Environmentally safe oil-field reagents for development and operation of oil-gas deposits

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Abstract. Sodium-carboxymethylcellulose and arabinogalactane inhibits the crystallization of calcium carbonate from a supersaturated aqueous solution at 80°C. The sizes of formed crystals CaCO₃ in the presence of arabinogalactane, sodium-carboxymethylcellulose and neonol AF 9-10 decrease on an average 7-12 μm and a change of their structure. It is expected, that the mechanism of inhibition is in specific adsorption polysaccharides and neonol on occurring crystalline surface of the calcium carbonate, both at the expense of electrostatic interaction of functional groups with Ca²⁺ ions, located on the surface of the crystal, and due to coordination and hydrogen bonds with oxygen atoms and HO-groups of additives. Oil-water emulsion rheology in the presence of neonol AF 9-10 has been studied. It is shown that neonol AF 9-10 decrease viscosity natural water-oil emulsion by 25 times. Addition of 5% neonol to water-oil emulsion leads to formation more than 20 stable emulsion forms of different density and composition. New highly effective “green” oilfield reagents have been developed on the basis of neonol and natural polysaccharides.

1. Introduction
The world’s explored oil reserves contain approximately 70% of heavy and extra-heavy oils, what is about 810 billion tonnes [1,2]. Extraction and transportation of high viscosity hard-to-recover oil requires development of new economically feasible technologies and reagents ensuring multi-phase flow flotation and crude oil viscosity reduction which represent water-oil emulsion of a w/o type, which are stabilized by lipophilic natural surfactants which are present in oil – asphaltenes, resins, naphthenic acids, etc. [3]. Among lots of reagents regulating the rheological properties of high viscosity oils, the most widely used are surfactants of various structure [4]. One type of perspective for this purpose surfactants is polyoxyethylated alkylphenols (neonols) whose effectiveness is not affected by
mineralization of water [5-8].

Compatibility with other reagents, interaction with formation water and influence on the properties of oil is essential in using oilfield reagents. Scaling on downhole oilfield equipment and bottom-hole formation zone is one of the most common types of complications in the technological processes of development and operation of oil and gas deposits [9,10]. Formation of slightly-soluble salts in bulk is the reason for stabilization of water-oil emulsions and decline in efficiency of demulsifiers used in oil treatment. The most common salt deposits include the natural mineral CaCO$_3$.

Results on the effect of neonol AF 9-10 on the rheology of natural water-oil emulsion Severo-Komsomolskoye oilfield was used to develop methods of controlling its viscosity. We investigated the properties of carboxymethyl cellulose, arabinogalactan and neonol on the scaling of calcium carbonate. The obtained results are used to create new “green” chemicals for oilfield chemistry.

2. Experimental part
A sample of water-oil emulsion of the Severo-Komsomolskoye oilfield was investigated. Anhydrous crude oil and water, separated from the emulsion, had the following physical and chemical characteristics: oil density – 0.9464 g/cm$^3$ at 20°C; density of separated water – 1.003 g/cm$^3$; water cut determined by the Dean and Stark method – 31.4%. Oil blend composition: wax – 7.0%, asphaltenes – 0.7%, resins – 4.3%. Reservoir water of the Severo-Komsomolskoye oilfield belongs to the calcium-chloride type and has the following characteristics: salinity – 13.2 g/l; pH – 8.1; ionic composition – Ca$^{2+}$ – 210.4; Mg$^{2+}$ – 79.0; Na$^+$ + K$^+$ – 4662.9; Cl$^-$ – 7927.9; HCO$_3^-$ – 292.8; SO$_4^{2-}$ – 7.4 mg/l.

Neonol AF 9-10 (“Nizhnekamskneftehim” OJSC), arabinogalactan (“Ametis” JSC) and sodium carboxymethylcellulose (Sigma-Aldrich) were used in this study. Water of the following ionic compositions was used as a reservoir water model: Ca$^{2+}$ – 270.55; Mg$^{2+}$ – 30.35; Na$^+$ – 3120.25; Cl$^-$ – 4492.10; HCO$_3^-$ – 1525.50 mg/l, prepared from analytically pure salts CaCl$_2$, MgCl$_2$ 6H$_2$O, NaCl, NaHCO$_3$.

