oil from water — one of the main advantages of this method is that it is applied in combination with other methods (thermal, chemical) and gives good results [47]. The mechanism of electric emulsion of oil emulsions is due to the fact that as a result of induction, the droplets are stretched along the chain of the electric field. Under the influence of the main and individual fields, the droplets move in a regular manner and collide to form large droplets. The analysis shows that the decomposition (demulsification) of oil emulsions due to the electric field is several times more efficient when the current is alternating with the direct current.

Results and discussions

Asphaltenes stabilize crude oil emulsions by various methods of action. When asphaltenes

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Fig. 4. Waterdrops stabilized with asphaltene and paraffin crystals [38].
are scattered on the surface, the layer formed in the water / crude oil field acts as a film, the hardness of which can be demonstrated by the formation of wrinkles in this area when the droplets are reduced to small sizes. They can also combine with resin molecules and prevent the droplets from coalescing by interaction (Figure 5).

![Figure 5](image)

**Fig. 5.** Asphaltenes combine with resins to prevent droplets from forming [38].

It follows from Equation (2) that the thickness of the adsorbed layer depends on the distribution of particles on the droplet surface, the size and mobility of the droplet surface, and the concentration of asphaltenes in the flow volume. At the volumes of \( Pe = 10^2 - 10^3 \) (\( D \approx 10^{-10} - 10^{-9} \text{m}^2/\text{c} \)), \( \gamma = 0.8, \Delta C/\rho_a \approx 10^{-5} \) \( \forall \) \( Sh = 10^4 - 10^5 \), we assume that \( \Delta/\alpha_r \approx 0.01 - 0.03 \).

The large values of the number, which are the result of the small values of the diffusion coefficient of the particles in the liquid, determine that in some cases the convective transport of the substance over the diffusion is predominant. Further compression of the adsorption layer under the influence of external disturbances and chemical transformations helps to increase the density of the layer and "age" the emulsions.

Figure 6 shows the values calculated for the adsorption isotherm of asphaltenes on the surface of water droplets (\( T = 40^0\text{C} \)) for North Caucasus oils [36] and Equation (3), where \( K=55, K_0=0.5 \).

![Figure 6](image)

**Fig. 6.** Dependence of the concentration of the adsorbed substance on the surface on the concentration of asphaltene [36].

**Conclusion**

In this study, we have proposed several efficient methods for the separation of oil emulsions. Our research has shown that formula (1) is consistent with many experimental data for oils from different fields. At the same time, as a result of equation (2), at values \( Pe = 10^2 - 10^3 \) (\( D \approx 10^{-10} - 10^{-9} \text{m}^2/\text{c} \)), \( \gamma = 0.8, \Delta C/\rho_a \approx 10^{-5} \) \( \forall \) \( Sh = 10^4 - 10^5 \), determined that \( \Delta/\alpha_r \approx 0.01 - 0.03 \).

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ASFALTEN-QATRAN BİRLƏŞMƏLƏRİNİN NEFT EMULSİYALARININ AYRILMASINA TƏSİRİNİN TƏDQİQİ

M.R.Manafov, F.R.Şixiyeva, K.I.Matiyev, V.I.Karimli


Açar sözlər: neft emulsiyası, asfalten, rezin, neft emulsiyalarının ayrılmış, su yağda, yağ suda.

ИССЛЕДОВАНИЕ ВЛИЯНИЯ АСФАЛЬТО-СМОЛЬНЫХ СОЕДИНЕНИЙ НА РАЗДЕЛЕНИЕ НЕФТЯНЫХ ЭМУЛЬСИЙ

М.Р.Манафов, Ф.Р.Шихиева, К.И.Матиев, В.И.Керимли

Разделение нефтяных эмульсий является важным этапом очистки сырой нефти от воды, минеральных солей и различных попутных загрязнений, асфальтосмолистых веществ и парафинов, содержащихся в нефти. При формировании и стабилизации нефтяных эмульсий в виде коллоидных частиц в масло большое влияние оказывают также нерастворимые дисперсные вещества. Примерами таких веществ являются микрокристаллы твердых парафинов, асфальтенов, сульфидов железа и других механических смесей. Эти вещества образуют прочный механический барьер для мелких капель воды, распределенных в масляной фазе, что препятствует отделению воды. В данной работе подробно изучено влияние различных соединений в составе нефти на разделение нефтяных эмульсий, предложена подходящая модель и представлена информация о перспективных методах разделения нефтяных эмульсий.

Ключевые слова: нефтяная эмульсия, асфальтен, резина, разделение нефтяных эмульсий, вода в масле, масло в воде.