Behavior of gellan in aqueous-salt solutions and oilfield saline water

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The influence of storage time and temperature on the behavior of low acyl gellan (LAG) was studied by viscometry and ^{1}H NMR spectroscopy without salt addition. The viscometric results revealed that the effectiveness of salts to enhance gelation of gellan changes in the following order: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$. The sol-gel and liquid-solid phase transitions of gellan solutions were observed upon addition of oilfield water containing 73 g L^{-1} of alkaline and alkaline earth metal ions. The effectiveness of salts to induce the separation of liquid and solid phases changes in the sequence: $NaCl > KCl > MgCl_2 \approx CaCl_2 \approx BaCl_2$. The hydrodynamic behavior of 0.5 wt.% gellan solution injected into the sand pack model with high (20 Darcy) and lower (2 Darcy) permeability is useful to model the oil reservoirs in the process of enhanced oil recovery.

Keywords: gellan; viscosity; rheology; sol-gel-sol transition; phase transition.

Тұзды-су ерітіндісі мен жер қабат суында гелланның қасиеттері

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Мақалада вискозиметрия және ЯМР ^{1}Н спектроскопия әдістерімен төмен ацилденген гелланның (ТАГ) сулы ерітіндісінің ұзақ уақытқа сақталу мерзімі мен температура әсері тұздардың қатысынсыз зерттелді. Гель түзу нәтижесіне жеке тұздардың әсері келесі қатар бойынша өзгеретіндігі анықталды: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$. Гелланның сулы ерітіндісінің золь-гель және гель-золь ауысуы сілті және сілтілік жер металлдарының иондары 73 г/л болатын жер қабат суын қосқанда байқалады. Сұйық және қатты фазаға бөліну нәтижесіне жеке тұздардың әсері келесі қатар бойынша өзгеретіндігі анықталды: $NaCl > KCl > MgCl_2 \approx CaCl_2 \approx BaCl_2$. Мұнай шығымын арттыру үрдісін модельдеу үшін 0,5% гелланның сулы ерітіндісі қолданылып, жоғарғы (20 Дарси) және төменгі (2 Дарси) өтімділіктегі құмды модельдің фильтрациялық қасиеті зерттелді.

Түйін сөздер: геллан; тұтқырлық; реология; золь-гель-золь ауысу; фазалық ауысу.

Поведение геллана в водно-солевых растворах и пластовой воде

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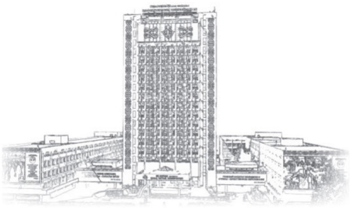
В работе методами вискозиметрии и ЯМР ^{1}Н спектроскопии изучено влияние времени хранения и температуры на вязкость водного раствора низкоацилированного геллана (НАГ) в отсутствие соли. Установлено, что влияние отдельных солей на эффективность гелеобразования изменяется в следующем порядке: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$. Золь-гель и гель-золь переходы водного раствора геллана наблюдаются при добавлении пластовой воды с минерализацией 73 г/л, содержащей ионы щелочных и щелочноземельных металлов. Влияние отдельных солей на эффективность разделения жидкой и твердой фазы изменяется в следующей последовательности: $NaCl > KCl > MgCl_2 \approx CaCl_2 \approx BaCl_2$. Для моделирования процесса увеличения нефтеотдачи с использованием 0,5%-ного водного раствора геллана были проведены фильтрационные исследования на насыпных песчаных моделях с высокой (20 Дарси) и низкой (2 Дарси) проницаемостью.

Ключевые слова: геллан; вязкость; реология; золь-гель-золь переход; фазовый переход.