The viscosity and rheological characteristics were determined with the rotary viscometer Haake Viscotester iQ. For the explored samples a shear test was used with the shear rate varying from 1 to 300 s$^{-1}$, at which the dependence of shear stress and viscosity on shear rate was determined. The influence of neonol AF 9-10 on the water-oil emulsion stability was studied using the integrated tool set for dispersion stability measuring “Turbiscan Tower” (Formulaction SA). The efficiency of the neonol AF 9-10, arabinogalactan and sodium carboxymethylcellulose as scale inhibitors was determined at a temperature of 80°C and concentrations of 10, 30 and 50 mg/l by the method, based on blocking of a 0.8 mm thick and 1.5 m long steel capillary with the occurring calcium carbonate deposits during pumping of the reservoir water model [11]. The sizes of resulting CaCO$_3$ crystals were recorded using the laser particle size analyzer Analysette 22 NanoTec plus.

3. Results and discussion
The reviews [12–14] consider interrelation between composition and structure, structural features of emulsions, which determine their rheological properties.

The object of our study was the natural water-oil emulsion of the Severo-Komsomolskoye field with viscosity of 1234 mPa·s at water cut 31.4%. Anhydrous crude oil has the API value of 19.5, calculated with the formula $141.5\times\rho_w/\rho_o - 131.5$, where $\rho_w = 1.003$ g/cm$^3$ - reservoir water density, and belongs to heavy oils according to classification of the American Petroleum Institute [15]. Microscopic analysis of the water-oil emulsion has shown that it is a “packed” in membranes emulsion of a water-in-oil type, containing water drops mainly of sizes less than 135 μm (Figure 1). This emulsion is stable, obviously, the stabilization due to the formation of the "armoring" layers of molecules of asphaltenes, resins and paraffin crystals at the interface of water and oil phases. It is well known that these oil components increase the stability of emulsions, creating a protective barrier around the water droplets [3, 16,17].
The conducted analysis of effective viscosity curves of shear rate has shown that in the temperature range of \(-10 \text{ to } +50 ^\circ\text{C}\) flowing of the crude oil obeys the Newton’s law, i.e. the emulsion behaves like a Newtonian fluid (Figure 2).

It should be noted that at low shear rates and temperature above 30\(^\circ\text{C}\) a non-monotonic change in viscosity is observed, what is apparently connected with the breakdown of crystal structure of paraffins (melting) and structural changes in asphaltenes “armoring” layer at the oil/water phase interface, since asphaltenes, being diphilic substances, can form hard 2-10 nm thick films on the surface of water droplets, consisting of resins and asphaltenes [3,18]. At temperature above 40\(^\circ\text{C}\) and shear rate of 9 s\(^{-1}\) effective viscosity does not depend on shear rate and approaches to an asymptote, what is connected with the breakdown of spatial coagulation-cristallization structure of high-molecular oil compounds.

The effect of neonol AF 9-10 on crude oil viscosity was studied at concentrations of 0.5, 1, 3 and 5\%. Based on the results of the conducted rheological studies of oil with neonol AF 9-10 addition it was established that the best viscosity decline is observed in samples with surfactant concentration of 3\%. Effective viscosity at 20\(^\circ\text{C}\) in the explored samples decreases by 25 times (Figure 3).
Figure 3. The influence of neonol AF 9-10 on dependence of crude oil effective viscosity on shear rate at concentrations of 0 (1), 0.5 (2), 1 (3), 3 (4) and 5% (5) at 20°С. μ – effective viscosity (Pa·s), γ – shear rate (1/s).

Figure 4. Dependence of crude oil effective viscosity on temperature in the presence of 3% neonol AF 9-10. ln(μ) – effective viscosity logarithm, 1/T – reciprocal temperature (1/K).

Containing 5% surfactant the oil viscosity increases what is connected with possible emulsification and stabilization of water-oil emulsion by neonol. Strongly pronounced non-monotonic change in oil effective viscosity in the presence of neonol AF 9-10 is due to, apparently structural changes in interfacial layer at the water/oil phase interface as a result of introduction of surfactant molecules into structures formed by asphaltenes and resins molecules and formation of various emulsion forms, including micelles, since critical concentration of micelle formation of neonol AF 9-10 is 0.082 mmol/l [19].

