Development of polymer emulsions stabilized with anionic polyelectrolytes

A V Khvatov¹, P A Sakharov¹, Yu K Lukanina¹ and E V Belenko²

¹ Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin str., 4, Moscow, 119334 Russia
² MIREA - Russian Technological University, 78 Vernadsky Avenue, Moscow, 119454 Russia

E-mail: hvatovanatoliy@gmail.com

Abstract. The colloidal-chemical principles of the formation of reversibly reversible microemulsions based on compositions of anionic polysaccharides, higher fatty acids, and non-ionic polyoxyethylated surfactants have been investigated. The structural formula of the interpolymer complex in the "polyelectrolyte - surfactant" system was proposed, and the molar ratios of the components were determined. The effectiveness of the developed polymer emulsions as drilling fluids for the construction of oil wells is shown.

More recently, the ever-increasing levels of inclined and horizontal drilling in low-permeable, difficult production horizons have placed new demands on the rational use of expensive reagents and on the quality of their technology. The basic condition for the prospect of a new technology in the field of well washing is to ensure a minimum material intensity of the selected system, capable of maintaining effective performance for the maximum number of cyclic effects on the compound.

In light of the above, the most promising flushing systems with high technological potential are solutions with a variable controlled number of dispersed phases, characterized by a pronounced encapsulating effect. Such solutions can be divided into emulsion systems in which an oil-soluble dispersed phase can be combined with both a polymer stabilizer and a colloidal clay fraction, as well as direct polymer emulsions (polyemulsions) that stabilize a hydrophobic colloid by using traditional polymer thickeners of an aqueous dispersion medium. In this case, the reversal of the dispersed phase in emulsion solutions is due to the presence of a reversible equilibrium "micellar surfactant solution ↔ direct surfactant emulsion", while in polyemulsions at the point of reversal, a reversible phase inversion occurs.

The most typical systems of this class are clay-emulsion solutions, in which the reversibly reversible component is nonionic oligomeric surfactants, for example, polyalkylene glycols, characterized by cyclic alternation of acts of intra- and intermolecular association under the influence of external - thermobaric or internal - solubilization factors [1, 2]. Such fluids perfectly preserve the stability of inclined wells, have a high carrying capacity, and minimize differential sticking during drilling. At the same time, the degree of dispersion of the oil-soluble surfactant phase is easily controlled under drilling conditions by changing the intensity of intermolecular hydrophobic interactions [3]. The loss of surfactant due to adsorption on the cuttings during the circulation of the solution is very low, which ensures the preservation of the efficiency of the system for a maximum time and does not require additional treatments, as well as the introduction of new duplicating...
reagents. Thus, the high efficiency of reversible colloidal systems in combination with the resource-saving nature of their use creates the prerequisites for large-scale industrial implementation of emulsion solutions as the most progressive and science-intensive technological solutions in the field of well construction.

Stable emulsion systems can be obtained by solubilizing hydrophobic higher fatty acid molecules in complex micelles formed by nonionic surfactants (polyalkylene glycols (PAG)) and anionic polysaccharides. Earlier, emulsion systems based on the following binary compositions were investigated: polysaccharide thickener (CMC) - higher tall oil fatty acids (TO); non-ionic emulsifier (PAG) - TM. Thus, the authors of [4-6] have studied the ability of higher fatty acids to solubilize in micellar solutions of PAG, which leads to the formation of a microemulsion, which significantly increases the lubricating and pseudoplastic properties of the drilling mud. It was noted that the introduction of HM into an aqueous solution of CMC or starch at the stage of swelling of the polymer reagent significantly increases the viscosity characteristics of the resulting structured liquid, increases the yield point of the system, and imparts inhibiting and hydrophobic properties to it. The source of technological modification of polysaccharide solutions, apparently, is the solubilization of fatty acids in the internal hydrophobic cavities of macromolecular helices, the sizes of which correspond to the effective volume of hydrocarbon radicals of fatty acids.

Gels based on concentrated surfactant solutions are also of a viscoplastic nature [7]. In such solutions, macromicellar aggregates interact at close range due to the formation of hydrogen, van der Waals, or ionic bonds, forming a cellular structure. The pseudoplastic nature of concentrated emulsions is due to the elongated elongated shape of supramolecular aggregates, which are easily oriented in the direction of the shear rate. Micellar solutions used in the practice of drilling and oil production have a low concentration of micelle-forming surfactants, no more than 5-10 times higher than the CMC. As a rule, such solutions include an oil-soluble solubilizate (hydrocarbons, higher fatty acids), which leads to the formation of axisymmetric micellar aggregates and, accordingly, the development of structure-forming and pseudoplastic properties [8, 9]. Unfortunately, compared to polymeric (crosslinked ionic bonds or biopolymer) structures, micellar gels are characterized by non-reproducible rheology under shear or thermal effects. Therefore, the development of new types of hydrogels - polymer-micellar, combining high structural and pseudoplastic properties characteristic of crosslinked polymer systems, and optimal technological characteristics (surface-active, lubricating, anti-filtration, inhibiting), inherent in concentrated micellar systems such as "surfactant-solubilizate".

