Production of Ethanolamine Salts and Amides of Carboxymethyl Cellulose (Promising Reagents for Oil Production)

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Abstract The research team has obtained functionalized nitrogen-containing polysaccharides based on affordable low-molecular carboxymethyl cellulose. 90 thousands and ethanolamines. The paper shows that due to the specific reversible adsorption that occurs when seeds are nucleating, these polysaccharides alter the shape of the emerging crystal, inhibit the aggregation and agglomeration of CaCO3 crystals, and reduce their size from 49.6 to 20.2 and 15.4 µm, respectively. Gravimetry shows that the corrosion rate of low-carbon steel 20 in a produced-water model is reduced when continuously running CO2 in the presence of synthesized polysaccharides. The protective effect of the functionalized CMC derivatives is 15.8 to 18.6 percent stronger than for the original biopolymer. The obtained polysaccharide derivatives could be of use for developing corrosion and scaling inhibitors.

1. Introduction
Advancements in today’s chemical use in production, including that of oil and gas, necessitates novel ‘green’ high-performance reagents that have multiple effects. Carboxymethyl cellulose sodium salt (NaCMC) is an affordable water-soluble polysaccharide; its physical and chemical properties, affordability, heat resistance, and biodegradability in aerobic and anaerobic conditions make it a good candidate for making new ‘green’ reagents for oil production [1-3]. Gravimetry and electrochemical tests have proven NaCMC to have anti-corrosion effects and to be a mixed (cathodic and anodic) corrosion inhibitor [4].

Injecting different functional groups into the glucose fragment of cellulose stabilizes it in waters of varying mineralization and makes its water solutions resistant to ions of some metals [5].

Injecting an amide group or quaternary ammonium groups into the molecule is expected to improve the solubility of carboxymethyl cellulose and to induce new applied properties (scaling and corrosion inhibition). To that end, this paper analyzes how carboxymethyl cellulose interacts with monoethanolamine, diethanolamine, triethanolamine, and urea.
2. Experimental part
The research team used NaCMC (1) from Aldrich with a molecular weight of 90 thousand and a degree of substitution of 0.7.

IR spectra were recorded by a Nicolet iS 10 Fourier spectrometer with OMNIC mathware at 400 to 4,000 cm⁻¹.

How CMC derivatives could inhibit the crystallization of calcium and barium salts was studied using mineral water models typical of oil fields in Western Siberia; the models had the following ion composition:
- \( \text{Ca}^{2+} - 250.8, \text{Mg}^{2+} - 85.3, \text{Na}^{+} - 3120.2, \text{Cl}^{-} - 4492.1, \text{HCO}_3^{-} - 1,720.5 \text{mg/l} \) (produced-water model, PWM, for the Priobskoye Field).
- \( \text{Ca}^{2+} - 4912.4, \text{Mg}^{2+} - 74.5, \text{Na}^{+} - 2863.0, \text{Cl}^{-} - 11758.7, \text{SO}_4^{2-} - 5,245.1 \text{mg/l} \) (sulfate water, SW).
- \( \text{Ba}^{2+} - 157.2, \text{Na}^{+} - 5966.3, \text{Cl}^{-} - 9180.4, \text{SO}_4^{2-} - 135.1 \text{mg/l} \) (barium water, BW) made from AR-graded \( \text{CaCl}_2, \text{MgCl}_2\cdot6\text{H}_2\text{O}, \text{NaCl}, \text{NaHCO}_3, \text{Na}_2\text{SO}_4 \) salts.

The effectiveness of polysaccharides against scaling was tested at 80ºC at 10, 30, or 50 mg/l by blocking a steel capillary with forming calcium sulfate and carbonate deposits. The produced-water model (PWM) contained \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^{+}, \text{Cl}^{-}, \text{HCO}_3^{-} \); the water was pumped at 1 ml/min through a 2.5 meters long, 1 mm ID stainless-steel capillary; the team recorded changes in pressure due to the deposition of \( \text{CaCO}_3 \) and \( \text{CaSO}_4 \).

Size of the emerging \( \text{CaCO}_3 \) crystals was measured by an Analysette 22 NanoTec plus laser diffraction particle-size analyzer.

