Polymeric stabilization of drilling drills with low content of solid phase

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Abstract. This article is devoted to identifying the relationship between the structure-forming properties of polymer stabilizers of clay suspensions (drilling fluids) and the structure of their macromolecules based on thermodynamic representations of the stability of polymer-dispersed systems. New types of polymer-micellar gels combining high structural and pseudo-plastic properties and optimal surface-active characteristics characteristic of concentrated micellar systems of the "surfactant-solubilizate" type are presented.

The use of polymeric thickeners and stabilizers for washing fluids pursues a variety of purposes, the most important of which are: reducing the filtration rate, ensuring sedimentation stability of drilling dispersion, controlling the rheological and structural-mechanical characteristics of the system, as well as implementing special technological requirements, for example, thermal stability, resistance to biodegradation, salt resistance, etc. Polymer reagents differ in the chemical nature of the monomers forming the macromolecular chain, the size of the molecular mass and the degree of ionization of the functional groups. The most common synthetic polymers are polysaccharide and polyacrylic series. In addition, starch derivatives, lignosulfonates, humates, as well as microbial polysaccharides (XC biopolymers) are often used as stabilizing agents. The esterified derivatives of cellulose (carboxymethyl cellulose (CMC), polyamionic cellulose (PAC), hydroxyethyl cellulose (HEC), carboxymethylxyethyyl cellulose (CMOEC), etc.) are polyelectrolytes containing hydroxyl, macromolecular, other these polymers are divided into anionic, cationic, amphoteric and nonionic. The solubility of nonionic compounds in water is due to the presence in their composition of hydroxyl and ether polar functional groups resistant to hardness salts.

An important non-ionic stabilizer is the starch reagent, which is the main component of cereal seeds (corn, wheat, rice) and tuber crops (potatoes and tapioca). Hydrolysis of starch produces glucose, as well as a small amount of fatty and phosphoric acids. The carbohydrate part of starch contains two polysaccharides - amylose and amylopectin. Amylose consists of long chains of α-glucose, the molecular weight of which varies from 10 thousand to 100 thousand (Figure 1).
Amylose contains a mixture of branched chain molecules (Figure 2).

Amylopectin contains a mixture of branched chain molecules (Figure 2).

The molecular weight of amylopectin varies from 40,000 to 100,000. Starch is used in drilling fluids only to reduce the filtration rate and is susceptible to enzymatic decomposition by many microorganisms (yeast, mold, bacteria).

In the chemical structure of biopolymers, a β-linked backbone containing D-glucose, D-mannose and D-glucuronic acid with one side chain for every 8 sugar residues and one 4,6D-glucose side chain for every 16 sugar residues takes part [1] (Figure 3).

The biopolymer macromolecule contains carboxyl, carbonyl and hydroxyl groups, as a result of which it is characterized by a high thickening ability, giving the drilling fluid highly pronounced pseudoplastic properties and resistance to polymineral aggression.

The success of using low-charged and non-ionic polymers (starch, biopolymer, HEC) in low-clay and non-clay drilling fluids is associated with ensuring the aggregate stability of the system, as well as with the formation of a three-dimensional structural grid. The stabilization of the disperse system and structure formation are interrelated processes in which the polymer provides the implementation of
structural-mechanical, sorption-solvate and electrostatic factors of system stability. There are several mechanisms of structure formation with the participation of a nonionic polysaccharide:

- in aqueous solutions of biopolymers, the tendency toward macrostructuring is very pronounced as a result of the formation of supramolecular spatial networks consisting of spiral structural units that are contacted by means of hydrogen and Van der Waals bonds. The biopolymer macromolecules, in addition to polar functional groups, also carry anionic carboxylate groups, the source of which is the structural units of pyruvic acid and glucuronic acid, located on the side branches inside the main (d) glucose helix. It is this shielding of the charged sections of the biopolymer macromolecule that apparently explains the unique reversibility and shear strength of hydrated macromolecular structures, which provide the solid, pseudoplastic nature of the rheological behavior of biopolymer solutions. This, in particular, is confirmed by the fact that the maximum solubility of biopolymers is observed at pH = 4–6, while the solubility region of conventional polyanionic stabilizers lies at pH > 8 [2];

- non-ionic polymers (XC-polymer, starch) form spatially structured systems when interacting with dispersed particles of high-grade bentonite in polymer-bentonite drilling fluids. An important property of such solutions is their pseudoplasticity, characterized by a pronounced dependence of the effective viscosity on shear rate;

