The effect of electrization on the properties of flowing water-oil emulsion

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Abstract. The electrization of the water-oil mixture is a negative factor, the study of which has so far been neglected. Electrostatic charges generated in the pipelines during oil transportation, are accumulated in oil-water mixture. It essentially changes the corrosion activity of the aqueous phase and enables water-oil emulsion stabilization. The purpose of the study is to determine the effect of electrostatic charges that are generated during oil transportation through pipelines on the stabilization of water-oil emulsions. It is established that the accumulation of electrostatic charges in the oil phase leads to the stabilization of the water-oil emulsion, i.e. to the increase of "water-oil" interfacial tension. It is shown that demulsifiers increase the redistribution of electrostatic charges between aqueous and oil phases. The proposed method preventing the stabilization of emulsion is based on reduction of electrostatic charges redistribution in “water-oil” system by introducing antistatic surfactants.

1. Introduction
Emulsions are disperse systems composed of two immiscible or slightly immiscible liquids, one of which is dispersed in another as fine droplets (globules). The dispersed liquid is internal or dispersed phase and the surrounding liquid is known as the external or continuous phase. When emulsion is formed the surface of the dispersed phase increases. So a certain work, which is concentrated on the phase boundary in form of the free surface energy must be expended for emulsification process. The energy spent for the formation of a unit of a boundary surface is called interfacial tension $\sigma$.

The mechanical strength of the surface layers of high-paraffin oil significantly depends on temperature. However, demulsifiers are particularly effective in reducing the interfacial tension. The more efficient the demulsifier is, the more it reduces the mechanical strength of the oil surface layer. The adsorption of dispersed demulsifiers on the water-oil surface, thickening of the interfacial layer and gellation lead to the fact that the emulsion “water in oil” becomes more stable in time than the one that has just been formed [1]. Increasing the stability of oil emulsions leads to an increase of energy costs at the stage of oil processing, since such emulsions are much more difficult to be destructed than fresh ones. Therefore, the study of this phenomenon is of great practical importance.

2. Formation and stabilization of emulsions
The formation and stabilization of emulsions depend on several factors:
• Surfactant properties of water and oil phases, largely dependent on the amount and activity of reagents introduced during oil production.
• The gas factor. Formation of gas bubbles caused by the pressure changes in oil-well tubing significantly increases the emulsion formation.
• The roughness of the inner surface of the pipe.
• The type of pump for emulsion extraction and pumping. The most stable emulsions are formed when using centrifugal pumps, less stable emulsions are formed when using rod and screw pumps.
• Fluid flow rate.
• The dispersion and dispersed phases ratio.
• The ability of liquid phases to accumulate electrostatic charges.

An important indicator for oil emulsions is their stability, i.e. the ability not to separate into oil and water during a certain period of time. Stability of a dispersed system is characterized by the stationarity of its main parameters: dispersion and equilibrium distribution of the dispersed phase in the medium. When considering the stability of oil emulsions (as well as the stability of any dispersed systems), two types of stability should be distinguished: kinetic (sedimentation) and aggregative.

Sedimentation stability is the stability of the dispersed phase towards the gravity, i.e. it is the ability of the system to resist the sedimentation or flotation of particles (globules) of the dispersed phase due to gravity. For dilute systems, the kinetic stability can be estimated as the reciprocal of the sedimentation (or flotation) rate of particles of the dispersed phase:

\[
K_s = \frac{1}{W_r} = \frac{g v_N}{2(\rho_b - \rho_H) r_p^2 g},
\]

where \(W_r\) – sedimentation rate of the dispersed phase particles; \(r\) – particle radius; \(\rho_b - \rho_H\) – difference between the densities of the dispersed phase and the dispersion medium, \(\text{kg/m}^3\); \(v\) – kinematic viscosity, \(\text{m}^2/\text{s}\); \(g\) – gravity, \(\text{m/s}^2\).

It follows from the equation that the increase of the viscosity of the dispersion medium, the decrease of the difference in densities of emulsified media and the water globules radius (particles of the dispersed phase) leads to the higher kinetic stability of the emulsions.

Aggregative stability is the ability of the system to preserve the dispersion and individuality of the dispersed phase particles [2].

The authors consider that the electrization of the water-oil mixture during its transportation through pipelines leads to the stabilization of oil emulsions; in addition, as a result of electrostatic charges accumulation, the redox potential (Eh), corrosiveness, water pH and acid number of oil are changed. When the emulsion moves along insulated steel pipelines with or without internal lining, electrostatic charges are redistributed between water and oil. In this case, as general, negative charges are accumulated in water, and positive charges are concentrated in oil due to the formation of carbocations [3].