The sedimentation stability of the water-dispersed \( \text{CaSO}_4 \) and \( \text{BaSO}_4 \) system as affected by polysaccharides was tested by a Turbiscan Tower (FormulationSA) dispersion stability instrument.

For gravimetry, the team used rectangular carbon steel 20 specimens sized 25×20×2 mm that had the following composition (wt.%): Fe — 99.31; C — 0.08; Si — 0.03; Mn — 0.40; Cr — 0.04; Ni — 0.03; Cu — 0.06; Al — 0.05. The surface of each specimen was cleaned with Ecowet Mirka p80 (230×280 mm) fine-grained sanding paper, washed with water, degreased with acetone, kept for 1 hour in a dessicator filled with GOST 3956-76 technical silica gel, then weighed using analytical scales. Tests were carried out at 20ºC over 6 hours in the PWM with polysaccharides added at 50 mg/l; the model was subject to continuous carbon dioxide saturation. After exposure, the specimens were cleaned of corrosion products, degreased, and weighed.

Carboxymethyl cellulose (HCMC, 2). 5.0 g of NaCMC 90 was added to 140 ml of a 20% \( \text{H}_2\text{SO}_4 \) solution in a 70% ethanol solution (pH=2 to 2.5), then mixed magnetically at room temperature over 20 minutes. HCMC was filtered by a blue-ribbon filter, washed with 70% ethyl alcohol until the sulfate-ion tests were negative, then dried in vacuum. Yield: 4.51 g (97%).

HCMC interaction with ethanolamines. 2 moles of ethanolamine per carboxyl group was added to a suspension of 1 g of NaCMC in 40 ml of distilled water in a 100-ml three-neck flask, then mixed at 80ºC over 5 hours. Isopropyl alcohol was used to cause sedimentation; the deposited solids were filtered and washed in a filter funnel with isopropyl alcohol, then dried in vacuum to reach constant mass.

Monoethanolamine CMC salt (3). 1 g of NaCMC and 0.422 (6.9 mmol) of monoethanolamine produced 1.034 g of the product, a yield of 85%.

Diethanolamine CMC salt (4). 1 g of NaCMC and 0.727 (6.9 mmol) of diethanolamine produced 1.222 g of the product, a yield of 89%.

Triethanolamine CMC salt (5). 1 g of NaCMC and 1.099 (6.9 mmol) of triethanolamine produced 1.414 g of the product, a yield of 93%.

CMC amide (6).
0.105 g (1.75 mmol) of urea was ground in a porcelain mortal with 0.5 g of NaCMC, then added to a flask with 10 ml of o-Xylol. The mixture was boiled over 2 hours; the solid product was filtered, washed with ethyl alcohol and dried in vacuum. The yield was 0.497 g (95%).

Figure 1 and Table 1 present the elemental analysis and IR spectra of NaCMC 90 of polysaccharides 1 to 6.

Table 1. Elements of polysaccharides 1 to 6.

| Polysaccharide | C, %     | H, %     | N, %     |
|---------------|----------|----------|----------|
| 1             | 35.81, 35.86 | 4.86, 4.91 | -        |
| 2             | 39.99, 40.04 | 6.16, 5.84 | -        |
| 3             | 35.62, 35.50 | 6.65, 6.81 | 2.99, 2.95 |
| 4             | 38.23, 38.38 | 6.30, 6.04 | 2.79, 2.81 |
| 5             | 39.14, 39.06 | 6.08, 6.00 | 2.66, 2.64 |
| 6             | 36.65, 36.99 | 5.70, 5.45 | 7.65, 7.98 |

3. Results and discussion
To synthesize CMC salts with ethanolamines and CMC amides, carboxymethyl cellulose sodium salt 1 was first converted into H-form 2 by processing 20% H₂SO₄ solution in a 70% ethanol solution at room temperature.

CMC 1 interacted most efficiently with a 2x molar surplus of ethanolamines was most effective at 80ºC in a water solution. In that case, the only products of reaction were monoethanolamine CMC salt 3, diethanolamine salt 4, and triethanolamine salt 5, yielded at 85%, 89%, and 93%, respectively.

