

## ENGINEERING SCIENCES

**MODELLING NANO-TECHNOLOGICAL PROCESSES OF OIL EMULSIONS FORMATION AND DESTRUCTION***Abasova Inara Afrail qizi,**Azerbaijan State Oil and Industry University, assistant, Azerbaijan, Baku*DOI: [https://doi.org/10.31435/rsglobal\\_ws/30112019/6759](https://doi.org/10.31435/rsglobal_ws/30112019/6759)**ARTICLE INFO****Received:** 15 September 2019**Accepted:** 17 November 2019**Published:** 30 November 2019**KEYWORDS**

armoring casings (AC),  
emulsified water drop (EWD),  
disperse composition (DC),  
sloping apparatuses (SA),  
energy barrier (EB).

**ABSTRACT**

It is shown that oil preparation process is related to nanotechnologies, since they are carried out at the Nano-dimensional level consisting in the charge interaction of mono and polyvalent ions being present in interacting environments of oil and reservoir (intermediate) water. Taking into account specific features (Nano-phenomena) of oil emulsion formation and destruction, a mathematical model for thermochemical oil dehydration process is proposed. As it is known, the main processes of formation and destruction of AC at the interfacial section (oil-water) occur at the molecular level, and molecular-surface phenomena (Nano-phenomena) are dominant in the process of oil preparation. First of all, this is the charge interaction of nano-dimensional particles, manifested in the form of physicochemical adsorption of natural emulsifiers on the surface of EWD, wetting the armoring casings of the latter (with corresponding demulsifier interaction), ion-exchange formation of a double electric layer (DEL) on surfaces of EWD and mechanical impurities (solid particles of clay, quartz, limestone, dolomite, iron sulfide, etc.). Consequently, the modeling of these processes is an urgent task, and the article is dedicated to above-mentioned problem.

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The most important components of oil preparation process determining its efficiency, are the removal of armoring casings (AC) from emulsified water drop (EWD) and separation of oil and water into separate phases [1]. AC formed on the surface of EWD as a result of physical-chemical adsorption of various types of Nano-dimensional natural emulsifiers (micellar asphaltene with a dispersion degree of 5 ... 15 nm, clay particles, the radii of equivalent spheres varying within 7 ... 40 nm, iron oxide nanoparticles - rods with 50... 100 nm length and about 10 nm in diameter, resins with a degree of dispersion of 0.3... 1 nm and so on) contained in oil, have structural-mechanical properties and prevent the coalescence of drops upon their contact. Therefore, the success of oil demulsifier process is largely determined by the degree of destruction at the molecular and supramolecular levels (0.1 ... 100 nm). In this case, the decisive role is played by the phenomena of charge interaction and wettability. According to the authors [2,3] wettability problem (molecular-surface processes occurring at interphase boundary) is one of the most important problems of Nano-science in oil-gas industry, including water-oil preparation. Academician RAN N.P. Laverov nanotechnologies are noted as the most important problems in the development of oil-gas production [4].

**The solution of the problem.** The most important indicator of oil emulsion (OE) is stability, i.e. the ability not to destruct and separate into oil and water within a certain time. On sustainability (kinetic and aggregative drops with AC) OE are greatly influenced by the following factors:

- coagulation and fragmentation of drops in a turbulent flow;
- disperse composition;
- physical-chemical properties of natural emulsifiers, forming armoring casings;
- the presence of DEL in EWD;
- temperature of miscible liquids (oil and water) and specific consumption of demulsifier;
- pH emulsified reservoir (intermediate) water.

**Coagulation and crushing of drops in a turbulent flow.** The turbulent flow of OE in pipelines is characterized by complex physical phenomena of coagulation and fragmentation of drops of a stochastic nature. Therefore, in order to describe this process, Fokker – Planck equation [5] can be used:

$$\frac{\partial P}{\partial \tau} = -K_R \frac{\partial}{\partial a} \left[ \left( \frac{m}{a} - a \right) P \right] + B \frac{\partial^2 P}{\partial a^2}, \quad m = m_R / K_R \quad (1)$$

$$\text{with the initial condition:} \quad P(a, \tau)_{\tau=0} = P_0(a), \quad (1a)$$

where  $m_R = 4KD_T\varphi$ ;  $B$  is coefficient;  $K_R, D_T$  are respectively the factors of fragmentation and turbulent diffusion,  $a$  is the average radius of drops;  $\varphi$  is volume fraction of water.