Let’s consider the mechanism of emulsions stabilization by electrostatic charges. The classic definition of Gibbs energy is the expression:

\[
G = U + PV - TS,
\]

where \(U\) – the internal energy; \(P\) – pressure; \(V\) – volume; \(T\) – temperature; \(S\) - entropy.
The Gibbs energy differential for a system with a constant number of particles, expressed in its own variables — by pressure $p$ and temperature $T$:

$$dG = -SdT + VdP .$$

For a system with a variable number of particles, this differential is:

$$dG = -SdT + VdP + \sigma dw + \sum \mu_i dn_i + \phi dq ,$$

where $\sigma$ – the surface tension;
$w$ – the area;
$\mu_i$ – the chemical potential of the $i$-th component, which can be defined as the energy that must be expended to add another particle to the system;
$n_i$ – the number of moles of the $i$-th component;
$\phi$ – the electric potential;
$q$ – the amount of electricity (charge).

This equation shows the Gibbs energy increment in terms of the algebraic sum of the increments of other types of energy. Obviously, the surface energy is able to transform into the following types of energy:

- Gibbs energy;
- thermal (heat) energy;
- chemical energy;
- mechanical energy;
- electrical energy.

The surface energy transformation into one of the listed types of energy corresponds to certain surface phenomena, such as changes in reactivity caused by changes in dispersion, adhesion and wetting, capillarity, adsorption, electrical phenomena.

The free energy of the system increases ($\Delta G > 0$) in the process of dispersion, the system is characterized by high $\sigma$ values at the phase boundary. An excess of free energy makes such systems thermodynamically unstable. They are characterized by spontaneous processes that reduce this excess.

The size of water droplets in emulsion is usually inversely proportional to the amount of energy expended in the process of fluid turbulization. The more energy is expended, the smaller the diameter of the droplet is, and, therefore, the larger their total specific surface area is. Emulsions instability is primarily associated with an excess of interfacial free energy. The surface energy $\sigma ds$ can transform into electrical (electrical and electrokinetic phenomena) energy. The value of surface tension can be influenced by the introduction of a surfactant. For example, demulsifiers, which are applied for emulsions destruction, reduce $\sigma$ at the phase boundary.

The tendency of a heterogeneous system to reduce the surface energy causes negative orientation of polar molecules, ions, electrons in the surface layer. As a result, the contacting phases (water-oil) acquire charges of opposite sign, equal in magnitude. In this case, according to the Gibbs energy increment equation the excess surface energy can be converted into electrical energy.

From the combined equations I and II of the thermodynamics beginning, we have

$$dG = \sigma dw + \phi dq$$

at $T, p, n$ – const.

Subtracting this equation from the equation of the total differential of the Gibbs energy, we obtain

$$wd\sigma + qd\phi = 0$$

or
\[ -q_w = \frac{d\sigma}{d\varphi} \]  

The last formula is called the Lippmann equation [4]. It defines the relationship between the charge, the potential of an electrical double layer and the surface tension of the medium in which it is formed. In the case of a two-phase system “oil-water”, the redox potential of water is meant to be electric potential. An increase in the redox potential of the system increases the formation energy of a double electric layer on the surface of water globules. This leads to mutual repulsion of the aqueous phase droplets, which complicates their coalescence. Thus, the accumulation of electrostatic charges by the aqueous phase significantly increases emulsion stability, which leads to an increase in energy consumption for its further destruction.

In real systems tending to equilibrium, the signs of \( q_w \) and \( \varphi \) coincide, and therefore, a decrease in the redox potential of water is accompanied by an increase of its surface tension.

The interaction between Van der Waals attraction and repulsion of double electric layers is described by the DLVO theory, named after the four scientists who developed it - Deryaguin, Landau, Verwey and Overbeek. When two particles approach one another, they are exposed to two forces having a different nature and opposite orientation:

- Van der Waals attraction force (\( F_A \)), depending on the specific surface and mass of the colloidal particle, as well as on the nature of the medium in which it is located;
- electrostatic repulsive force (\( F_R \)), depending on the surface charge of the particles.

The resultant of these two forces, \( F = F_A + F_R \), significantly exceeds the Van der Waals force, which can, therefore, be neglected, and, at the same time, determines the direction of the process towards the aggregation (adhesion) of particles, provided that the following inequality is valid: \( F_A > F_R \) (in absolute value) or in the direction of their mutual repulsion, if \( F_R > F_A \). There is an opposition between these forces, which determines the stability of dispersed systems. The attraction prevails at short and at large distances between particles. At intermediate distances, the repulsion of double electric layers, provided by highly charged surfaces with not very high concentrations of electrolyte in a dispersion medium, can exceed the attraction forces. When the particles come very close to each other, there is a very strong repulsion due to the electron clouds overlapping - Brownian repulsion. It is obvious that repulsion is possible due to the formation of an electric double layer (Stern layer) at the boundary of the globe.

Thus, in order to break the stability of the emulsion (to coagulate) it is necessary to reduce the electrostatic repulsive force, which leads to the necessity of the colloidal particles surface charges neutralization. This is exactly what can be obtained by adding so-called demulsifiers into the water. According to the double layer theory, optimal coagulation can be achieved by introducing a reagent that allows to reduce electrokinetic potential value (i.e. potential formed on the surface of the electric double layer) to zero.

3. Results and discussion

It has been experimentally established that the introduction of demulsifiers into emulsion, along with the initial decrease in the “water-oil” interfacial tension in course of time leads to an increase in electrostatic charges redistribution, which significantly increases the surface tension. Thus, at a certain distance from the point of dispensing the demulsifier into the pipeline, a charge sufficient for further stabilization of the original emulsion will be accumulated.