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1. Introduction

According to a literature survey, a huge amount of publications is devoted to polysaccharides, in particular gellan, which is produced by the bacterium *Pseudomonas elodea* and consists of a tetrasaccharide repeating unit of D-glucose, D-glucuronic acid, D-glucose, and L-rhamnose [1-3]. Review article [4] comprehensively considers the structure, rheology, gelation, topology, and application aspects of gellan. The coil-helix conformational and sol-gel phase transitions of gellan gums induced by temperature, salt addition, pH change etc. were the main subject of the most research [5, 6]. A series of publications cover a formation of interpenetrating networks with participation of gellan and natural polymers [7-9].

It is commonly accepted that gellan gum exhibits a conformational change from the disordered state (single chain) to the ordered state (double helix) with decreasing temperature, and the gelation is considered to be mediated by the double-helix formation and the association of such helices enhanced by the presence of mono- and divalent alkaline and alkaline earth cations. Monovalent counter ions are responsible for the screening of the electrostatic repulsion between adjacent molecules and promote coil-helix transition and association between gellan molecules while divalent ions form the ionic bonding between two carboxyl groups. It has been established that the extent of aggregation and effectiveness in promoting gel formation by addition of ions follows this order: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. This sequence coincides well with increasing of the ionic radius of cation species. The higher effectiveness of divalent cations in comparison with monovalent cations may be attributed to additional crosslinking of gellan chains due to cooperative binding (or “bridging”) of the divalent cations between glucuronate residues according to their ionic radii. Divalent cations seem to bind directly with gellan molecules to form aggregates of gellan helices with the effectiveness of $Ca^{2+}>Mg^{2+}$ [10-13].

The sol-gel technology is one of effective ways to design materials with definite chemical and physical mechanical properties. Transformation of sol to gel state proceeds with an increase of either concentration of disperse phase or under the action of external factors (concentration of polymer, temperature, time, pH medium, ionic strength etc.).

Rheological properties of deacylated gellan gel are superior to those of other common polysaccharide gels such as agar, κ-carrageenan, and alginate at similar concentrations. According to these authors, the hardness, brittleness, and elasticity of gellan gel at 0.5% is comparable to, and its stiffness is much higher than, 1% K-carrageenan, 1.5% agar, or 4.0% gelatin gels [14].

Earlier [15] we have demonstrated for the first time that the sol-gel transition of gellan can successfully be used for enhanced oil recovery (EOR). The remarkable property of gellan was plugging of high drainage channels in oil reservoirs. According to oilfield tests provided at Kumkol oilfield (South Kazakhstan), the technological effectiveness of an oil recovery reached 2000 tons of oil per 1 ton of injected gellan that is comparable with the best results obtained for linear poly(acrylamide) cross-linked by chromium ions.

In the present paper, we have studied the viscosity, rheology, sol-gel and gel-sol transformations of low acyl gellan in the presence of both NaCl, KCl, $MgCl_2$, $CaCl_2$ and oilfield saline water containing 73 g L^{-1} of alkaline and alkaline earth metal salts. The obtained results will be useful to select optimal conditions of gellan gelation to be injected into oil reservoir for application in EOR.

2. Experimental

2.1 Materials

Food grade low acyl gellan (LAG) purchased from "Zhejiang DSM Zhongken Biotechnology Co., Ltd.", China, was used without further purification. Gellan contained mainly K ion (17.9 ± 0.088 wt.%). The elemental composition of the gellan was determined on X-ray fluorescence analyzer Epsilon 3 SW LTU PANalytical (The Netherlands). Gellan was dispersed in distilled water at room temperature (25 ±1°C) under vigorous magnetic stirring. Gellan concentrations selected for experiments varied from 0.2 to 1 wt.% on a dry weight basis. Low molecular weight salts, NaCl, KCl, $CaC1_2$ and $MgCl_2$, purchased from JSC "Reactiv", Russia, were used without further purification. The oil field water from "Kumkol" oil reservoir with a density of 1.05 g cm^3 and pH 6.68 composed of 22.5 g L^{-1} of Na^+ and K^+, 3.8 g L^{-1} of Ca^{2+}, 0.85 g L^{-1} of Mg^{2+}, and 43.9 g L^{-1} of Cl^- was used.

