Inhibitors based on new polysaccharides in technological processes of oil production. Efficiency of inhibition of scale formation and influence on stability of water-oil emulsion

A V Fakhreeva¹², A I Voloshin³, A G Telin⁴, L A Magadova⁵, L V Spirikhin² and V A Dokichev²,³

¹Ufa State Aviation Technical University, Karl Marks st. 12, Ufa, Bashkortostan, 450008 Russia
²Ufa Institute of Chemistry, Russian Academy of Sciences, Oktyabrya pr. 71, Ufa, Bashkortostan, 450054 Russia
³OOO RN-BashNIPIneft³, Sochinskaya st. 12, Ufa, Bashkortostan, 450103 Russia
⁴OOO Ufa-NTC, Aksakov st. 59, Ufa, Bashkortostan, 450076 Russia
⁵National University of Oil and Gas «Gubkin University», Leninskiy pr. 65/1, Moscow, 119991 Russia
E-mail: alsu.allagulova@mail.ru

Abstract. Functionalized nitrogen-containing polysaccharides based on available low molecular weight sample of carboxymethylcellulose (CMC) with a molecular mass of 90 thousand and mono-, di- and tri- ethanolamine were obtained. The study of CMC salts with ethanolamine as inhibitors of salt deposition was carried out at 80 °C by capillary testing. It was shown that at the concentration of 10-30 mg/l these salts inhibit the processes of scale deposition of CaCO₃ and their efficiency is 53-80%. Rheological and sedimentation characteristics of artificially obtained water-oil (w/o) emulsions based on oil of the Priobskoye oilfield without and in the presence of low molecular weight sodium salt of carboxymethylcellulose (NaCMC) were studied. It was found that the NaCMC does not increase the viscosity and stability of W/O emulsions at concentrations of 50, 100, 200 mg/l.

1. Introduction
In the technological processes of development and operation of oil and gas fields, scale deposition in the bottom-hole zone of the formation, on downhole oilfield equipment and in the processes of oil preparation is one of the most common types of complications [1-4]. Scale deposition occurs as a result of crystallization of inorganic salts in the event that there is an excess of the actual concentration of scale-forming ions in mineralized water over the equilibrium concentration with changes in temperature and pressure.

The group of the most common scale deposits includes slightly soluble native minerals CaCO₃, CaSO₄, BaSO₄. Oilfield reagents based on phosphorus-containing compounds and organic polymers are widely used to prevent scale formation [4-7], the disadvantages of which include low thermal stability, high toxicity and relatively low efficiency in inhibiting sulfate deposits.

In recent decades, we can note intensive research in the field of search and development of new inhibitors of scale deposition based on polysaccharides [8], which is in good agreement with the general...
trend of "green" development of the processes of chemigation of modern industries, including oil and gas production.

Sodium salt of carboxymethylcellulose is one of the most accessible water-soluble polysaccharides, the physicochemical properties of which, as well as the availability, thermal stability, biodegradability in aerobic and anaerobic conditions determine the search and creation of new "green" oilfield reagents on its basis [9-11].

Without experimental data, it is difficult to assess the degree of influence of the polysaccharides on the properties of crude oil, the effectiveness of other oilfield reagents used in oil production. Therefore, the use of polysaccharides in oil production should be carried out only after studies of the impact on the production process and demulsification processes of w/o emulsions, which will prevent possible complications of the operation of oil preparation plants [12]. It is known that some polysaccharides can both stabilize and destroy w/o emulsion [13, 14].

This article presents the results of the synthesis of new mono-, di-, triethanolamine salts of CMC, their effectiveness in inhibiting the formation of calcium carbonate from supersaturated mineralized water. The results of studies of the effect of NaCMC, which is an effective inhibitor of scale deposition [15] on the viscosity and stability of the w/o emulsions of the Priobskoye oilfield, are considered.

2. Experimental part
NaCMC (1) produced by Aldrich with a molecular weight of 90 thousand was used in the work; the degree of substitution was 0.7.

The IR spectrum of polysaccharides was taken on the spectrometer "Nicolet iS10" on the prefix NPVO Diamant in the range of 400-4000 cm\(^{-1}\).

Carboxymethylcellulose (H-CMC), (2). To 140 ml of 20% \(\text{H}_2\text{SO}_4\) solution in 70% ethanol solution (\(\text{pH} = 2-2.5\), 5) was added 5.0 g NaCMC and stirred on a magnetic stirrer, at room temperature for 20 minutes. H-CMC was filtered on a filter "blue ribbon", washed with 70% ethyl alcohol to a negative test for sulfate ions, dried in a vacuum. The yield of 4.51 g (97%).