The solution of equation (1) is generally presented as follows

$$P(a, \tau) = a^\theta \exp\left(-\frac{K_R a^2}{2B}\right) \sum_{n=0}^{\infty} C_n L_n^{(a)}\left(\frac{K_R a^2}{2B}\right) e^{-2K_R n \tau}, \quad (2)$$

where  $a = (\theta - 1)/2 = (m_R - B)/2B$ ;  $L_n(a)$  are Laguerre functions;  $C_n$  is the integration constant;  $\tau$  is time;  $\theta = m_R/B$  are frequency of drops collisions;  $n$  is the order of Laguerre function change, starting from zero.

Using the initial condition (1a) and the orthogonality condition of Laguerre function,  $C_n$  is defined:

$$C_n = \frac{\left( \theta^{\frac{\theta+1}{2}} \int_0^\infty P_0(a) L_n^{(a)}(K_R a^2 / 2B) da \right)}{\left( m_R^{\theta+1} \cdot 2^{\frac{\theta-1}{2}} a \left( n + \frac{\theta+1}{2} \right) n! \right)}. \quad (3)$$

Thus, equations (2) and (3) allow us to establish the dependence of the distribution function of emulsified water on the size of drops, taking into account their coagulation and fragmentation on the duration of the specified physical phenomena, as well as on  $m_R, K_R$  and  $P_0(a)$ , characterizing the process.

When  $\tau \rightarrow \infty$ , taking  $L_n^{(a)}(K_R a^2 / 2B) = 1$  from equation (2), we obtain the asymptotic values of the distribution:

$$P_\infty(a, \tau) = C_0 a^\theta \exp\left(-\frac{K_R a^2}{2B}\right), \quad C_0 = \left(\frac{K_R}{2B}\right)^{\frac{\theta+1}{2}}. \quad (4)$$

The average limiting dimension of EWD can be written as follows:

$$a_\infty = \int_0^\infty P_\infty(a, \tau) da = \sqrt{\frac{m_R^2}{2K_R B}} \Gamma\left(\frac{m_R}{2B}\right). \quad (5)$$

$$\text{Introduce the relation } \frac{a_\infty}{a_0} = \sqrt{M \frac{m_R}{2B}} \Gamma\left(\frac{m_R}{2B}\right).$$

Consequently, the ratio  $a_\infty/a_0 \sim M^{1/2}$  determines the predominance of coagulation or fragmentation of EWD in a turbulent flow.

Determine the coordinates of the maximum value of limiting distribution from the condition

$$\frac{\partial P_\infty(a, \tau)}{\partial a} = C_0 \theta a^{\theta-1} \exp\left(-\frac{K_R a^2}{2B}\right) - C_0 a^\theta \frac{K_R}{B} \exp\left(-\frac{K_R a^2}{2B}\right) = 0. \quad (6)$$

Reducing non-zero parameters, we have  $a_{\infty} = (m_R / K_R)^{1/2}$ .

Consequently, the maximum value of the distribution shifts towards smaller dimensions with decreasing  $m_R / K_R$  and toward larger drop dimensions with increasing  $m_R / K_R$ .

**Disperse composition of OE.** The higher the dispersion of OE, the more kinetically stable it is, since all other things are equal. However, due to a significant increase in the interface ( $S$ ), oil-water obtained by dispersing acquires a large supply of free surface energy  $F$  defined by the formula  $F = \sigma S$ , and becomes thermodynamically unstable; here  $\sigma$  is the free energy of a surface unit associated with the lack of equilibrium of charges around the molecules of the boundary layer. Such a system will tend to spontaneously go into a stable state by reducing  $F$ , which in turn can be done in two ways: by reducing  $S$  or surface tension  $\sigma$ . The last factor is exclusively widely used in the conditions of oil-gas production companies for the destruction of OE. This factor is controlled by the dosage of the corresponding chemical agent [6] and temperature [7].