2.2 Methods

The viscosity of aqueous gellan solutions was measured on the Ubbelohde viscometer at 25±0.1°C. Proton NMR spectra of gellan were registered on JNM-ECA 400 (JEOL) at 30°C. The total salinity of oilfield water was determined on SevenCompact^{TM} S230 (Mettler-Toledo, Switzerland). The elemental composition of oil field water was analyzed with an X-ray fluorescence analyzer (Epsilon 3 SW LTU, PANalytical, Netherlands).

3. Results and Discussion

3.1 H^1 NMR spectra of gellan

Proton spectra of gellan in D_2O represent a set of resonance lines that are difficult to interpret comprehensively. Therefore, the proton signals belonging to each saccharide units were only identified. High frequency signal with 5.08 ppm corresponds to H-1 α-anomer of L-ramnose. The presence of ramnopiranosol residue is justified by signal at 1.25 ppm corresponding to protons of methyl radicals. Signals at δ = 4.66 and 4.48 ppm can correspond to 1,4-α- and 1,3-β-glucopiranosol units, respectively. The presence of glucoronic acid is verified by downfield signal at δ = 4.64 ppm. Identification of proton signals of gellan is represented in Fig.1 and Table 1.

3.2 Influence of storage time and temperature.

The influence of storage time on solution behavior of gellan is shown in Fig.2. The time dependence of viscosity of gellan at the interval of concentration 0.2-0.5% is similar. The viscosity has the minimal value at the fifth day of storage, followed by the increase and further slight changes. Slightly decreasing viscosity of gellan with time is probably connected with a destruction of gellan associates stabilized by hydrogen bonds.

A viscosity of gellan solutions gradually decreases with an increase of a temperature (Fig. 3). Initial values of the viscosity considerably differ at 25°C, however, they more

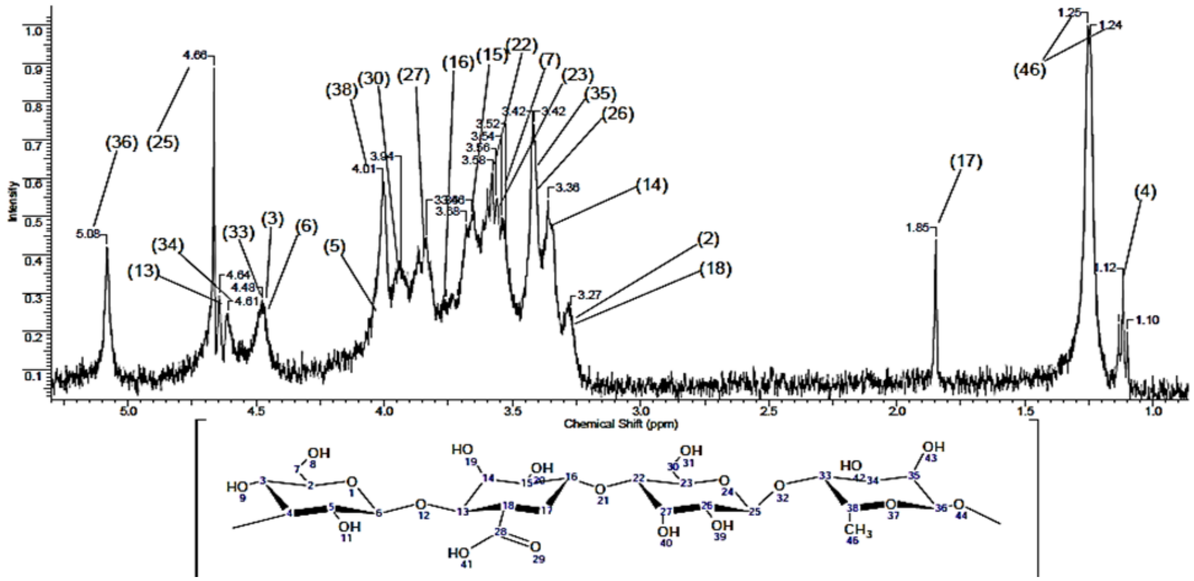


Figure 1 – Structural unit of gellan and its H^1 NMR spectra in D_2O at 30°C

Table 1 – Characteristic chemical shifts of H^1 NMR spectra of gellan

Chemical shift, ppm	Fragment of saccharide
5.08; 1.25	1,4-α-L-ramnose
4.66	1,4-α-D-glucose
4.48	1,3-β-D-glucose
4.64	1,4-β-D-glucoronic acid

