Concentrated salt-resistant emulsions of the "oil in water" type used for the development of oil and gas wells

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Abstract. Currently, water-based and hydrocarbon-based oil and gas well silencing fluids are widely used. The most promising liquids for silencing and developing wells are direct emulsions, whose viscosity can be regulated by changing the concentration of the "oil" phase. Urgent task is to develop polymer-free structured emulsion compositions for developing and silencing low-temperature oil and gas wells that are stable when the water phase is saturated with sodium or potassium chlorides. For use in protected areas, the developed formulations should use vegetable oils and esters based on them as the oil phase, along with hydrocarbons.

Currently, water-based and hydrocarbon-based oil and gas well silencing fluids are widely used. The first group includes solutions of mineral salts, foams, fresh and reservoir waters, as well as direct emulsions. Hydrocarbon-based liquids include commercial or thickened oil and invert emulsions with an aqueous phase content of up to 80% vol. Among the disadvantages of hydrocarbon systems, we can distinguish their blocking effect due to capillary forces that are realized when mineralized reservoir water is displaced from the pore space, which can lead to the formation of persistent water-oil emulsions in the reservoir. In addition, oil-based compounds have increased combustibility and a low level of environmental safety for the environment.

Sodium chloride (halite), which has the optimal combination of low cost and high availability in comparison with other salts, is the most widely used as silencing fluids for low-temperature gas wells. Sodium chloride is usually used for the preparation of silencing liquids with a density of up to 1.18 g/cm³. For the preparation of liquids with a density of 1.18 to 1.30 g/cm³, calcium chloride is used, and for the preparation of silencing liquids with a density of more than 1.30 g/cm³, potassium carbonate (potash), as well as other salts or mixtures thereof can be used. Water brines are thickened with polymer additives based on polysaccharide derivatives to reduce the level of filtration of the water phase into the productive layer. Polymers are limited in solubility in a saline medium, so their aqueous solutions are close to dispersions in properties. Water-polymer compositions may also contain a highly dispersed filler and surfactant for hydrophobizing the pores of a productive formation. The article [1] describes an oil and gas well silencing fluid containing a surfactant, a polymer emulsion, a highly dispersed hydrophobic material, and an aqueous solution of mineral salt. The presented composition has insufficient insulating properties and increases the water content of the extracted hydrocarbons. A polysaccharide gel for silencing wells containing mineralized water, a polysaccharide thickener, a
boron crosslayer, diethanolamine, Quaternary ammonium compounds, and a mixture of non-ionic and anion-active surfactants has low sedimentation stability and complexity of preparation [2]. Polymer gels based on high-molecular polyacrylic derivatives, magnesium or calcium chloride and surfactants [3] reduce reservoir properties due to high filtration rate and significant adsorption activity of macromolecules of the thickener. As a result, the use of anion-active polymers and surfactants in the silencing liquid in combination with concentrated solutions of mineral salts leads to the formation of highly dispersed precipitation, as well as blocking adsorption layers that are impervious to hydrocarbons.

Replacement of polymer thickeners with oligomeric and low-molecular-weight alcohol-containing components (triethanolamine, polyglycols, aliphatic alcohols, etc.) [4, 5] in combination with saturated aqueous solutions of alkaline and alkaline earth metals provides the required level of inhibition of hydrate formation, but does not allow to effectively regulate the rheological, filtration and inhibitory characteristics of the system. For example, a silencing liquid based on triethanolamine and a solution of calcium chloride reduces the permeability of terrigenous zones as a result of increasing the volume of water-sensitive minerals and reducing the porosity of the formation [4]. The low viscosity of the silencing fluid, which does not contain polymer thickeners, makes it ineffective when silencing highly permeable reservoirs, since the absorption volumes increase and the time of well development increases. Included in many liquids the aqueous solution of calcium chloride causes the formation of high viscosity oil-water emulsion, coagulation of clay particles and precipitation of insoluble solid inorganic salts in the channels of the filter layer, which leads to increased water saturation in the productive formation, reduce permeability of the reservoir hydrocarbon and increases the water content of hydrocarbons. Disadvantages of silencing fluids based on polyglycol [5] are the propensity to foam and the presence of sodium hydroxide in the polyglycol composition, which interacts with carbonate rocks to form water-insoluble salts, and also causes swelling and dispersion of clay minerals, reducing the permeability of the bottom-hole zone of wells and their productivity coefficient.

The most promising liquids for silencing and developing wells are direct emulsions, whose viscosity can be regulated by changing the concentration of the "oil" phase. To ensure the stability of such emulsions in mineralized water, low-viscosity derivatives of lignosulfonates, polysaccharides, and oligomers based on acrylate or sodium methylsiline are used [6-8]. Direct emulsions contain up to 40% of hydrocarbons (diesel fuel, gas condensate) and are stabilized mainly by oil-soluble emulsifiers. A common disadvantage of emulsion compositions is their low stability at a high concentration of mineral salts in the water phase, which is 10-25%. This narrows the range of regulation of the specific gravity of the silencing fluid, and also does not allow you to completely abandon the use of anionic polymer stabilizers.

