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Development of drilling muds based on anionic and nonionic polysaccharides

The present article is devoted to development of new drilling muds based on anionic (gellan, xanthan) and nonionic (starch) polysaccharides. The results of DSC and viscometric and rheological measurements of gellan, mixtures of gellan — xanthan and gellan-corn starch in absence and presence of NaCl, KCl, $MgCl_2$, $CaCl_2$ and bentonite are presented. The influence of temperature, pH medium, concentration of polysaccharides and salts on the rheological characteristics and conformational transitions of gellan, gellan-xanthan and gellan-starch mixtures was studied. The rheological behavior of 0.2–1.0 wt.% gellan solutions at various temperature, pH medium and content of NaCl, KCl, $MgCl_2$, $CaCl_2$ and bentonite is well described by Ostwald–de Waele and Herschel–Bulkley equations. The coil-helix conformation and sol-gel phase transitions of gellan induced by temperature, salt addition, and pH are key factors to design of drilling muds. Model experiments show that the gellan in combination with xanthan and starch are effective agents to stabilize borehole walls and isolate water inflow. Effective drilling muds based on gellan-starch and gellan-xanthan-starch mixtures in the presence of bentonite and KCl were obtained. The formulated recipes can be used for drilling of wells at unfavorable geological conditions.

Key words: colloids, drilling muds, gellan, interpolymer complexes, viscosity.

Introduction

Low acyl gellan (LAG) which is produced by the bacterium *Pseudomonas elodea* consists of a tetrasaccharide repeating unit of D-glucose, D-glucuronic acid, D-glucose, and L-rhamnose [1, 2]. The review of Morris et al. [3] comprehensively considers the structure, rheology, gelation, topology, and application aspects of LAG. The coil-helix conformational and sol-gel phase transitions of LAG gums induced by temperature, salt addition, pH change and etc. were the main subject of many studies [4, 5].

It is commonly accepted [1; 2; 6] that LAG gum exhibits a conformational change from the disordered state (single chain) to the ordered state (double helix) induced by temperature decrease, while the gelation is considered to be mediated by the double-helix formation and the association of such helices, which is enhanced in the presence of mono- and divalent alkaline and alkaline earth cations [7, 8]. The main difference between the monovalent and divalent cations is that the monovalent cations shield the electrostatic repulsion between the $-COO^-$ while the divalent cations rather suppress electrostatic repulsion and form interchain ionic bonds with carboxylic groups of the glucuronic acid units resulting in the aggregation of the double helices [9].

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

Natural polysaccharides like starch, carboxymethyl cellulose, xanthan and others are widely used in formulation of low-clay-content and clay-free polymer drilling fluid for drilling of vertical and lateral wells [10–12]. However, the high price, low thermal and microbiological stability significantly limit the application of polysaccharides for drilling muds [10].

Earlier [13–15] we have demonstrated for the first time that the LAG solution can be successfully used for enhanced oil recovery. The remarkable property of LAG was plugging of high drainage channels in oil reservoirs.

The idea of using LAG as key component of drilling muds is based on its ability to undergo the conformational and phase transitions under the influence of temperature, low molecular salt additives, and pH medium. This should ensure the effective capacity of LAG containing solutions to strength the walls of the well by forming polymer-clay filter cake, to control the adsorption of water and clean the down hole from cuttings.

In the present paper the viscometric, rheological, conformational and phase behavior of LAG and LAG-xanthan mixtures at various concentrations of polysaccharides, salt content, temperature and pH are investigated. Based on these studies novel LAG-containing drilling muds with good rheological, filtration and cake-formational characteristics have been developed.

Experimental part

Materials

LAG is an anionic extracellular bacterial polysaccharide discovered in 1978 [8]. It consists of repeated tetrasaccharide units: 1,3-linked β-D-glucose, 1,4-linked β-D-glucoronic acid, 1,4-linked β-D-glucose, and 1,4-linked α-L-rhamnose.