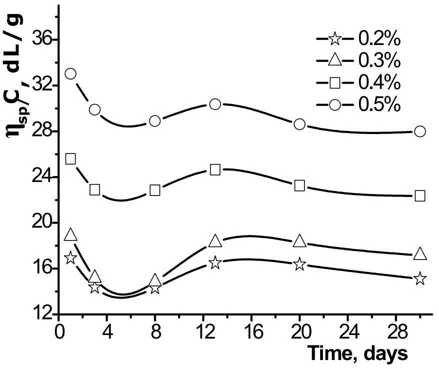


Figure 2 – Dependence of the viscosity of gellan on a storage time

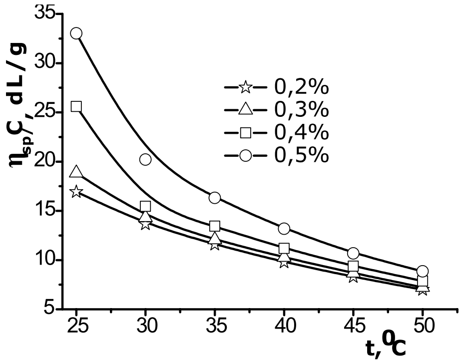


Figure 3 – Dependence of the viscosity of gellan on a temperature

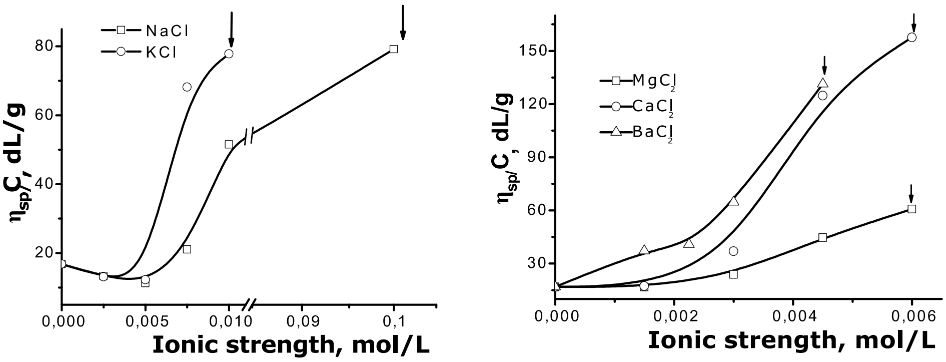


Figure 4 – Dependence of the viscosity of 0.2% gellan on the ionic strength of the solution adjusted by alkaline and alkaline-earth metal salts. Arrows point at a gel formation

or less fit together at 50°C. This may be connected with a gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds. One can suggest that in oil reservoir, gellan solution will be stable to biodegradation during 1 month, however, with a reduced viscosity at high temperature.

3.3 Influence of one- and two-valent alkaline and alkaline earth metal ions

According to viscometric measurements, the effectiveness of salts to enhance gelation changes in the following order: $BaCl_2$ > $CaCl_2$ ≈ $MgCl_2$ > KCl > NaCl (Fig. 4). This order is in good agreement with the results presented in [12] found for gellan. The higher effectiveness of divalent cations in comparison with monovalent cations may be attributed to additional crosslinking of gellan chains due to cooperative binding (or "bridging") of the divalent cations between glucuronate residues according to their ionic radii [13,14]. The critical concentration of salts, expressed as the ionic strength of the solution, leading to sol-gel and gel-sol phase transitions of 0.2% gellan solution are summarized in Table 2.