The interaction at close distances (i.e., the repulsive force between molecules that occurs when their electron clouds overlap) is called the exchange interaction \( U_{exc} \). The energy of exchange interaction is calculated on the basis of quantum mechanics, according to the Pauli principle. Other intermolecular interaction forces can be considered in the framework of classical electrostatics. The total interaction energy can be represented by the following expression:
\[ U = U_{\text{ele}} + U_{\text{ind}} + U_{\text{dis}}, \] (8)

where \( U_{\text{ele}} \) - the energy of the electrostatic interaction;
\( U_{\text{ind}} \) – the energy of induction interaction;
\( U_{\text{dis}} \) – dispersion-interaction energy \([5]\). The charge generated during emulsion electrization increases the total interaction energy due to an increase in the energy of electrostatic interaction. Thus, for this case, the Gibbs energy increment is determined only by the change in the electrostatic interaction energy between the emulsion components:

\[ \Delta G = U_{\text{ele}} = \sigma \Delta w + \psi \Delta q, \] (9)

where \( \Delta G \) – Gibbs energy increment;
\( \Delta w \) – change of the contact area of the dispersed phase with the dispersion medium;
\( \Delta q \) – the charge generated when the emulsion is electrified.

The effect of accumulated electrostatic charge on the surface tension of water globules is described by the following equation:

\[ \sigma = \frac{\psi \Delta q}{d w} \] (10)

These equations explain the experimental increase of water surface tension along with the increase of electrostatic charges redistribution. Low values of the redox potential, corresponding to a higher accumulated charge, lead to a significant decrease in the corrosivity of water and to a greater stabilization of the oil-water emulsion \([6-8]\). Figure 1 represents a scheme for stabilizing a water-oil emulsion under the conditions of electrostatic charges redistribution.

![Figure 1](image-url)

Figure 1. Scheme for stabilizing a water-oil emulsion under the conditions of electrostatic charges redistribution: 1 – change of “water-oil” interfacial surface tension along the length of the pipeline without surfactant; 2 – increase in surface tension along the length of the pipeline with a demulsifier; 3 – “water-oil” interfacial tension with antistatic surfactant; \( \sigma_1 \) – the surface tension of water at the beginning of the pipeline; \( \sigma_D \) – the surface tension of water in the presence of a demulsifier; \( \sigma_A \) – the surface tension of water in the presence of an antistatic surfactant; \( \alpha \) – the angle of increase of interfacial tension due to electrostatic interactions; \( \beta \) – the angle of increase of interfacial tension due to the influence of the demulsifier.
The “water-oil” interfacial surface tension increases in the absence of surfactants due to the electrostatic interaction energy, which increases along the length of the pipeline proportionally to \( \sigma_{water-oil} \).

In this case, with an increase in the length of the pipeline \( l \), the electrization of the emulsion and, consequently, its stability, increases. Introduction of demulsifiers reduces the surface tension of water \( \sigma_{water-oil} \), which contributes to a better coalescence of water droplets. However, transporting an emulsion with a demulsifier increases electrization, the electrostatic interaction energy along the length of the pipeline increases proportionally to \( \sigma_{water-oil} \). In this case, the electrization proceeds more intensively, therefore \( \beta > \alpha \). At a certain critical length of the pipeline \( l_{cr} \), accumulated energy will be sufficient to block the properties of the demulsifier. When the pipeline length is \( l > l_{cr} \), the interphase surface tension will increase to degree when the emulsion will stabilize, i.e. the effect of the demulsifiers application in this area will disappear.

Introduction of antistatic surfactants reduces emulsion electrization and keeps the interaction energy between the particles of water and oil low and constant along the length of the pipeline. In this case, the surface tension of water has lower values and does not increase with increasing pipeline length. Thus, the stability of the emulsion is reduced, which ensures cost reduction for its destruction.

4. Conclusion

1. Electrostatic charges are accumulated when the “water-oil” emulsion moves along pipelines. In this case, a positive charge accumulates in the oil phase, and a negative charge – in the water phase. These processes occur both in pipelines lined with polymeric materials and in steel pipelines that have only external insulation.

2. There is a change in the redox potential, corrosivity and the pH of the aqueous phase, as well as the “water-oil” interfacial surface tension as a result of “oil-water” emulsion electrization.

3. Introduction of demulsifiers, along with the initial decrease in “water-oil” interfacial tension during the emulsion transportation through the pipeline causes an increase in its electrification, which leads to inversion of demulsifier properties and significantly increases the surface tension of water.

4. Introduction of antistatic surfactants reduces the electrization of the emulsion and keeps “water-oil” interfacial surface tension low and constant along the length of the pipeline. In this case, the stability of the oil-water emulsion is reduced, which significantly reduces the cost of its destruction.

5. Application of antistatic surfactants reduces accumulation of positive electrostatic charges in the oil phase and increases pH of the aqueous extract, that allows to reduce the corrosion rate of equipment for oil processing and storage.

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