Xanthan gum is also a microbial exopolysaccharide produced by bacterium *Xanthomonas campestis* [16, 17]. It consists of repeated pentasaccharide units composed of two D-glucopyranosyl units, two mannopyrasonyl units and D-glucopyranosyluronic acid in the molar ratio 2.8:2.0:2.0

Corn starch is commercial product was purchased from «Jarkent corn-molasses plant» (Almaty region, Kazakhstan). Structural formula of corn starch is shown in [18].

Low molecular weight salts: NaCl, KCl, $CaC1_2$ $MgCl_2$ and bentonite $(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ purchased from JSC «Reactiv», Russia, were used without further purification.

Methods

The viscosity of aqueous LAG solutions was measured by Ubbelohde viscometer at 25±0.1 ºC. The rheological behavior of polysaccharide solutions was monitored with the help of Rheolab QC, Anton Paar (Austria). The approximation of results was performed by Ostwald–de Waele and Herschel–Bulkley models to find the rheological and conformational characteristics (shear stress — τ_0, plastic viscosity — η, consistency index — K and nonlinearity factor — n). The DSC and dDSC characteristics of samples were determined with the help of DSC Eva Setaram (France). Static shear stress (SSS) measurement was performed by means of the instrument SNS-2 (Russian Federation) [10; 19]. Water yield of the drilling muds (WY) was determined by VM-6 instrument (Russian Federation) [19]. The thickness of the filter cake (δ) was measured by the instrument WIKA IV-2 (Russian Federation).

Result and discursion

Thermal and storage stability of LAG [20]

Figure 1 represents the DSC and dDSC curves of LAG within temperature range from –30 to 300 ºC. DSC curve shows the endothermic peak at 95 ºC with melting enthalpy –264.5 $J \cdot g^{-1}$. The second endothermic peak at 251.1 ºC corresponds to LAG decomposition temperature — LAG enthalpy of which is equal to 98.99 $J \cdot g^{-1}$. Thus, LAG is thermally stable polysaccharide, which in solid state melts within the temperature interval at 31–178 ºC.

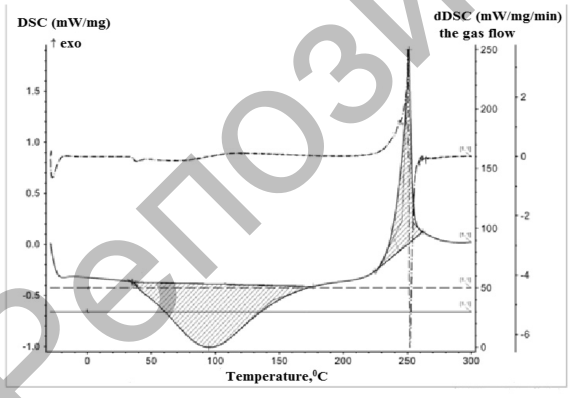

Figure 1. The results of DSC and dDSC analysis of LAG

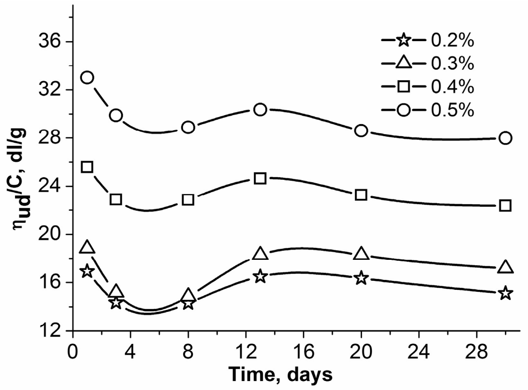

Figure 2. The intrinsic viscosity of LAG solutions versus storage time pH = 6.4; T = 25 ºC

One of the main requirements to drilling muds is the stability of rheological characteristics versus time. Especially it concerns to polysaccharides, which are able to undergo biodegradation [11, 12,19]. In this regard, the viscosity of LAG solutions was studied as a function of storage time. As seen from Figure 2 the viscosity of LAG in concentration range of 0.2–0.5 wt.% decreases up to 15–18 % after 4 days, while the further slightly changes of the viscosity (during the following 30 days) are within the limits of experimental error and may be considered as constant.