3.4 Influence of oilfield water

One of the remarkable properties of gellan is its ability to undergo sol-gel and gel-sol transitions in oilfield brine water of Kumkol oil reservoir containing mono- and divalent cations,

Table 2 – Sol-gel and gel-sol phase transitions of 0.2 wt.% gellan solution in the presence of various salts

Salt type	Critical value of the ionic strength inducing the sol-gel transition[a], (mol L^{-1})	Critical value of the ionic strength inducing the gel-sol transition[b], (mol L^{-1})
$BaCl_2$	0.0045	0.036
$CaCl_2$	0.006	0.036
$MgCl_2$	0.006	0.036
KCl	0.01	0.15
NaCl	0.1	0.20
[a]According to viscometric data; [b]Visual observation.		

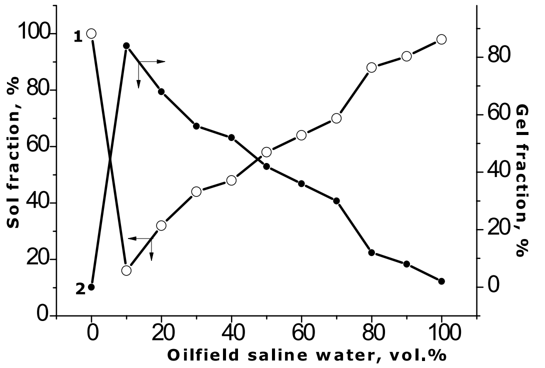


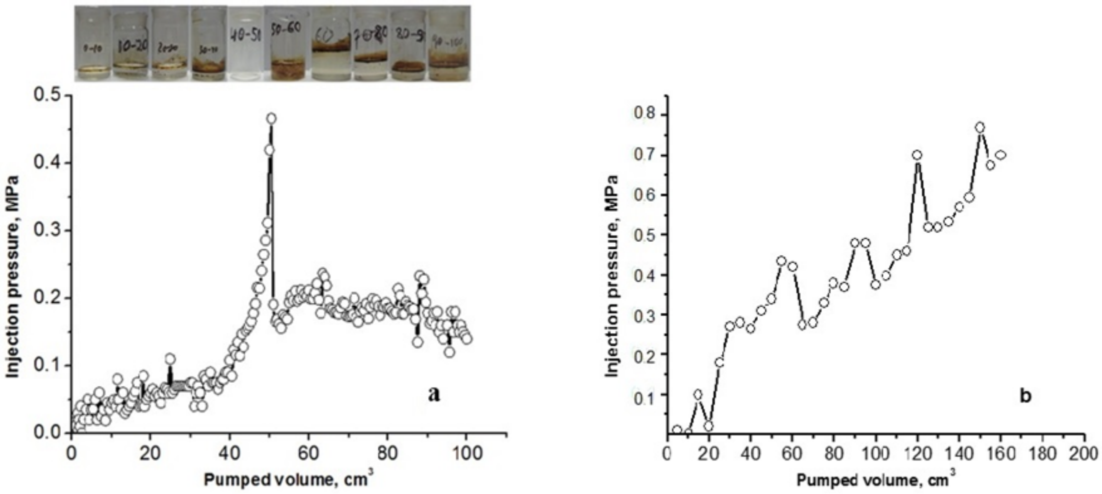
Figure 5 – Dependence of the amount of sol (1) and gel (2) fractions of 0.5 wt.% gellan solution upon addition of oilfield water with a salinity 73 g L^{-1}

such as Na^+, K^+, Ca^{2+} and Mg^{2+} with a total salinity 73 g L^{-1}. Addition of 10-30 vol.% oilfield saline water to aqueous solution of gellan causes the gel formation (sol-gel transition) while in the presence of ≥ 40 vol.% oilfield saline water, transformation of gellan from the gel to sol (gel-sol transition) takes place (Fig. 5). Sol-gel transition of gellan in oilfield water may be beneficial for extraction of oil from saline reservoirs. First of all, pumping aqueous solution of gellan into the injection well will be easy due to low viscosity of polymer. Secondly, the gel slug that is formed after contacting with underground saline medium can move to the deep stratum and can block or reduce the flow capacity of high-permeability channels without damaging less-permeable hydrocarbon-productive zones. Consequently, injecting water (water flooding) should penetrate as much as possible into the less-permeable zones so that oil can be displaced from these poorly swept zones.