Interaction of H-CMC with ethanolamine. To the suspension of 1 g H-CMC in 40 ml of distilled water in a three-neck flask of 100 ml, ethanolamine was added at the rate of 2 mol per carboxyl group and stirred for 5 hours at a temperature of 80 °C. the precipitated solid product was filtered and washed on a SCHOTT’s funnel with isopropyl alcohol and dried in vacuum to a constant mass.

Monoethanolamine salt of carboxymethylcellulose (3). From 1 g H-CMC and 0.422 g (6.9 mmol) of monoethanolamine 1.034 g (3) was obtained. The yield 3 of 85%.

Diethanolamine salt of carboxymethylcellulose (4). From 1 g H-CMC and 0.727 g (6.9 mmol) diethanolamine 1.22 g (4) was obtained. The yield 4 of 89%.

Triethanolamine salt of carboxymethylcellulose (5). From 1 g of H-CMC and 1.033 g (6.9 mmol) triethanolamine, 1.414 g (5) was obtained. The yield 5 of 93%.

Elemental analysis data and IR spectra of CMC and ethanolamine salts of CMC 1-5 are presented in figure 1 and table 1.

| polysaccharide | C, %       | H, %       | N, %       |
|----------------|------------|------------|------------|
| 1              | 35.8, 35.9 | 4.9, 4.9   | -          |
| 2              | 40.0, 40.0 | 6.2, 5.8   | -          |
| 3              | 35.6, 35.5 | 6.7, 6.8   | 3.0, 2.9   |
| 4              | 38.2, 38.4 | 6.3, 6.0   | 2.8, 2.8   |
| 5              | 39.1, 39.1 | 6.1, 6.0   | 2.7, 2.6   |

The effect of NaCMC and its functional derivatives on the inhibition of \(\text{CaCO}_3\) formation was determined at a temperature of 80 °C and a polysaccharide concentration of 10, 30 and 50 mg/l by a method based on blocking the steel capillary formed by calcium carbonate crystals. The reservoir wa-
The model (RWM) was pumped at a rate of 1 ml/min through a 2.5 m long stainless-steel capillary with an internal diameter of 1 mm and the dynamics of the pressure drop in the capillary caused by the deposition of CaCO$_3$ was recorded.

The effectiveness of inhibition of calcium carbonate formation was determined by the formula (1):

$$E = 100 \times \frac{\Delta P_1 - \Delta P_2}{\Delta P_1}$$

where $\Delta P_1$ is the pressure drop on the capillary when pumping RWM without polysaccharides; $\Delta P_2$ is the pressure drop on the capillary when pumping RWM with polysaccharides.

To prepare emulsions, a sample of oil from the Priobskoye oilfield was used as a hydrocarbon phase. Anhydrous oil had the following physical and chemical characteristics: oil density 0.876 g/cm$^3$ at 20°C; water cut determined by the Dean-Stark method − 0%. Component composition of oil: paraffins − 3.6%, asphaltenes − 2.6%, resins − 15.2%. The formation water of the Priobskoye field had the following characteristics: mineralization − 13.2 g/l; density −1.01 g/cm$^3$; pH = 8.1; ionic composition: Ca$^{2+}$ − 250; Mg$^{2+}$ − 85.0; Na$^+$ + K$^+$ − 3048; Cl$^-$ − 4425; HCO$_3^-$ − 1658 mg/l.

The preparation of emulsions without polysaccharides was carried out by mixing the aqueous and hydrocarbon phases in a ratio of 1:1 at room temperature for 30 min using a mechanical stirrer at a speed of 1400 rpm. In a container put the oil in droplets and when mixing the injected aqueous phase for 10 min, after which the composition was stirred 20 min [12].

Water-oil emulsion in the presence of polysaccharides was obtained by dissolving in RWM of the Priobskoye oilfield the calculated amount of polysaccharide (H-CMC and arabinogalactan). The density of water samples was determined by a standard method using an aerometer.

Rheological characteristics (viscosity@shear rate) of artificial emulsions were determined on rotary viscometer RHEOTEST RN4.1, designed to measure the dynamic viscosity of the liquid and rheological studies. For the studied samples, a shear test was applied when the shear rate changed in the range from 1 to 300 c$^{-1}$, at which the dependence of the shear stress and viscosity on the shear rate was determined.