Until now, it has been possible to obtain stable direct emulsions only under conditions of relatively low salinity of the aqueous phase of the system (less than 10 - 12% in terms of sodium chloride concentration) and within a limited temperature range - not higher than 80° C. The thermal stability of the direct emulsion begins to decrease sharply with an increase in the salt concentration in the aqueous phase, since the electrostatic stability of the system is disturbed. This is accompanied by the development of coalescence - microdroplets of the emulsion enlarge and the formation of "cream" occurs - phase separation, when the oil is concentrated in the form of a thick layer of invert emulsion on the surface of the aqueous phase. The temperature at which the phase separation of the direct emulsion occurs (phase inversion temperature (TIP)) depends both on the type and nature of the emulsifier and on the charge of the coagulating salt cation. When passing from sodium chloride to calcium and aluminum salts, the TIP of the emulsion decreases. The stability of the direct emulsion also changes with a variable pH level of the system and when using emulsifiers with a variable (pH-dependent) value of the hydrophilic-lipophilic balance (HLB). So, by selecting the emulsification conditions, the pH level of the medium and the concentration of the emulsifier, it is possible to achieve a reversible reverse transition of the direct emulsion to the opposite one, which is quite often used for drilling in variable mining and geological conditions. So, in [4, 10], reversibly reversible emulsion drilling fluids are described, the phase transformation in which occurs as follows: a surfactant complex and a part of the dispersed phase (water) are added to the inverse emulsion, due to this, the transition of the inverse emulsion into the direct emulsion occurs, and then by adding a new complex of
surfactants, the resulting direct emulsion can be converted into reverse. Moreover, a similar reverse conversion can be carried out for direct emulsions.

It was found that when unsaturated higher fatty acids, for example, oleic acid (OA), are introduced into aqueous PAG solutions, a significant decrease in Tp occurs. PAG (Figure 1). At the same time, the interfacial tension of solutions at the interface with air increases (Figure 2).

![Figure 1](image)

**Figure 1.** Changes in the cloud point of aqueous PAG solutions with a molecular weight of 2500 and a content of OE units of 30, 50, 70% (mol.) (Respectively, curves 1, 2 and 3) with the introduction of OA.
Figure 2. Influence of OA on the interfacial tension of aqueous PAG solutions at the interface with air. The molecular weight of PAG is 2500, the content of OE units is 30, 50, 70% (mol.) (Curves 1, 2, 3, respectively).

The mass concentration of PAG in aqueous solution in all experiments was 0.3 g/dl. The interfacial tension reaches its maximum value when the mass ratio between PAG and OA is 3: 7, respectively. The molar ratio between PAG and OA, at which $\sigma_{12}$ is maximum, is as follows: $\approx 1:28$. It was found that with the introduction of PAG and OA into an aqueous solution of NaCMC (molecular weight 122800, degree of carboxymethylation 0.98), the increase in $\sigma_{12}$ with an increase in OA concentration slows down (Figure 3). At a NaCMC concentration of 0.5 g/dl, $\sigma_{12}$ stabilizes (changes very slightly with an increase in the OA content in the system).
The discovered ability of NaCMC to stabilize the interfacial tension of aqueous PAG solutions is apparently explained by the redistribution of PAG molecules in an aqueous solution, some of which are involved in the emulsification of OA, while the other interacts with functional groups of NaCMC, forming interpolymer structures, the formation mechanism of which can be studied by the viscometric method. The curves were obtained for the dependence of the flow time of NaCMC solutions on the concentration of PAG (molecular weight 2500, content of OE units 85 mol%) (Figure 5). Regardless of the degree of NaCMC polymerization (low molecular weight (CMC-LW), medium molecular weight (CMC-MW) and high molecular weight (CMC-HW) samples were studied), with an increase in the concentration of PAG, a decrease in the relative viscosity is first observed, which then begins to grow again at a concentration of PAG above 10 - 11 g/l, which, apparently, indicates the interaction of PAG with NaCMC with the formation of intermolecular complexes. The most probable mechanism for the interaction of PAGs with NaCMC is their association through a counterion similar to crown ethers (Figure 4). The molar ratio between substituted (containing a carboxymethyl group) anhydroglucose cycles NaCMC and OE-PAG units at the inflection point of the viscometric curves (Figure 5) is ~ 1:8, respectively.
The effect of a mixture of PAG and OA on the rheological properties of an aqueous solution of NaCMC was studied. The experimental scheme was as follows: a mixture of PAG and OA (in the previously selected molar ratios of PAG: OA = 1:28) in an amount of 10 g was introduced into an aqueous solution of NaCMC with a volume of 100 ml. After that, the solution was stirred for 10 min. on a high-speed mixer (5000 min⁻¹). Then the solution was placed in a measuring cup of a rotary viscometer and the rheological properties were measured at 3, 6, 100, 200, 300, and 600 min⁻¹. The measurement results were used to construct rheological curves and calculate the ultimate strength (τₛ) and yield (τₒ) of the system, as well as the values of plastic (ηₚ) and effective (at 600 min⁻¹) (ηₑ) viscosities. The concentration dependences of the plastic and effective viscosities are shown in Figure 6.
Figure 6. Dynamics of changes in the plastic (curve 1) and effective (curve 2) viscosities of an aqueous solution of NaCMC containing PAG (3 g/dl) and OA (7 g/dl).