3.5 Behavior of gellan solution in a sand pack model

It is also interesting to study the flow behavior of gellan solution in a sand pack model. It is expected that the gellan solution in the course of injection into oil reservoir will undergo coil-helix conformation and sol-gel phase transitions. The sand pack model with absolute gas permeability and pore volume that are equal to 20 Darcy and 47 cm^3 (porosity – 38%), respectively, was initially saturated with brine water with salinity of 73 g L^{-1}. The brine saturated sand pack was flooded by crude oil with viscosity 1.218 mPa s and density – 0.772 g cm^{-3}. As a result, the initial oil and water saturation became equal to 73.2% and 26.7% respectively. The temperature of the sand pack model was kept at 62°C during the whole filtration experiments. Water flooding was simulated by injection of brine into the sand pack model under the flow rate of 0.5 cm^3 min^{-1}. After pumping of 2 pore volumes (1 pore volume is equal to 50 cm^3) of water through the model, the oil displacement coefficient was equal to 49%. After completion of water flooding, the 0.5 wt.% gellan solution under the same flow rate was injected into the sand pack. The hydrodynamic behavior of gellan solution within the sand pack model is seen from the dependence of injection pressure on the pumped volume (Fig. 6).

As seen from Fig. 6a, the injection pressure sharply increases up to 0.47 MPa after injection of 40 cm^3 of gellan solution, and it dramatically decreases down to 0.2 MPa after injection of 50 cm^3 of gellan solution. Such behavior of gellan is interpreted as follows. When the gellan solution penetrates into the high permeable channels (or pores) it contacts with brine and gelation process is enhanced. Formation of gel particles within the pores decreases the permeability and increases the injection pressure. Injection of 10-40 cm^3 of gellan solution into the sand pack saturated by brine and oil is accompanied by displacement of oil-containing liquid (no. 1-4 inset). Accumulation of gel particles inside of high



Pore volume is 50 cm^3; temperature is 55°C, flow rate is 0.5 cm^3 min^{-1}.

Figure 6 – Changing of injection pressure during the filtration of 0.5 wt.% gellan solution through the sand pack model with permeability of 20 (a) and 2 Darcy (b)

permeable channels and severe plugging of the sand pack model takes place between 40 and 50 cm^3 of injected gellan solution. Plugging of high permeable zones of sand pack model by gellan gel is accompanied by the absence of squeezed out liquid (no.5 inset). Some portion of gellan gel generated inside of the porous media is displaced out of the model after injection of 50-60 cm^3 gellan solution. The breakthrough of gel plug leads to a sharp decrease of injection pressure together with continuous displacement of oil and water mixture from the sand pack model (no. 7-10 inset). The permeability of porous media and gellan concentration play a crucial role in plugging mechanism. When the permeability of porous media is extremely high (for instance, 20 Darcy) the gelation of gellan takes place only once, causing sharp increase and decrease of pressure. Periodically increase and decrease of injection pressure (oscillation of pressure) is observed for the sand pack model with lower permeability (Fig. 6). For example, the oscillation behavior of 0.5 wt.% gellan solution was detected inside of the sand pack model with permeability 2 Darcy. The hydrodynamic behavior of 0.5 wt.% gellan solution presented in Fig.4b may be explained in the following way. When 0.5 wt.% gellan solution penetrates into the brine saturated sand pack model, it preferentially occupies high permeable channels and plugs them (injection pressure increases). Accumulation of gel particles in high filtration channels leads to involvement of new channels to be plugged. When gellan solution finds such channels it flows into it (injection pressure decreases).