Studies have shown that disperse composition (DC) is the only integral indicator of OE state at the entrance to the sloping apparatuses (SA), since such changes in the values of any flow parameters as the rate of formation and destruction of armoring casings (AC), coalescence and fragmentation of EWD ultimately reflected in OE DS. Taking into account the importance of this factor, we have developed a method for determining the density of distribution of emulsified water by drop size (8). According to this method, the distribution obtained in an industrial environment has the following form:

$$f(r) = \frac{4ab}{S} \cdot r / \left( a + \frac{b}{S} r^2 \right). \quad (7)$$

Coefficients  $a$ ,  $b$  and  $S$  are determined through hydrodynamic and rheological parameters of the flow at SA inlet.

**Physical-chemical properties of natural emulsifiers, forming adsorption protective casings on the interface surface.** The stability of emulsions is greatly influenced by stabilizing substances, called emulsifiers, which form adsorption protective casings on the surface of drops that prevent the coalescence of these drops. Such substances with high surface activity, as asphaltenes, naphthenes, resins, paraffin, metal porphyrin complexes and fine disperse inorganic substances consisting of clay, iron sulfides, sand and rocks, take part in the formation of adsorption casings. An increase in the concentration of Nano-dimensional colloidal particles, such as clay and iron sulfides, increases the mechanical strength of armoring casings [1].

**The presence of DEL in EWD.** The stability of OE to a large extent also depends on the electric charge on the surface of EWD. This is due to the fact that when two different phases (oil, water) come in contact, and especially when they move relative to the interface boundary, electric charges are transferred from a phase with a higher electric potential value to a phase with a smaller value. This transition leads to the formation of a charge in one phase and an equal, but opposite charge in another. Thanks to mutual attraction, these opposite charges remain at the interface boundary, forming DEL [9]. This source considers the formation of DEL in a suspension of drilling mud. In contrast, we consider the formation of DEL in EWD (in oil-water interphase section). From fig. 1, it can be seen that some counter ions are fragilely held on the surface and tend to move away from it, forming a diffuse ionic atmosphere around the particle. In addition to the attraction of ions, opposite sign of surface charge repulses ions of the same sign. As a result of the manifestation of these opposing forces, distribution of positive and negative ions arises, as schematically shown in Fig. 1, *a*. For EWD, the surface charge is negative and exchange cations (asphaltene) act as counter ions.

The distribution of ions in DEL leads to a change in the potential from the maximum on the surface of EWD to zero in the bulk of oil solution (see Fig. 1, *b*). The layer of cations closest to the surface of EWD, known as the "Stern layer", is associated with this particle and mixes with it, while the ions in the diffuse part of DEL have independent mobility.

As it can be seen from fig. 1, *c*, when two EWD approach each other with identical surface charges, a repulsive force appears, therefore, disperse EWD with DEL leads to OE stability.

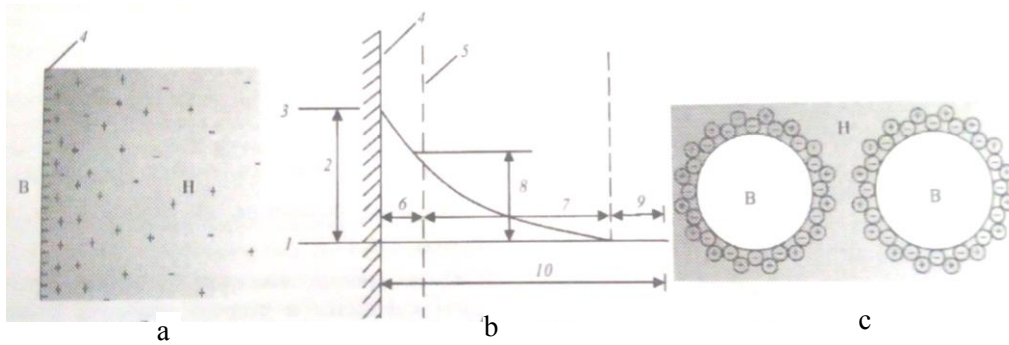


Fig. 1. Double electric layer on the surface of EWD

a - the model of the diffuse part of the electric double layer; b - a diagram illustrating zeta ( $\xi$ )-potential: 1- liquid potential; 2 - Nernst potential; 3- potential of armoring casings; 4- armoring casings of EWD; 5 - shear plane; 6- adsorbed part of EWD; 7- diffusive part of EWD; 8 - potential; 9- the bulk of solution; 10- distance from a solid; b - mutual repulsion scheme of two EWD of the same charge surface; B - disperse phase (water drop); H - disperse medium (oil)

Simultaneously with the electric repulsive force (ERF) ( $U_{EL}$ ) between DEL of the same sign, long-range dispersion force of Van-der-Waals-London ( $U_D$ ) attraction between EWD also moves. The stability of OE, in addition to the above mentioned factors, also depends on the sign and magnitude of the interaction, which is the sum of these forces:  $U = U_{EL} + U_D$ .