- polymer structured solutions are obtained by complexation using polyvalent metal ions, characterized by a large charge and a small ionic radius. Metals whose ions have a large hydration capacity include Cr, Al, Ca, Zr, Ti. To enhance the thixotropic properties of biopolymer solutions, trivalent chromium salts are introduced into them, the effect of which is due to the ability to form multinuclear complex compounds, for example, aquacomplexes, in the inner sphere of which water molecules and hydroxyl groups are contained. The coordinating ability of cations depends on their ionic potential (ratio of ion charge to its radius) [3], in accordance with the value of which complexing agents are located in the following order: Al> Fe> Cu> Ni> Mn. The thixotropic properties and viscosity of polymer solutions containing one or another complexing agent are directly proportional to its ionic potential. Thus, Al3 + cations are capable of very tightly coordinating the hydroxyl and carboxyl groups of polysaccharide derivatives in the pH range of <6, while a three-dimensional gel structure of the Ecorish solution is formed on the basis of the complex of iron (III) salts and HEC [4].

The requirement to control the structural and mechanical characteristics of drilling fluids is also presented to polyanions, which are less prone to complexation, however, form adsorption layers on the surface of clay particles, characterized by a long-range order.

The purpose of this article is to identify the relationship between the structure-forming properties of polymer stabilizers and the structural features of their macromolecules based on thermodynamic ideas about the stability of polymer-dispersed systems that can perform useful work. If, as a result of reagent treatment, the mud filtration rate increases, then this means that negative work has been performed on the system (ΔAf <0). Moreover, regardless of the change in the rheological properties of the system, the structural work performed by the system is also negative (ΔAs <0). If the filtration rate decreases, then the system itself does a positive job: ΔAf > 0, ΔAs > 0.

The gradient of the resulting operation of the mud system can be found as follows:

\[ \nabla A = T \mathbf{i} \]

This is the scalar product of the unit vector \( \mathbf{i} \) and the tensor \( T \), which is the result of the product of the gradients of the work produced by the system:

\[
T = \nabla A \cdot \nabla A_f = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \mathbf{i}_{\mu \nu} = \mathbf{i}_{\mu \nu} T_{\mu \nu}
\]

Having calculated the value of \( \nabla A \), the differential value of the resulting system operation \( dA \) is determined. Drilling fluid, being an open system, can perform positive work only due to loss of free energy:

\[ dG < -dA, \]

\( \therefore \) : \( dG < 0. \)
Therefore, in order for the system to perform positive work, it is necessary to have a supply of free energy, the change of which is associated with the positive work of the system:

\[ dA = -k \cdot dG \]

The coefficient \( k \) characterizes the completeness of the conversion of free energy into useful work \( dA \). In an isothermal irreversible process, when a certain amount of energy \( \delta Q \) is transferred to the system, entropy production is observed in accordance with the ideas of R. Clausius (for an isolated system), which is expressed by “uncompensated” heat (\( \delta Q' \)):

\[ \delta Q = TdS - \delta Q' \]

Chemical treatment of the drilling fluid, which is an isobaric-isothermal process, should be accompanied by a decrease in the free energy level of the system \( (\Delta GS <0) \). Suppose that as a result of introducing a polymer component, the system does a positive job \( (\Delta A > 0) \), accompanied by a decrease in the filtration index. The system before polymer processing \( (\Delta A_1) \) and after it \( (\Delta A_2) \) is expressed by the equations:

\[ \Delta A_1 = -k \cdot \Delta G_1 = -k(\Delta H_1 - T \cdot \Delta S_1) \]
\[ \Delta A_2 = -k \cdot \Delta G_2 = -k(\Delta H_2 - T \cdot \Delta S_2) \]

During the production process, the enthalpy of the system does not change \( (\Delta H_1 = 0, \Delta H_2 = 0) \), therefore, the operation of the drilling system before and after chemical treatment has an entropy character:

\[ \Delta A_1 = -k \cdot T \cdot \Delta S_1 \]
\[ \Delta A_2 = -k \cdot T \cdot \Delta S_2 \]

Define the work performed by the system as a result of chemical treatment:

\[ \Delta A = \Delta A_2 - \Delta A_1 = k \cdot T \cdot (S_1^1 - S_1^2), \]

where: \( S_1^1 \) - level of system entropy before chemical treatment; \( S_1^2 \) is the entropy level of the system after chemical treatment.