To characterize the process of separation of w/o emulsion in the absence and in the presence of polysaccharides, a complex system “Lumi Fuge Stability Analyser” was used to study dispersions on the basis of a multi-seat analytical centrifuge. The device allows you to quickly characterize any process with phase separation, calculate the rate of delamination depending on the centrifugal forces.

Micrographs of w/o emulsion were obtained using a microscope “Micromed 3” (LOMO) at a magnification of 400 times.

3. Results and discussion

For the synthesis of CMC salts with ethanolamines and CMC amides, the sodium salt of carboxymethylcellulose (1) was pre-converted to H-form (2) by treatment with a 20% H$_2$SO$_4$ solution in a 70% ethanol solution at room temperature.

The interaction of carboxymethylcellulose (1) with a 2-fold molar excess of ethanolamines is most successful in an aqueous solution at 80 °C. Under these conditions, the only reaction products are monoethanolamine (3), diethanolamine (4) and triethanolamine (5) carboxymethylcellulose salts formed with yields of 85, 89 and 93% respectively.

In the IR spectra of the obtained compounds, 3-5 valence oscillations of O-H groups are manifested in a wide frequency range of 3000-3600 cm$^{-1}$, absorption bands characteristic of carboxylation are observed in the region of 1577-1585 cm$^{-1}$, and for the ammonium group at ~ 2870 cm$^{-1}$ (figure 1).
It is known that NaCMC can form sufficiently stable complexes with the Ca\(^{2+}\) ion [16, 17]. Therefore, assuming that functionalized polysaccharides can prevent the precipitation of calcium salts from supersaturated aqueous solutions and inhibit scale deposition; studies were conducted on its effect on the crystallization process of CaCO\(_3\).

The study of CMC salts with ethanolamines as inhibitors of salt deposition at a temperature of 80 °C showed that at a concentration of 10-30 mg/l, the reagents inhibit the processes of scale deposition of CaCO\(_3\) and their efficiency is 53-80% (figure 2).

The efficiency with respect to inhibition of calcium carbonate at a concentration of 10 mg/l is higher for ethanolamine salts of CMC than for NaCMC. At higher concentrations, this effect disappears. Considering the efficiency of inhibition may be noted that in the range from 3 to monoethanolamine diethanolamine and triethanolamine salt of CMC 5, it decreases.

It is important that the reagents used in the production and preparation of oil are compatible with reservoir water and oil, and do not have a negative impact on w/o emulsions. In order to obtain data on the effect of polysaccharides on the stability of emulsion, we studied the rheological and sedimentation characteristics of artificially produced w/o emulsions based on oil from the Priobskoye field without and in the presence of 1.

To solve the problem of the effect of polysaccharide on the properties of w/o emulsion, emulsions containing 50% of model water with and without polysaccharide were prepared. The concentration of NaCMC in the aqueous phase of the emulsion was 50, 100, 200 mg/l. The density of water-oil emulsions without polysaccharide was 0.940 g/cm\(^3\), for the emulsion in the presence of NaCMC, the density practically did not change.
The rheological curve of oil in the Priobskoye field at a temperature of 20 °C deviates only slightly from Newton’s law. The viscosity of oil at a shear rate of 2.8 s\(^{-1}\) is 34.6 mPa·s. The viscosity of w/o emulsion is 578 mPa·s and has increased more than 16 times compared to oil. The dependence of viscosity on shear rate is typical for a typical visco-plastic non-Newtonian liquid (figure 3). The viscosity of w/o emulsion in the presence of H-CMC at a concentration of 50 mg/l decreases by more than 30% at low shear rates. Moreover, the effect of reducing the viscosity of w/o emulsion is greatest at a concentration of 50 mg/l with increasing concentration; the effect of reducing the viscosity is less (figure 4). It can be assumed that with the increase in the concentration of polysaccharide, the properties stabilizing the w/o emulsion are manifested, in particular, in the formation of the armor layer at the phase separation. This effect of the polysaccharide is quite consistent with the known literary results [13,14].