Of special interest are the nitrogen-containing cellulose derivatives whose structure, aside from hydroxyl groups, contain amides, which are considered promising corrosion inhibitors. They can be conveniently synthesized by carbonic acids interacting with urea. For instance, boiling CMC with urea in o-Xylol at 140ºC converts carboxyl groups into amide groups and yields 95% of CMC amide 6.
In the IR spectra of the produced compounds 3 to 5 valent oscillations of O-H groups were observed across a wide frequency spectrum of 3,000 to 3,600 cm$^{-1}$, the carboxylation-typical absorption bands were in a range of 1,577 to 1,585 cm$^{-1}$, while the ‘ammonium band’ was at ~2,870 cm$^{-1}$.

NaCMC is known to form stable low-solubility complexes with Ca$^{2+}$ [6,7]. The authors hereof assumed that CMC salts and monoethanolamines can prevent the sedimentation of calcium salts from oversaturated water solutions and inhibit scaling; the next step was to test their effect on the crystallization of calcium carbonate.

How NaCMC and its functional derivatives affected the inhibition of CaCO$_3$ formation was assessed at 80ºC with polysaccharide concentrations of 10, 30, or 50 mg/ml; the method was based on blocking a steel capillary with emerging calcium carbonate crystals. The produced-water model was pumped at 1 ml/min through a 2.5 meters long, 1 mm ID stainless-steel capillary; the team recorded changes in pressure due to the deposition of CaCO$_3$, see Figure 2.

Inhibition performance shown in Table 2 was found by the formula (1):

\[
P_p = \frac{100 \times (\Delta P_1 - \Delta P_2)}{\Delta P_1}
\]

where $\Delta P_1$ is the difference in pressure in the capillary when pumping PWM with no polysaccharide;

$\Delta P_2$ is the difference in pressure in the capillary when pumping PWM with polysaccharide.

Capillary testing of the scaling inhibiting capacity of CMC salts with ethanolamines at 80ºC showed that at 10 to 30 mg/l, the reagents were able to inhibit CaCO$_3$ scaling with a performance of 53% to 80%, see Table 2. At to 10 mg/l, this solution was more efficient than NaCMC. At higher
concentrations, it wasn’t. Considering the inhibiting performance, it should be noted that it lowered from monoethanolamine 3 towards diethanolamine and triethanolamine 5.

Table 2. CaCO₃ inhibition performance of polysaccharides 1, 3 to 5.

| Polysaccharide | Concentration, mg/l | Performance, % |
|---------------|---------------------|----------------|
|               | 10                  | 30            | 50            |
| 1             | 42                  | 74            | 70            |
| 3             | 80                  | 77            | 75            |
| 4             | 60                  | 62            | 62            |
| 5             | 53                  | 53            | 26            |

Where CMC salts with ethanolamines were present, crystals turned out to be far smaller, see Figure 3. The average size of emerging crystals dropped from 49.6 µm (no polysaccharides) to 15.4–20.2 µm.

The sedimentation stability of the water-dispersed CaSO₄⁺ and BaSO₄⁻ system both in the presence and in the absence of functionalized polysaccharides was tested by a TurbiscanTower (FormulactionSA) dispersion stability instrument.

In the absence of polysaccharides, there was formed a fine suspension of crystals that settled as a result of aggregation and agglomeration; the solution lightened. In that case, the Turbiscan Stability Index was the highest of any observation, see Figure 4a and 4b.

Scaling inhibition performance was found by the formula (2). Table 3 shows the results.

\[ \mathcal{E} = \frac{TSI_0 - TSI_{ing}}{TSI_0} \]  

where \( TSI_0 \) is the stability index with no polysaccharide; \( TSI_{ing} \) is the stability index with the polysaccharide.

Figure 3. Crystal-size distribution of CaCO₃ as affected by polysaccharide 3 at 0 (1), 10 (2), 30 (3) и 50 (4) mg/l, 80°C in the PWM, \( n \) is the vol.% of crystals, \( d \) is diameter, µm.

Figure 4a. How 3 affected the deposition of CaSO₄ at 25°C at 0 (1), 10 (2), 30 (3), 50 (4), 100 (6) mg/l, where \( \tau \) is time, min, TSI is the Turbiscan Stability Index.