Influence of pH medium on rheological behavior of LAG and LAG-xanthan solutions

Influence of pH on the rheological behavior of LAG was studied for 0.5 and 1 wt. % LAG solutions (Fig. 3*a*). The maximal value of shear stress is registered at pH = 7.5. The subsequent increase of pH leads to decrease of the shear stress due to increasing of the ionic strength of solution [20]. The shape of all flow curves is characteristic for pseudoplastic fluid that is common for gel forming structures [21].

Flow curves of LAG-xanthan solutions (Fig. 3*b*) significantly differ from the flow curves of LAG. All flow curves of LAG-xanthan solutions are located in the area of anomalously low shear stress. The average ratio of the shear stress values for solutions of LAG and LAG-xanthan mixture (1:1) with the same shear rate equal to 2.5. Besides the effect of ionic strength at pH above 7.5 is minimal or absent. Such anomaly behavior of LAG-xanthan solutions is apparently caused by the formation of interpolymer complexes (IPC) between macromolecules of LAG and xanthan.

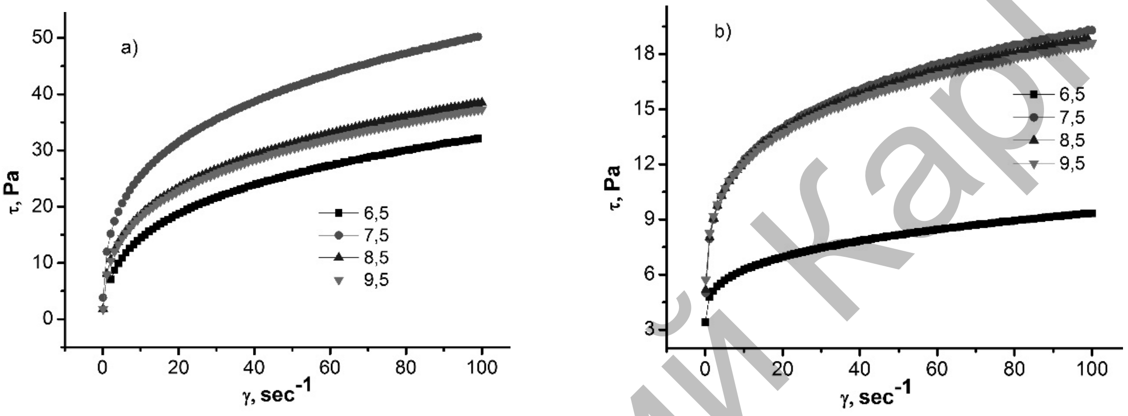

Figure 3. Shear stress versus shear rate curves of 1 wt.% LAG (*a*)
and LAG-xanthan (1:1) (*b*) solutions at different pH values; *T*=25 ºC

For detailed analysis of flow curves of LAG and LAG-xanthan solutions shear stress- shear rate dependences were processed by Shvedov-Bingham (1), Ostwald-de Waele (2) and Herschel-Bulkley (3) equations [22]:

$$\tau = \tau_0 + \eta \times \gamma; \tag{1}$$

$$\tau = K \times \gamma^n; \tag{2}$$

$$\tau = \tau_0 + K \times \gamma^n, \tag{3}$$

where τ — shear stress; γ — shear rate; τ_0 — yield point; *K* — consistency index; *n* — nonlinearity factor.

Correlation coefficient *R* was used to match the curves with their corresponding models, R^2 in ideal case should be equal to unity. The results are shown in Tables 1 and 2.

Table 1

**The rheological characteristics of LAG and LAG-xanthan solutions at different pH,
1 wt.% total polysaccharide concentration and 25 ºC**

pH	LAG/xanthan weight ratio	Rheological parameters of Herschel-Bulkley equation							
		after 1 min of solution immobility				after 10 min of solution immobility			
		τ_0, Pa	*K*, Pa·s	*n*	R^2	τ_0, Pa	*K*, Pa·s	*n*	R^2
9.5	1/0	0	8.837	0.322	0.995	0	13.092	0.257	0.998
8.5	1/0	0	5.414	0.414	0.996	0	13.173	0.262	0.998
7.5	1/0	0	11.309	0.322	0.999	0	17.5.49	0.253	0.998
6.5	1/0	0.223	0.009	1.138	0.987	0.127	0.158	0.911	0.797
9.5	1/1	0.823	5.821	0.219	0.996	1.973	6.13.	0.216	0.997
8.5	1/1	0.779	5.739	0.226	0.997	0.341	7.528	0.195	0.997
7.5	1/1	1.637	5.285	0.249	0.996	0.384	7.386	0.204	0.997
6.5	1/1	3.862	0.144	0.617	0.988	0	2.273	0.230	0.992