Thus, permanent plugging of different channels by gellan gel leads to constant redirection of gellan solution to lower and lower permeable pores. Such step-by-step plugging of high and low permeable channels is responsible for periodic increase and decrease of injection pressure.

4. Conclusion

Structural unit of gellan consisting of four saccharide units was identified by H^1 NMR spectra. The viscosity of gellan at the interval of concentration 0.2-0.5% is stable at least during one month. The viscosity of gellan solutions gradually decreases with an increase of a temperature due to destruction of hydrogen bonds leading to disaggregation of macromolecular associates. The effectiveness of salts to enhance gelation of gellan changes in the following order: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$ that is in good agreement with literature data. The sol-gel and gel-sol transitions of gellan were observed upon addition of various amounts of oilfield saline water to aqueous solution of gellan. The hydrodynamic properties of gellan solutions in sand pack model are determined by permeability of channels. The flow behavior of 0.5 wt.% gellan solution injected into the sand pack model of high (20 Darcy) and low (2 Darcy) permeability is different. When the permeability of porous media is high, the gelation of gellan takes place only once, causing rapid increase and decrease of pressure. Periodically, increase and decrease of injection pressure (oscillation of pressure) was observed for the sand pack model with low permeability. The brine-initiated gelation of gellan is perspective for plugging of the high-permeable channels of oil reservoir and as a shut-off agent in polymer flooding technology.

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References

1 Kohei K., Jun-ichi H., Shiro M. Effects of monovalent cation and anion species on the conformation of gellan chains in aqueous systems // Carbohydrate Polymers. – 2005. – Vol.61., Is.2. – P.168-173.

2 Khandker S.H., Katsuyoshi N. Chain release behavior of gellan gels (2009) Progress in Colloid and Polymer Science. – 2009. – Vol.136. – P.177-186.

3 Tako M., Teruya T., Tamaki Y., Konishi T. Molecular origin for rheological characteristics of native gellan gum // Colloid Polymer Science. – 2009. – Vol.287. – P.1445-1454.

4 Morris E.R., Nishinari K., Rinaudo M. Gelation of gellan // Food Hydrocolloids. – 2012. – Vol.28. – P.373-411.

5 Mariella D., Pasquale D., Vittorio C., Yoshiaki Y., Hiroshi U., Kanji K. Synthesis and physicochemical characterization of gellan gels // Macromolecules. – 2001. – Vol.34. – P.1449-1453.

6 Tuan-Chew T., Wan-Teck F., Min-Tze L., Azhar M. E. Comparative assessment of rheological properties of gelatin or gellan in maize starch – egg white composite gels // Journal of King Saud University – Science. – 2014. – Vol.4. – P.311-322.

7 Popa M., Dumitriu C.L., Sunel V. Interpenetrated polymeric networks based on gellan and poly(vinyl alcohol) // Polymer-plastic Technology and Engineering. – 2004. – Vol.43. – P.1503-1516.

8 Claudia C., Davide B., Cristina L., Andrea M., Pietro M. Preparation and characteriz // Journal of Materials Science-materials in Medicine. – 2011. – Vol.22. – P.263-271.

9 Kousaku O., Masanori Y., Ayako N., Norio N., Hiroyuki Y. Biodegradation of chitosan-gellan and poly(L-lysine)-gellan polyion complex fibers by pure cultures of soil filamentous fungi // Journal of Polymers and the Environment. – 2000. – Vol.8. – P.59-66.

10 Ogawa E., Matsuzawa H., Iwahashi M. Conformational transition of gellan gum of sodium, lithium and potassium types in aqueous solutions // Food Hydrocolloids. – 2002. – Vol.16. – P.1-9.

11 Lin D., Xinxing L., Zhen T. Critical behavior at sol-gel transition in gellan gum aqueous solutions with KCl and $CaCl_2$ of different

concentrations // Carbohydrate Polymers. – 2010. – Vol.81. – P.207-212.