Figure 4b. How 3 affected the deposition of CaSO₄ at 80°C at 0 (1), 10 (2), 30 (3), 50 (4), 100 (6) mg/l, where \( \tau \) is time, min, TSI is the Turbiscan Stability Index.
Table 3. CaSO₄ and BaSO₄ inhibition performance of sodium CMC (1) and CMC ammonium salts (3-5).  

| Concentration of polysaccharide, mg/l | 1   | 3   | 4   | 5   |
|--------------------------------------|-----|-----|-----|-----|
| Calcium sulfate inhibition performance, % |     |     |     |     |
| 10                                   | 81  | 83  | 77  | 77  |
| 20                                   | 93  | 91  | 81  | 86  |
| 30                                   | 96  | 92  | 81  | 94  |
| 50                                   | 95  | 92  | 83  | 94  |
| 100                                  | 96  | 93  | 82  | 93  |
| Barium sulfate inhibition performance, % |     |     |     |     |
| 10                                   | 5   | 52  | 30  | 49  |
| 20                                   | 58  | 73  | 53  | 51  |
| 30                                   | 37  | 83  | 67  | 71  |
| 50                                   | 74  | 85  | 54  | 74  |
| 100                                  | 10  | 91  | 37  | 54  |

Compared to the original NaCMC, CMC salts with ethanolamines had retained their strong inhibitory effects against calcium carbonate and sulfate. Injecting an ammonium group induced a protective effect against barium sulfate.

How polysaccharides 1 and 3 to 5 affected steel 20 corrosion was assessed by gravimetry per GOST 4 9.905-2007. Corrosion rates were measured on rectangular steel specimens sized 20x25x2 mm. Tests were carried out at room temperature 20ºC over 6 hours in a Priobskoye field PWM. Carbon dioxide was supplied consistently to the water solution throughout the experiment; the polysaccharide concentration was 50 mg/l. Uniform corrosion rate $K$, g/(m²∙h) and the protective effect were calculated by the formulas 3 and 4:

$$K = \frac{m_0 - m_t}{S \cdot \tau}$$  \hspace{1cm} (3)

$$Z = \frac{(K_0 - K) \cdot 100}{K_0}$$  \hspace{1cm} (4)

where:

- $m_0, m_t$ are the specimen weights before and after testing, respectively, g;
- $S$ -is the specimen surface area, m²;
- $\tau$ is the exposure time, h.
- $K_0$ is the corrosion rate with no polysaccharide, g/m²∙h
- $K$ is the corrosion rate with polysaccharide, g/m²∙h

Table 4 presents the corrosion rates as found by the formula 1.
Table 4. Corrosion rates returned by gravimetry, polysaccharide concentration of 50 mg/l, PWM.

| Polysaccharide | # | Δm, g | S, m² | Corrosion rate K, g/(m²·h) | Mean K, g/(m²·h) | Protection degree Z,% |
|---------------|---|-------|-----|-----------------|----------------|-----------------|
| No polysaccharide | 1 | 0.0050 | 0.00115373 | 0.7223 | 0.7211 | - |
| 1 | 0.0046 | 0.00114158 | 0.6715 | 0.6899 | 4.3 |
| 2 | 0.0049 | 0.00115303 | 0.7082 | | |
| 3 | 0.0038 | 0.00115458 | 0.5485 | 0.5556 | 22.9 |
| 2 | 0.0039 | 0.00115499 | 0.5627 | | |
| 4 | 0.0037 | 0.00115749 | 0.5327 | 0.56025 | 22.3 |
| 2 | 0.0040 | 0.00113428 | 0.5877 | | |
| 5 | 0.0038 | 0.00114715 | 0.5521 | 0.5759 | 20.1 |
| 2 | 0.0041 | 0.00113912 | 0.5999 | | |

Gravimetry showed that the corrosion rate of low-carbon steel 20 in PWM containing CO₂ was 0.721 g/m²·h; polysaccharides thus had a protective effect that was 15.8% to 18.6% higher for functionalized CMC derivatives than for the original biopolymer.

4. Conclusion
The obtained nitrogen-containing carboxymethyl cellulose derivatives with ethanolamines and urea effectively inhibit calcium and barium sulfate and carbonate deposition and are no less efficient than the original NaCMC; besides, they are better against carbon dioxide corrosion of steel 20.

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