The curve of dependence of water-oil emulsion viscosity logarithm in the presence of 3% neonol AF 9-10 on reciprocal absolute temperature in coordinates lnμ – 1/T shows breaks at temperatures of 10 and 23.6 °С (Figure 4). Temperature dependencies in the temperature ranges 0 – +10°С, +10 – +20°С and +25 – +50°С obey the Arrhenius equations ln(μ) = 2461.3·T^-1 - 10.70, ln(μ) = 15100·T^-1 - 53.25 and ln(μ) = 7427·T^-1 - 26.18, respectively. Activation energy of viscous flow in the temperature range 0 to +10°С is 62.0 kJ/mole, from +10 to +20 °С – 126 kJ/mole and from +25 to +40 °С – 20.5 kJ/mole. At temperatures of 10 and 23.6 °С the water-oil emulsion structure changes from less ordered to ordered (high activation energy) to the least ordered. Low value of effective activation energy is apparently connected with a parallel process of destruction of hydrocarbon bonds of water with oil components (the process ends at temperature of 35 – 40°С). Viscosity values at 35 and 40°C are corrected from approximation of the flow curve by the Bingham equation: μ = Kγ^n.
its interaction with oil components during formation of solvate layers of the dispersed phase.

The study of the effect of neonol AF 9-10, arabinogalactan and sodium carboxymethylcellulose (NaCMC) on the scaling process (calcium carbonate crystallization) by capillary blocking at temperature of 80°C has shown that at concentrations of 50, 20 and 30 mg/l, respectively, the reagents inhibit CaCO$_3$ scaling processes and their efficiency makes ~90-98%. The capillary does not occur deposition of calcium carbonate crystals by passing saline water during the experiment.

Data on the formed CaCO$_3$ crystals size distribution by the action of neonol, arabinogalactan and sodium carboxymethylcellulose, obtained with the laser particle size analyzer has shown that in their presence a decrease in the average size of crystals by ~7-12 μm is observed.

Electron micrographs of CaCO$_3$, formed in the presence of NaCMC, indicate polymorphism of calcium carbonate (Figure 5). The sample, obtained in the absence of polysaccharide, contains elongated aragonite crystals, which is the most thermodynamically stable phase under the specified conditions. During CaCO$_3$ crystallization in the presence of NaCMC formation of aragonite is practically not observed. The crystals are irregular-shaped particles with rounded faces.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{Electron micrograph of CaCO$_3$ crystals, obtained without (a) and in the presence of (b) NaCMC}
\end{figure}

Sedimentation stability of the formed aqueous dispersed CaCO$_3$-NaCMC systems was studied at 80°C and NaCMC concentrations of 10, 20, 30, 50 and 100 mg/l using the Turbiscan Tower device. In the absence of NaCMC a finely dispersed suspension of crystals, which settle as a result of aggregation and agglomeration [21], is formed and clarification of the solution is observed (Figure 6). In this case stability index of the TSI dispersed system has the highest value for the entire observation time.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{The effect of NaCMC on the CaCO$_3$ scaling process at concentrations of 0 (1), 10 (2), 20 (3), 30 (4), 50 (5), 100 (6) mg/l at 80°C. TSI — Turbiscan stability index, $\tau$ — time (min).}
\end{figure}
At NaCMC concentrations more than 10 mg/l the TSI value decreases, indicating an increase in stability of NaCMC-CaCO$_3$ and NaCMC-CaSO$_4$ dispersed systems. Within three hours formation and precipitation of CaCO$_3$ crystals did not occur, which illustrate high efficiency of NaCMC as a scale inhibitor.

The main reason for the effect of neonol, arabinogalactan and NaCMC on crystal formulation of calcium carbonate may be considered to be their specific adsorption on the emerging faces of calcium carbonate both due to electrostatic interaction of ionized carboxyl groups with Ca$^{2+}$ ions, located on the crystal surface, and due to coordinate and hydrogen bonds with oxygen atoms and HO-groups of carbohydrate fragments [22,23]. In particular, NaCMC macromolecules in aqueous medium have conformation of elongated coils with sizes of hypothetically straight-line sections of 13-18 nm (approximately 25 glucose cellulose monomers), corresponding to sizes of the formed calcium salts nanoparticles [24]. Such interaction leads to formation of polymer forms without distinct morphological features and to changes in calcium carbonate particles size. According to the mode of action, these reagents can be referred to the threshold-action scale inhibitors, since their specific adsorption on the emerging faces of microcrystalline calcium carbonate nucleus, which leads to slowing of the crystals growth and their suspension in solution at concentration above the deposition level.

The study of the effects of neonol, arabinogalactan and sodium carboxymethylcellulose on the process of calcium carbonate crystallization inhibition has shown that they are promising as environmentally safe inhibitors of calcium carbonate scaling.

4. Conclusion
It was stated that neonol AF 9-10 leads to a significant decrease in effective viscosity of the natural water-oil emulsion of the Severo-Komsomolskoye oilfield, inhibition of calcium carbonate crystallization and, along with the “green” scale inhibitors – arabinogalactan and sodium carboxymethylcellulose, is an effective oilfield reagent.

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