Thus, an urgent task is to develop polymer-free structured emulsion compositions for developing and silencing low-temperature oil and gas wells that are stable when the water phase is saturated with sodium or potassium chlorides. For use in protected areas, the developed formulations should use vegetable oils and esters based on them as the oil phase, along with hydrocarbons. The stability of the direct emulsion, which is a microdispersed oil phase (OF) (with an acid number of 80 mg (KOH)/g) distributed in fresh water, reaches a maximum in the pH range = 9 - 9.5, corresponding to the highest degree of electrostatic protection. In the absence of an emulsifying surfactant, the stability of the OF emulsion dispersed in the aqueous phase is very low. The rate of coalescence of oil droplets is proportional to the difference in densities of dispersed phase and dispersion medium, droplets OF the radius and inversely proportional to the viscosity of the water phase. Therefore, drops of the oil phase in direct emulsions must be stabilized with the addition of non-ionic oxyethylated surfactants (OS). The combination of the electrostatic factor of stabilization of emulsions due to the presence of negatively charged carboxylate groups on the surface of micelles and the sorption-solvate protective effect of hydrated adsorption layers of surfactants allows creating a sufficient potential energy barrier of the order of 20*k*T, which increases the half-life of the oil drop
to several years [9]. The structure of the protective barrier formed in a freshwater dispersion medium is shown in (Figure 1).

Figure 1. Formation of an adsorption layer of an oxyethylated surfactant on the surface of an oil drop.

Oxyethylated surfactants provide stability of the direct emulsion only if the dispersion medium is a good solvent for polyoxyethylene chains that are distributed near the drop surface and are linked to the carboxyl groups of OF by hydrogen bonds. Therefore, polyoxyethylene surfactant chains provide the implementation of a steric stability factor that occurs when entropy decreases when the adsorption layers interpenetrate when neighboring droplets converge.

Electrostatic stabilization of direct emulsion microdrops is not sufficient when the ionic strength of the water phase increases when the 1-1-valence electrolyte (NaCl) is dissolved. The destruction of the emulsion (floculation consolidation of the droplets with the formation of the top layer of "cream") is due to two reasons: a critical lowering of the electrostatic repulsion between the drops in the transition to the isoelectric condition (coagulation concentration) and decrease the solubility of surfactants, which is accompanied by the degeneration of the entropy factor, which becomes the cause of the hydrophobic attraction dehydrated adsorption layers of adjacent particles OF.

To ensure the stability of the direct emulsion under conditions of saturation of the aqueous phase with electrolyte, it is necessary to introduce an additional structural and mechanical stability factor, which is realized as a result of interpolymer complexation between carboxylate groups on the surface of OF micelles and the substituent associations of divalent cations of alkaline earth or transition metals Me²⁺ (Ca²⁺, Mg²⁺, Cu²⁺, Fe²⁺) [10, 11] (Figure 2).

Figure 2. Formation of a structural-mechanical barrier on the surface of microemulsion droplets due to interpolyelectrolyte complexation of Me²⁺-[EO]₅ substituent associates with COO⁻-groups.

Podand poly-cationic associates are formed as a result of the coordination of divalent ions (Me²⁺) within the crown-like five-membered oxy-ethylene cycles of surfactant molecules: Me²⁺-[EO]₅. At the same time, 1 structural unit of the substandard polycation Me²⁺-[EO]₅ electrostatically shields 2 COO⁻-groups, so the structural stability coefficient (Kₘₚ) of the emulsion is equal to the ratio of the amounts of substances of the components of the interpolymer complex (IPC), taking into account its stoichiometry. Accordingly, the steric stability factor of the emulsion (Kₛ) describes the entropic stabilization of the system and is determined by the ratio of five-membered oxyethylene cycles and carboxyl COOH- groups.
When the mass ratio between surfactant and OF changes, the stability and rheological properties of the direct emulsion undergo significant changes, which is associated with different levels of electrostatic and structural-mechanical stabilization of the system (Table 1).

**Table 1.** Colloidal-chemical properties of a direct emulsion with a different ratio of the oil phase (OF) and nonionic surfactant.

| Colloidal-chemical properties of the emulsion | Mass ratio of OF: surfactant in emulsion (100 g) |
|-----------------------------------------------|-----------------------------------------------|
| Acid number OF, mg(KOH)/g                      | 80:20  | 65:35  | 50:50  | 30:70  |
|                                               | 80     | 80     | 80     | 80     |
| The mass ratio of the phases «water-in-oil»   | 85:15  | 85:15  | 85:15  | 85:15  |
| NaCl concentration in the aqueous phase of the emulsion, % wt. | 26     | 26     | 26     | 26     |
| Degree of dissociation COOH-groups          | 39,5   | 39,5   | 39,5   | 39,5   |
| Number (υ) of COOH-groups OF, mol            | 0,026  | 0,021  | 0,017  | 0,009  |
| υ (COO⁻-groups) OF, mol                      | 0,017  | 0,014  | 0,011  | 0,006  |
| υ (surfactant), mol                          | 0,005  | 0,009  | 0,012  | 0,017  |
| υ (EO)₅, mol                                 | 0,009  | 0,015  | 0,022  | 0,031  |
| υ Ca²⁺, mol                                  | 0,0022 | 0,0022 | 0,0022 | 0,0022 |
| υ (COO⁻) as part of the IPC: [Ca-(EO)₅⁺₂⁻COO⁻], mol | 0,0044 | 0,0044 | 0,0044 | 0,0044 |
| υ (Me²⁺)/υ (COO⁻)                           | 0,26   | 0,32   | 0,42   | 0,67   |
| υ [EO]₅/υ (COOH)                            | 0,17   | 0,50   | 1,04   | 2,96   |