In the NaCMC concentration range of 3.5 - 5 g/dl, a significant increase in the solution viscosity occurs, which is accompanied by the transition of the system to a solid state (Figure 6). In this case, the resulting solid-like system has thixotropic properties - the ultimate strength of the structure $\tau_s$ increases with time (Figure 7).

In parallel with measuring the rheological properties, the “breakdown” voltage ($U_b$) of the system was determined, which increases many times in the range of NaCMC concentrations from 3.5 to 5 g/dl (Figure 8). This indicates that phase inversion occurs in the system, leading to the formation of an inverse emulsion, in which water is a dispersed phase. With the formation of an inverse emulsion, the electrical conductivity of the system decreases many times, and the "breakdown" voltage on the electrodes, accordingly, increases.

The minimum concentrations of PAG, NaCMC and OA required for the formation of an inverse emulsion are $1.2 \times 10^{-2}$, $25 \times 10^{-2}$, $2.85 \times 10^{-4}$ mol/l, respectively.

The formation of an inverse emulsion is apparently associated with the revealed effect of stabilization in the presence of NaCMC of the interfacial tension of an aqueous PAG solution at a low level when oleic acid is introduced into the system. At a sufficiently high concentration of NaCMC (about 3.5 g/dl), PAG retains high surface activity and acts as an emulsifier. The presence of a polymer (NaCMC) in the system ensures the realization of the structural and mechanical factor of stability of the inverse emulsion, which apparently explains its stability at a very high volumetric content of the aqueous phase: the volumetric ratio “aqueous phase: oleic acid” is $\approx 13:1$, respectively.
Figure 7. Dependence of the static shear stress (ultimate strength) of an aqueous solution containing 3 g/dl PAG and 7 g/dl OA on the concentration of NaCMC. Before measurements, the solution remained at rest for 1 min. (curve 1) and 10 min. (curve 2).

Figure 8. Change in voltage "breakdown" of the medium with an increase in the concentration of NaCMC in the system.

Currently, the developed polyemulsions are a completely new type of disperse systems, characterized by reversible phase reversion due to the action of chemical factors - changes in the acidity or mineralization of the medium, or the introduction of emulsifiers. Moreover, both traditional
nonionic oxyalkylated surfactants and polymer stabilizers subject to conformational fluctuations in the hydrophilic-lipophilic balance can act as the main object of reversion in polyemulsions. The use of emulsion systems makes it possible to successfully regulate the hydrophilic-hydrophobic properties of drilling fluids, which creates obvious prerequisites for solving the problem of increasing oil recovery in low-permeability reservoirs, as well as optimizing the technology for constructing inclined and horizontal wells.

References
[1] Belenko E V, Vakhrushev L I and Penkov A I 1999 J. Construction of oil and gas wells on land and at sea 1-2 pp 21–24
[2] Belenko E V and Vakhrushev L I 2007 J. Environmental protection in the oil and gas complex 8 pp 28-32
[3] Belenko E V 2007 J. Environmental protection in the oil and gas complex 7 pp 28-32
[4] Koshelev V N, Vakhrushev L P, Belenko E V and Lushpeeva O A 2002 J. Oil industry 8 p 76
[5] Belenko E V, Sakharov P A and Khvatov A V 2020 New materials and advanced technologies Sixth Interdisciplinary Scientific Forum with International Participation (Moscow: Center for scientific and technical solutions) pp 662-664
[6] Belenko E V, Khvatov A V and Sakharov P A 2020 IOP Conference Series: Materials Science and Engineering 921(1) 012002
[7] Abramzon A A 1988 Surfactants (Leningrad: Chemistry) p 200
[8] Gorbunov A T, Zabrodin D P, Petrakov A Sh and Koretsky A F 1984 J. Oil Industry 5 pp 33-37
[9] Kochmar O S, Bodan A N, Gud L N and Kochmar B V 1985 J. Oil Industry 3 pp 39-43
[10] Ilyasov S E, Popov S G, Okromelidze G V et al. 2011 J. Territory of oilgas 11 pp 16