Table 2

The rheological characteristics of LAG and LAG-xanthan solutions at different pH, 1 wt.% total polysaccharide concentration and T=25 ºC

pH	LAG/xanthan weight ratio	Rheological parameters of Ostwald–de Waele’ equation					
		after 1 min of solution immobility			after 10 min of solution immobility		
		K, Pa·s	n	R^2	K, Pa·s	n	R^2
9.5	1/0	5.654	0.411	0.968	7.241	0.367	0.970
8.5	1/0	4.605	0.448	0.991	7.420	0.368	0.970
7.5	1/0	7.50	0.394	0.988	11.359	0.330	0.984
6.5	1/0	0.053	0.768	0.982	0.012	0.983	0.708
9.5	1/1	6.642	0.201	0.996	8.072	0.179	0.996
8.5	1/1	6.513	0.208	0.996	7.873	0.189	0.996
7.5	1/1	9.851	0.102	0.875	7.769	0.197	0.997
6.5	1/1	2.944	0.161	0.972	1.234	0.336	0.969

As seen from Tables 1 and 2, the flow curves of LAG and LAG-xanthan solutions at pH 7.5, 8.5 and 9.5 are described in the best way by Herschel-Bulkley model, which takes into account the yield stress characteristic of the gelling systems. At pH 6.5 the flow curves of LAG and LAG-xanthan solutions are poorly described by the equations 1–3. The appearance of yield stress (τ_0) for flow curves of LAG solution at pH 6.5 and LAG-xanthan solution in the range of pH 6.5–9.5 confirms the gelation of the system [23]. This is probably due to participation of polysaccharides in complexation reaction. The difference in consistency index of LAG and LAG-xanthan solutions after 1 and 10 minutes of immobility is indicated on the thixotropic behavior of polysaccharide systems. Thixotropic phenomenon is more pronounced for LAG solutions, that is favorable for suspending of drilled cuttings [21].

Temperature dependent rheology of polysaccharides

Comprehensive information on the rheological properties of LAG, xanthan and LAG-xanthan mixture as a function of temperature and salt content is necessary to predict the behavior of drilling muds. In this regard, shear stress-shear rate dependences of polysaccharide solutions at different temperatures and salt concentrations were analyzed using the equations describing the flow curves of Newtonian and non-Newtonian fluids.

The shear stress-shear rate curves of 0.5 wt.% LAG solution registered at temperature interval between 25 and 55 ºC show the pseudoplastic behavior (Fig. 4*a*). Newtonian flow of LAG solution is observed at 60–70 ºC. Step-by-step transformation of LAG solution from pseudoplastic behavior to Newtonian may be explained by «melting» of double stranded structure of LAG and formation of LAG macromolecules in random coil conformation at higher temperature [3].