![Graph](image-url)
Figure 3. Change in the coefficients of structural (Kst) and steric (Ks) stability of the emulsion with an increase in the mass fraction of oil in the surfactant composition.

As a result of lowering the stability coefficients, the stability of the direct emulsion with increasing oil concentration in the system also decreases, which can lead to the transition of the system to a state characterized by a deep secondary potential minimum. This is a fairly stable energy state in which the oil droplets are as close to each other as possible, but retain their integrity. In this case, the emulsion acquires high structural-mechanical and rheological properties, acquiring the features of a strong gel (Figure 4).

![Figure 4](image_url)

Figure 4. Change in the rheological properties of the direct oil emulsion in the composition OF: surfactant (total concentration of the complex OF + surfactant = 15 % by weight).

The increase of the static strength of the structure (GEL) and dynamic viscosity (η) with increasing concentration of the oil phase indicates the presence of long-range order interactions between the dispersed particles of the emulsion resulting in the development of hydrophobic complexation by overlapping adsorption layers of adjacent particles, between which there is an electrostatic barrier. Further convergence of the droplets is prevented by a structural-mechanical barrier due to the presence of IPC at the phase interface. On the contrary, when the oil concentration is low, the distance between the microdrops increases, which prevents hydrophobic interactions; the stability of the emulsion increases significantly, and the structural spatial grid of dispersed particles disappears. Increasing the oil concentration above 80%wt. it is impractical, since it leads to an increase in coagulation processes and stratification of the emulsion with an insufficient level of steric and structural-mechanical stabilization (Ks < 0.1; Kst < 0.1).
It is convenient to characterize the stability of emulsions by the phase inversion temperature (PIT), which is the transition temperature of the direct emulsion to the reverse. To determine the PIT, the direct emulsion was stirred at 8000 rpm with increasing temperature and identified by the sharp drop in conductivity when added to an aqueous dispersion medium (Figure 5, a) passes into a state with an oil dispersion medium. In the temperature range above PIT, after mixing is stopped, the emulsion usually breaks down to form a three-layer structure: the lower layer of water, the middle thin layer of the bicontinual emulsion, and the upper layer of oil (Figure 5, b).

![Figure 5. Stratification of the direct emulsion when heated above PIT.](image)

The direct emulsion PIT decreases with increasing electrolyte concentration in the water phase, as well as with additional introduction to the system relative to the polar oil phase as a solubilizer. The more polar the oil is (it contains multiple bonds, phenyl groups, branches of the hydrocarbon skeleton, etc.), the lower the typhoid. In addition, PIT is lowered by additives that increase the polarity of the oil phase – fatty acids and alcohols. Additives less polar, but well soluble in water, significantly increase PIT. Figure 6 shows a change in the PIT of direct emulsions containing different ratios of OF: surfactants, with an increase in the concentration of sodium chloride.

![Figure 6. Dependence of PIT emulsions containing different ratios of OF and surfactant on the concentration of NaCl (total concentration of OF + surfactant = 15 % by weight).](image)
Increasing the surfactant concentration increases the PIT of the emulsion in conditions of high electrolyte concentration, which is associated with an increased role of the electrostatic and structural-mechanical mechanisms for system stabilization.

The advantages of the electrostatic method of stabilization of direct emulsions are the minimum number of system components, a wide range of variations in rheological characteristics and PIT, and the absence of adsorption active reagents in the polymer composition. To increase the stability of direct emulsions and expand the temperature range of their use (increasing the PIT), it is necessary to increase the coefficients of steric and entropic stability of the system by increasing the concentration of oxyethylated surfactant, reducing the volume fraction of the oil phase, or using special additives that reduce the acid number of the oil. With an increase in the electrolyte concentration in the aqueous phase of the emulsion, the PIT decreases, remaining at a sufficient level (>40°C) in full salinity conditions for the use of emulsion compositions in low-temperature wells. Additional solubilization of polar oil-soluble components (fatty acids and esters of vegetable oils) leads to the development of coalescence and reduction of the PIT emulsion. On the contrary, the introduction of non-polar hydrocarbons (alkanes, polyolefins, mineral oil), as well as polyatomic alcohols (triethylene glycol, propylene glycol, glycerin) into the emulsion provides a moderate increase in PIT as a result of the hydrotropic effect.

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