The magnitude of the positive operation of the drilling fluid system is greater, the lower the entropy \( (\Delta S <0) \) of the system after chemical treatment. Thus, chemical treatment of the drilling fluid with a general decrease in the free energy level of the system should lower its entropy. This conclusion allows us to formulate the basic requirements for polymer reagents as structural agents and reducing agents for filtering washing fluids.

The introduction of the polymer into the drilling fluid must be accompanied by an exothermic thermal effect \( (\Delta H <0) \), which ensures the solubility of the reagent in the dispersion medium, while the entropy of the system should decrease \( (\Delta S <0) \). Therefore, polymer macromolecules must contain a large number of hydrophilic functional groups, both non-ionic type (polyoxyethylene chains) and those capable of dissociation. The optimal polymer should be a polyanion or polycation, in the macromolecules of which the charged fragments alternate with nonionic (hydroxyl, hydroxyethyl, carbonyl) groups.

The requirement of a negative enthalpy of dissolution of the polymer reagent determines the choice of polymers capable of chemisorption on the surface of the particles of the dispersed phase. Moreover, the higher the molecular weight, the higher the affinity of the polymer to the surface of the adsorbent.

In drilling fluids, the dispersed phase is mainly represented by bentonite particles, the crystal lattice of which is formed by two structural elements consisting of 3 layers. One structural element consists of two outer silicon-oxygen tetrahedral networks with silicon atoms in the centers. Between the two silicon-oxygen tetrahedrons is an aluminum-oxygen octahedral network. Adjacent packets face each other with the same layers. The weak bond between the layered packets and the possibility of water and some cations penetrating between them explains the high ion-exchange ability of bentonite clays and their strong swelling in water. Particles of a clay dispersed phase have a lamellar structure: the faces of three-layer packets are negatively charged (as a result of dissociation of surface silanol groups), and the edges are positive. As a result, polyanions are prone to chemisorption on the edges of aluminosilicate packets, and polycations are adsorbed on their faces and enter the interlayer space. Polyanions increase the negative charge of dispersed particles, helping to stabilize the system, while polycations neutralize the clay surface, causing the development of coagulation. With an excess of
polycation concentration, recharging of the surface of a dispersed particle can take place, acquiring a positive potential, which will ensure the implementation of the electrostatic stability factor of the system.

Effective polymer treatment of the drilling fluid is accompanied by a decrease in the entropy of the system. This means that macromolecules must be integrated into the hydrogen bonds of the existing coagulation structure, reducing the concentration of “free” water. The state of the aqueous phase in the drilling fluid system can be judged by the change in its relative hydrophilicity, which is directly dependent on the time of spin-spin relaxation of water protons, determined by the method of nuclear magnetic relaxation (NM relaxation) [5, 6]. The introduction of the polymer should be accompanied by an increase in the fraction of water protons that are tightly coordinated in the adsorption layers on the surface of the dispersed phase (spin-spin relaxation time $T_2$ of the order of $10^{-2}$ s), as well as an increase in the fraction of “exchange” water in ion hydration shells ($T_2$ of the order of $10^{-1}$ s). The requirement of low entropy also determines the choice of polymers with a maximum molecular weight and a limited number of macromolecular conformations. Therefore, polymers of regular structure, the macromolecules of which form stable spiral structures, are most in demand.

Let us dwell in more detail on the micellar structures of nonionic surfactants. It is known that gels based on concentrated solutions of nonionic surfactants are of a viscoplastic nature. In such solutions, micromolecular aggregates interact at close distances 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 an elongated elongated form of supramolecular aggregates, which are easily oriented in the direction of shear rate. Micellar solutions used in drilling and oil production practice have a low concentration of micelle-forming surfactants, not more than 5-10 times higher than the critical micelle formation concentration (CMFC). Typically, such solutions include 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 [7]. Unfortunately, compared to polymer (crosslinked ionic bonds or biopolymer) structures, micellar gels are characterized by irreproducible rheology under shear or thermal stresses. 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, antifiltration, inhibitory) characteristic of concentrated micellar systems of the “nonionic surfactant-solubilizate” type is highly relevant."