Imposition of electrostatic and disperse interactions is presented in Fig. 2. The ordinate axis shows upward values of electrostatic repulsion energy, downwards - values of attraction energy. The distance between the particles is plotted on the abscissa axis (10-12). In fig. 2, b, the secondary minima (potential wells) of EWD interactions at different values of DEL surface potentials are shown. The curve depicted by the dotted line corresponds to the dispersion energy of attraction.

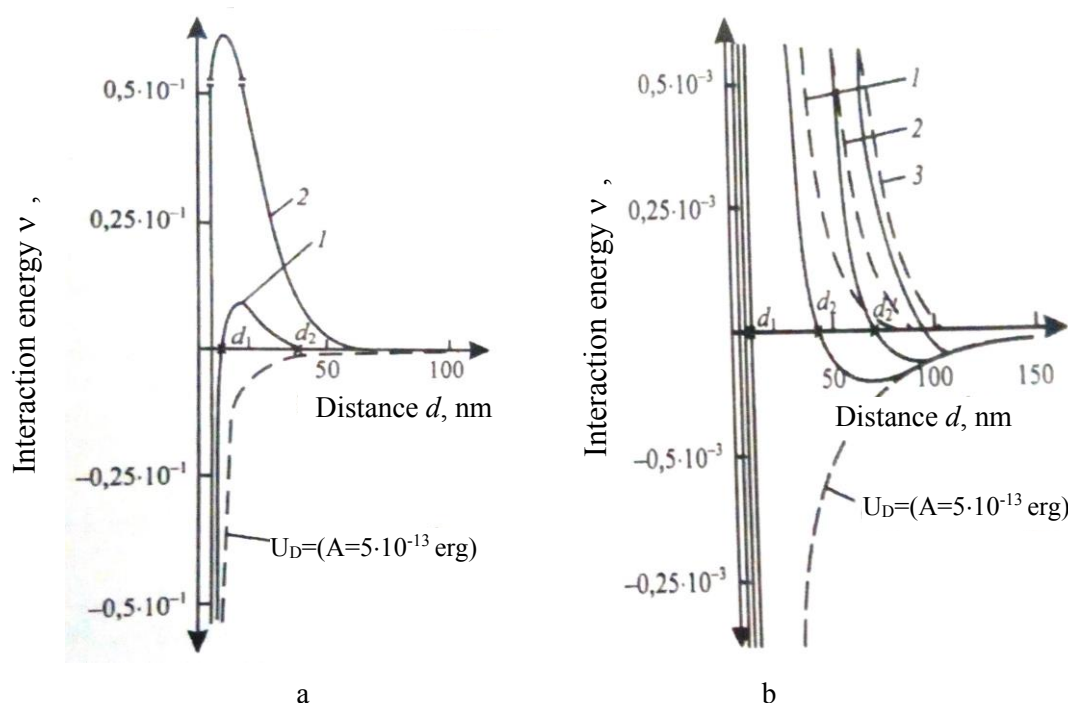


Fig.2. Interaction energy as distance function:

a -  $A = 5 \cdot 10^{-13}$  erg. and  $J = 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  and surface potential:

1 -  $\psi_0 = 20 \text{ mV}$ ; 2 -  $50 \text{ mV}$ ; b -  $A = 5 \cdot 10^{-13}$  erg. (for visualizing secondary lows image):

1 -  $\psi_0 = 20 \text{ mV}$ ; 2 -  $50 \text{ mV}$ ; 3 -  $200 \text{ mV}$ .