![Figure 3. Dynamic viscosity as a function of shear rate of Priobskoye oil field and oil-water emulsion prepared without polysaccharide.](image)

![Figure 4. Dynamic viscosity as a function of shear rate for w/o emulsion without polysaccharide and in the presence of 50, 100, 200 mg/l NaCMC.](image)

According to the results obtained from the transmission data (transmission profiles - “fingerprints”), the w/o emulsion of the Priobskoye oilfield is sufficiently stable, which is confirmed by the relatively low rate of emulsion delamination and the relatively low value of the Lumi Fuge instability index (figure 5). In the presence of polysaccharide, w/o emulsion is markedly destabilized, especially at a concentration of 100 mg/l (figure 5 and table 2).

| The profiles of transmittance | Kinetics of demulsifications |
|------------------------------|------------------------------|
| w/o emulsion without polysaccharide | w/o emulsion in the presence of 100 mg/l NaCMC |
Figure 5. Transmission profiles and demulsification kinetics for w/o emulsion without polysaccharide and in the presence of 100 mg/l NaCMC.

Table 2. Instability Index Lumi Fuge

|                  | Emulsions without additives NaCMC | Emulsions with additives NaCMC |
|------------------|-----------------------------------|--------------------------------|
| w/o emulsion     | 0.18                              | 0.21                           |
| w/o emulsion (50% water/50% oil) | 0.18                              | 0.21                           |
| 50 mg/l          | 0.21                              | 0.17                           |
| 100 mg/l         | 0.30                              | 0.36                           |
| 200 mg/l         | 0.17                              | 0.17                           |

Thus, NaCMC does not increase the stability of the w/o emulsion of the Priobskoye oilfield. For w/o emulsion samples without polysaccharide (figure 6a), as well as in the presence of 100 mg/l NaCMC (figure 6b), micrographs were obtained using at a magnification of 400 times. From the photo it can be seen that in the presence of NaCMC water globules have large sizes, causing less stability of the emulsion over time.

Figure 6. Micrographs of w/o emulsion without polysaccharide (a), in the presence of 100 mg/l NaCMC (b).

4. Conclusion
On the basis of carboxymethylcellulose ethanolamine salts, new highly effective inhibitors of calcium carbonate deposits were obtained, which are superior in efficiency to NaCMC.

It was found that the sodium salt of carboxymethylcellulose does not increase the effective viscosity and stability of VNE at concentrations of 50, 100, 200 mg/l.

Acknowledgement
The research is performed under the scope of the State Order of the Ministry of Education and Science of the Russian Federation (№ 4.2703.2017/ПЧ) on subject №АААА-А17-1170011910021-8.

References
[1] Crabtree M, Eslinger D, Fletcher P et al. 2002 Oilfield Rev. 11 N3 30-45
[2] Olajire A A 2015 J. Pet. Sci. Eng. 135 723-737
[3] Pereyma A A 2015 Oil Industry N2 84-87
[4] Kashchavtsev, V E, Mishchenko, I T 2004 Soleobrazovanie pri dobyche nefti (Scaling in Oil Extraction), Moscow: Orbita-M p 140
[5] Sawada K 1997 Pure Appl. Chem. 69 N5 921-928
[6] Reddy M M 1977 J. Cryst. Growth. 41 N2 287-295
[7] Ishmiyarov E R, Rakhimova N T, Latypova D R et al. 2015 Russ. J. of Applied Chem. 88 N7 1174-1177
[8] Voloshin A I, Gusakov V N, Fakhreeva A V et al. 2018 Neftepromislovoe delo (Oilfield engineering) N11 60-72
[9] Fakhreeva A V, Gusakov V N, Voloshin A I et al. 2016 Russ. J. Appl. Chem. 89 N12 1541-1545
[10] Dokichev V A, Fakhreeva A V, Voloshin A I et al. 2018 Equipment and technologies for oil and gas complex 5 43-48
[11] Klemm D. Cellulose / Klemm D, Schmauder H 2002 Biopolymers 6 275-319
[12] Graifer V I, Lazarev G A, Leontiev M I. 1973 Neftepromislovoe delo (Oilfield engineering) N2 21-23
[13] Hippmann S, Ahmed S S, Fröhlich P et al 2018 Colloids and Surfaces A: Physicochemical and Engineering Aspects 553 71-79
[14] Martínez-Palou R, Mosqueira M de L, Zapata-Rendón B et al. 2011 J. of Petroleum Science and Engineering 75(3-4) 274-282
[15] Fakhreeva A V, Voloshin A I, Telin A G et al IOP Conference Series: Materials Science and Engineering 2019 525 012050
[16] Zakharov N A, Ezhova Zh A, Koval’ E M et al. 2005 Inorg. Mater. 41 509-515
[17] Backfolka K, Lagergeb S, Rosenholmc J et al. 2002 J. of Colloid and Interface Science 248 5–12.