As the polymer base of the polymer-micellar system (hydrogel), we will choose derivatives of polysaccharides bearing hydroxyethyl and carboxymethyl groups — CMOEC, and as nonionic surfactants — polyalkylene glycol (PAG) — a random copolymer of ethylene and propylene oxides characterized by a hydrophilic-lipophilic balance value of 3. Tall oil (TM), in which the content of fatty acids is 60%, acts as a hydrophobic solubilizate. We studied the structure formation in the ternary system “polymer (CMOEC) - PAG - TM”, in which PAG micellar complexes acquire a surface charge due to the introduction of a neutralizing alkaline agent (HA) into the system. The main structure-forming element in such a system (dispersed phase) is, apparently, the hydrophobic surface of the polysaccharide skeleton, the hydrophilic cavities inside which are occupied by mixed PAG micelles and TM fatty acids, which form hydrogen and ionic bonds with functional groups (hydroxyethyl and carboxylate anions) of CMOEC.

The compositions of the obtained polymer-micellar hydrogels with the same content of TM acids are given in Table 1. As can be seen, an increase in the mass fraction of the alkaline agent allows one to achieve a decrease in the content of the polymer stabilizer (CMOEC) and micelle former (PAG) at a constant concentration of hydrophobic solubilizate (TM).

| № experience | CMOEC, % | PAG, % | TM, % | HA, % | Filtration rate, cm³ / 30 min | Clay minerals | Coefficient of friction |
|---------------|---------|--------|-------|-------|-----------------------------|--------------|-----------------------|

Table 1. Compositions and technological properties of polymer-micellar hydrogels.
The results of the study of the technological characteristics of the obtained hydrogels are presented in Table 1. As can be seen, an increase in the mass fraction of HA in the polymer-micellar hydrogel leads to a slight increase in the filtration rate and a decrease in the initial rate of swelling of clay minerals in the hydrogel medium. On the other hand, by increasing the degree of neutralization of TM fatty acids, system No. 3 has the best lubricating properties.

The rheological properties of the gels were investigated on a FANN viscometer company Baroid (USA). Experiments show that as a result of an increase in the concentration of an alkaline agent, there is a decrease in the viscosity characteristics, as well as the yield strength of the gel system. However, with an increase in the mass fraction of HA, the static shear stress of the gels increases, which is apparently due to the structural effect of neutralized fatty acids. The effect of temperature on the rheological characteristics of polymer-micellar gels was also studied. Upon heating, there is a gradual decrease in the viscosity and structural characteristics, as well as a slight decrease in the pseudoplastic properties of the gel, which, however, remain at a high level even at 80 °C.

It should be noted that the mass fraction of fatty acids in the composition of HMs significantly affects the properties of polymer-micellar hydrogels. The effect of the mass fraction of fatty acids in the composition of HM on the technological properties of hydrogel solution No. 3 was studied (Table 1). Table 2 presents the technological parameters of such hydrogels, differing only in the content of alkaline agent.

**Table 2.** Investigation of the influence of the mass fraction of fatty acids in HM on the technological properties of polymer-micellar gel based on CMOEC.

| The content of HA, % | Mass fraction of fatty acids in TM, % | Effective viscosity, MPa·s | Plastic viscosity, MPa·s | Static shear stress, dPa | Consistency Index (Ostwald-Weil Model) | Degree indicator (Ostwald-Weil model) | Coefficient of friction | Filtration parameter, cm / 30 min |
|---------------------|-------------------------------------|---------------------------|--------------------------|------------------------|----------------------------------------|--------------------------------------|------------------------|-------------------------------|
| 1,35                | 60                                  | 119                       | 43                       | 85/90                  | 28                                     | 0,29                                 | 0,02                   | 6                             |
| 0,89                | 79                                  | 140                       | 60                       | 30/35                  | 12,7                                   | 0,35                                 | 0,007                  | 6                             |
| 0,22                | 97                                  | 150                       | 65                       | 16/18                  | 7,3                                    | 0,45                                 | 0,007                  | 5,5                           |

As can be seen, an increase in the concentration of fatty acids in the composition of tall oil can reduce the concentration of alkaline agent necessary to ensure complete colloidal solubility of the hydrophobic solubilizate. It is easy to notice that an increase in the content of fatty acids in TMs (Table 2) affects the properties of hydrogels in a similar way to a decrease in the concentration of an alkaline agent at a constant concentration of fatty acids (Table 1): there is an increase in the viscosity characteristics of the system with a simultaneous decrease in structural and pseudoplastic properties, as well as lubricating and anti-filtration indicators are improved.