12 Masahiko A., Yuko O., Takayuki N. Swelling behavior of covalently cross-linked gellan gels // Journal of Physical Chemistry. – 2000. – Vol.104. – P.6755-6760.

13 Yoko N., Rheo T., Katsuyoshi N. Viscoelasticity and phase separation of aqueous Na-type gellan solution // Biomacromolecules. – 2010. – Vol.11. – P.187-191.

14 Camelin I., Lacroix C., Paquin C., Prbvost H., Cachon R., Diviest C. Effect of chelatants on gellan gel rheological properties and setting temperature for immobilization of living bifidobacteria // Biotechnology Progress. – 1993. – Vol.9. – P.291-297.

15 Gussenov I.Sh., Ibragimov R.Sh., Abilkhairov D.T., Kudaibergenov S.E. Novel brine initiated gel technology for water shutoff operations. Proceedings of the Conference "New Knowledge in the Area of Drilling, Production, Transport and Storage of Hydrocarbons", High Tatras, Slovakia. – 2014. – P.152.

References

1 Kohei K, Jun-ichi H, Shiro M (2005) Carbohyd Polym 61:168-173. *http://dx.doi.org/10.1016/j.carbpol.2005.04.011*

2 Khandker SH, Katsuyoshi N (2009) Prog Coll Pol Sci S 136:177-186. *http://dx.doi.org/10.1007/978-3-642-00865-8_25*

3 Tako M, Teruya T, Tamaki Y, Konishi T (2009) Colloid Polym Sci 287:1445-1454. *http://dx.doi.org/10.4236/fns.2014.53035*

4 Morris ER, Nishinari K, Rinaudo M (2012) Food Hydrocolloid 28:373-411. *http://dx.doi.org/10.1016/j.foodhyd.2012.01.004*

5 Mariella D, Pasquale D, Vittorio C, Yoshiaki Y, Hiroshi U, Kanji K (2001) Macromolecules 34:1449-1453. *http://dx.doi.org/10.1021/ma001185x*

6 Tuan-Chew T, Wan-Teck F, Min-Tze L, Azhar ME (2014) Journal of King Saud University – Science 26:311-322. *http://dx.doi.org/10.1016/j.jksus.2014.02.001*

7 Popa M, Dumitriu CL, Sunel V (2004) Polym-Plast Technol 43:1503-1516. *http://dx.doi.org/10.1081/PPT-200030259*

8 Claudia C, Davide B, Cristina L, Andrea M, Pietro M (2011) J Mater Sci-Mater M 22:263-271. *http://dx.doi.org/10.1007/s10856-010-4217-z*

9 Kousaku O, Masanori Y, Ayako N, Norio N, Hiroyuki Y (2000) J Polym Environ 8:59-66. *http://dx.doi.org/10.1023/A:1011517903510*

10 Ogawa E, Matsuzawa H, Iwahashi M (2002) Food Hydrocolloid 16:1-9. *http://dx.doi.org/10.1016/S0268-005X(01)00024-8*

11 Lin D, Xinxing L, Zhen T (2010) Carbohyd Polym 81:207–212. *http://dx.doi.org/10.1016/j.carbpol.2010.02.013*

12 Masahiko A, Yuko O, Takayuki N (2000) J Phys Chem 104:6755-6760. *http://dx.doi.org/10.1021/jp0001539*

13 Yoko N, Rheo T, Katsuyoshi N (2010) Biomacromolecules 11:187–191. *http://dx.doi.org/10.1021/bm901063k*

14 Camelin I, Lacroix C, Paquin C, Prbvost H, Cachon R, Diviest C (1993) Biotechnol Progr 9:291-297. *http://dx.doi.org/10.1021/bp00021a008*

15 Gussenov ISh, Ibragimov RSh, Abilkhairov DT, Kudaibergenov SE (2014) Novel brine initiated gel technology for water shutoff operations. Proceedings of the Conference "New Knowledge in the Area of Drilling, Production, Transport and Storage of Hydrocarbons", High Tatras, Slovakia. P.152.