At point  $d_1$ , the forces of attraction and repulsion between particles are mutually destroyed. At this point, the particles can connect with each other, forming large agglomerates. However, before they can get closer to each other at such a distance, they must overcome the energy barrier (DEL). As the curves show, with an ionic strength of  $10^{-3} \text{ mol} \cdot \text{l}^{-1}$  and the Hamaker constant  $A = 5 \cdot 10^{-13}$  [12], the surface potential of 20 mB is already sufficient to prevent complete coagulation. If the surface potential decreases, then the energy barrier (EB) decreases and in comparison with  $KT$ , the values show that the system will undergo slow coagulation. The transition from high stability through slow coagulation to fast (i.e., the disappearance of EB) is continuous, without a sharp coagulation point. In this case, as it is shown by the results of our studies, when the distance between the drops is less than 50 nm, rapid thinning and interfacial film breaking and fusion (coalescence) of drops begin.

In contrast to suspensions in OE, in the interaction of EWD, two factors should be considered, namely: the possibility of the distortion of drops during their interaction and the presence of a diffuse layer inside the drops themselves. If the drops are stabilized due to the repulsion of double layers, then a close approach (due to turbulence and the temperature of OE flow) contributes to flattening of the surfaces; The potential EB counteracting the contact of drops (disjoining pressure) will be greater than the estimated undeformed spheres. In this case, the effective radius of curvature increases. The influence of the internal diffuse layer consists in the neutralization of a surface charge part by internal counter ions, leading to a decrease in the surface potential. Therefore, for this reason, the effect of DEL will be relatively weaker in the inverse emulsion (B/H) than in the straight line.

As it can be seen from fig. 2, EWD interactions occur at Nano-dimensional distances. In addition to the theory of DEL, there is also a solvation theory explaining the dependence of high aggregative stability of OE on the formation of a sufficiently powerful layer of DC molecules on the surface of EWD, which preclude particle fusion during a collision, and the theory of the structural-mechanical barrier, according to which the stability of OE is determined by the formation of adsorption casings on the surface of EWD with high structural viscosity.

**The temperature of the mixed liquids (oil and water) and specific consumption of demulsifier.** In order to make the coalescence process of EWD occur, it is necessary to eliminate (destroy) AC on the surface of the latter from the dispersed medium formed by the oleophilic colloidal stabilizers. Such a structural-mechanical barrier preventing the decrease of film thickness when the drops approach each other and thereby preventing their coalescence, can be destroyed only with an increase in temperature and introducing more surface- active substances into the system (than natural colloidal stabilizers), called demulsifying agents (DA). With increasing temperature, the stability of OE decreases, since in this case the mechanical strength of AC, especially containing refractory paraffin and ceresin wax, decreases, resulting in the coalescence of drops and destruction of OE. According to P.A. Rebinder's theory and his schools, DA molecules, possessing a greater surface activity than the natural stabilizers of OE, displace the latter from the oil-water interface. In this case, the DA molecules must first destroy (peptize) the AC. Being adsorbed on the colloidal particles of OE natural stabilizers, the DA molecules change their wettability, which contributes to the transition of these particles into the aqueous or oil phase. The adsorption layers formed in their place from the DA molecules practically do not have noticeable structural-mechanical properties, which contributes to the rapid coalescence of EWD with such casings during their effective collision.

**pH of emulsified reservoir water.** The pH value of the reservoir water also has a significant effect on the stability of OE. The influence of hydrogen factor pH impacts on the elastic properties of the surface layers, and its degree of influence on various oils varies. With increasing pH, rheological properties of the surface layers at the oil-water interface boundary are reduced, which entails the separation of OE. The pH value depends on the ionic composition of the reservoir water, in which many common salts are dissolved, decomposing (dissociate) into anions - ... .. and cations ... .. The radii of the listed ions do not exceed 1 nm. These ions are involved in the formation of DEL and AC.

In conclusion, as a result of the research, it was found that the processes of thermochemical preparation of oil is related to Nano-technologies, since the processes of formation, stability and destruction of oil emulsions are determined by the charge interaction of Nano-dimensional particles (asphaltenes, metal porphyrin complexes and petroleum resins, ions of reservoir water, clays, etc.) Taking into account the specific features (Nanophenomena) of oil preparation process, mathematical models of the coagulation and fragmentation process of EWD in the turbulence flow and the distribution of emulsified water in drop dimensions at the OA inlet are proposed. Molecular surface



phenomena that contributes to the formation of AC was analyzed. A structural model is proposed for the formation of DEL on the EWD surface and the stability of OE depending on the sign and magnitude of the interaction energy, which consists of the sum of the electrostatic repulsion energy and the van der Waals-London attraction energy.

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