In the course of the studies, it was established that it is possible in principle to obtain structured hydrogel systems by stabilizing solubilization microemulsions with polysaccharide water loss reducers. Thus obtained polymer-micellar hydrogels combine high structural and pseudoplastic properties characteristic of biopolymer solutions, as well as significant inhibitory and lubricating characteristics inherent in saturated emulsion systems. However, the preparation of such emulsions in a drilling environment is rather laborious due to the multi-stage emulsification process and the low efficiency and productivity of the most common drilling dispersants. A modern engineering solution designed to facilitate the management of the properties of polymer-micellar hydrogels and transfer them to the category of real industrial systems is the concept of flushing liquids with a reversible
dispersed phase. Polymer-micellar hydrogels are a completely new type of dispersed systems, the main objects of reversion in which can be both oligomeric polyalkylene glycols and polymer stabilizers that are subject to conformationally induced fluctuations in the hydrophilic-lipophilic balance. In most reversible emulsion systems, a reversible emulsifier plays an important role, which, depending on the acidity of the medium, acts alternately as a stabilizer of direct and reverse emulsions. In polymer-micellar systems, the role of a reversible emulsifier can be played by nonionic surfactants that provide phase reversal without changing the ionic strength, as well as the acidity of the medium. For example, the management of the properties of a hydrogel emulsion, including polysaccharide derivatives (CMC, CMOEC, PAC, etc.) and hydrophobic solubilizate (unsaturated higher fatty acids, polypropylene glycols, triglycerides, etc.), is provided by the introduction of an invert emulsifier with HLB = 3-8, which leads to the formation of a reverse emulsion. Translation of the reverse emulsion into a direct one can be easily carried out by adding an ethoxylated surfactant with HLB = 16-18.

Consider the effect of the concentration of the polysaccharide reagent on the technological parameters of a reversible hydrogel emulsion. In this case, we select CMC as the polysaccharide base of the polyemulsion, and oleic acid as the hydrophobic solubilizate. The roles of the invert emulsifier and emulsifier of direct emulsions in such a system are performed, respectively, by polyalkylene glycol with HLB = 3 and neonol. At the first stage of the introduction of PAG into the mixture of CMC and oleic acid, we obtain a highly viscous invert emulsion with a practically zero filtration index and one hundred percent inhibitory activity with respect to the swelling of clay minerals. At the next stage, the addition of neonol to an invert hydrogel emulsion leads to the formation of a less viscous direct emulsion with a simultaneous deterioration in filtration and inhibitory properties. If we now reduce the concentration of CMC in the initial mixture with oleic acid, then the viscosity and structure of the newly formed invert hydrogel emulsion are not as high as in the previous case with a higher polymer concentration. In addition, there is a slight decrease in filtration and inhibitory properties. The direct emulsion obtained after the addition of neonol is also characterized by a decrease in the main technological indicators, in comparison with a similar hydrogel emulsion with a high content of polysaccharide reagent. That is, the technological properties of the hydrogel emulsion at different stages of the reversal cycle with a decrease in the concentration of the polysaccharide reagent approach some average values.

Unlike biopolymer washing systems, a hydrogel emulsion is characterized by increased water repellent and surface-active characteristics. In addition, the additional enhancement of hydrophobic interactions in polysaccharide macromolecules due to the use of PAG in the composition of the polyemulsion helps to increase the degree of stabilization of filtration properties in harsh operating conditions. Thus, at the present stage, emulsions based on polymer-micellar hydrogels are the most advanced systems for the construction of horizontal shafts in productive horizons.

Based on the considered example of creating polymer-micellar hydrogels, it can be concluded that the rule of lowering entropy requires polymers to form a unified spatial structural network in the volume of the dispersion medium of the drilling fluid, approaching the liquid-crystalline state. The system can perform the maximum work, the chemical treatment of which contributes to the transition from a coagulation to a condensation structure with minimal entropy. An example is the preparation of a cement mortar, which during the transition to a condensation structure (at the beginning of setting) generates a large amount of heat (ΔH <0). Structures close to condensation also have various hydrogels, including the above-described biopolymer solutions “crosslinked” with salts of polyvalent metals. To form a spatial network, the polymer macromolecules should not have too high a charge - the molar fraction of ionic groups is preferred from 50 to 70 mol%.

Thus, in the production of effective chemical treatments of the drilling fluid, including polymer reagents, one should be guided by the requirement of providing a significant exothermic effect while reducing the entropy of the system. Optimal polymer stabilizers should have a large molecular weight, an average charge level of macromolecules, a regular macromolecular structure with a periodic alternation of charged and non-ionic functional groups. The advantage is the ability of the polymer to
chemisorb on the surface of the particles of the dispersed phase, as well as the tendency to form coherent dispersed systems (gels) with a spatial structure.

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