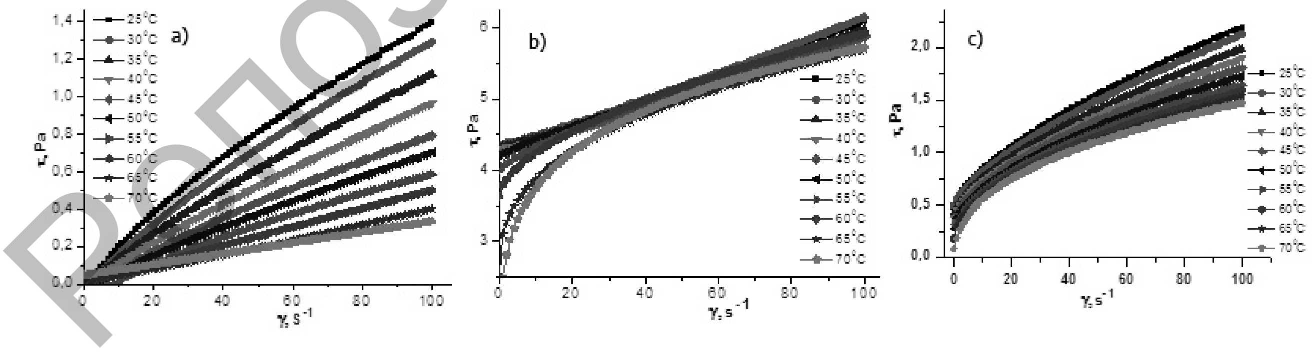

Figure 4. The shear stress-shear rate curves of 0.5 wt.% LAG (*a*), xanthan (*b*) and LAG-xanthan (2:1) (*c*) solutions at the interval of temperature 25–70 ºC

In the temperature range 25÷40 ºC the 0.5 % xanthan solutions are typically viscoelastic fluids. At the interval of 40÷65 ºC the gradual transition from viscoelastic flow to pseudoplastic flow is observed. The mixture of LAG-xanthan throughout the temperature range behaves like a pseudoplastic fluid, further having a yield stress at t<50 ºC. Such behavior 0.5 % solution of LAG-xanthan mixture (2:1) is probably due to formation of IPC.

Influence of salts on rheological behavior and gel formation of polysaccharides [20]

Oilfield water may participate in the formation of a filter cake on the surface of the borehole wall contacting with drilling fluid. This process may occur even in the case of clay-free drilling muds by the hydrogel formation of a filter cake on the well surface. This is particularly actual in the conditions of high permeability and fracturing the rock [21].

The viscometric measurements were performed with 0.2 wt.% LAG solution because the reduced viscosity of 0.5 wt.% LAG is extremely high and difficult to measure. Dependence of the reduced viscosity of 0.2 wt.% LAG on the ionic strength of the solution adjusted by addition of $BaCl_2$, $CaCl_2$, $MgCl_2$ and oilfield water with the salinity 73 $g{\cdot}L^{-1}$ is shown in Figure 5. According to viscometric data the effectiveness of salts to enhance gelation changes in the following order: $BaCl_2 > CaCl_2 \approx MgCl_2 >$ oilfield water. This order is in good agreement with the results found for LAG by the authors [24].

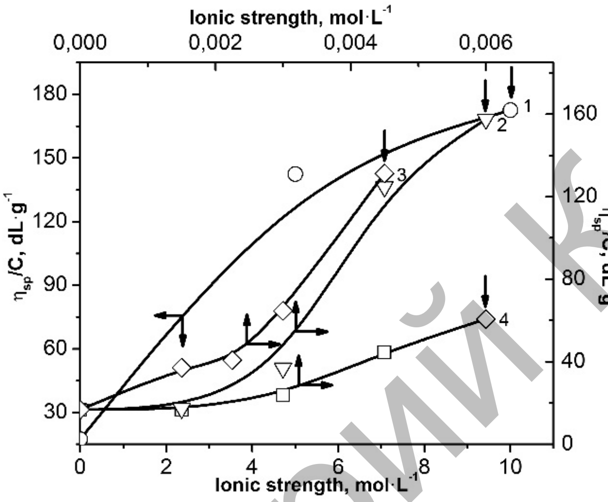

Figure 5. Dependence of reduced viscosity of 0.2 wt.% LAG on the ionic strength of the solution adjusted by addition of oilfield water with the salinity 73 $g{\cdot}L^{-1}$ (*1*), $CaCl_2$ (*2*), $BaCl_2$ (*3*), $MgCl_2$ (*4*). Arrows show the start of the gelation process. Temperature is 25 ºC

Dependences of shear stress versus shear rate for LAG and LAG-xanthan solutions in the presence of NaCl, KCl, $CaCl_2$, $MgCl_2$ and oilfield water are shown in Figure 6. Increasing of shear stress as a function of shear rate follows by the order: Oilfield water > $CaCl_2$ > $MgCl_2$ > KCl > NaCl (Fig. 6*a*).

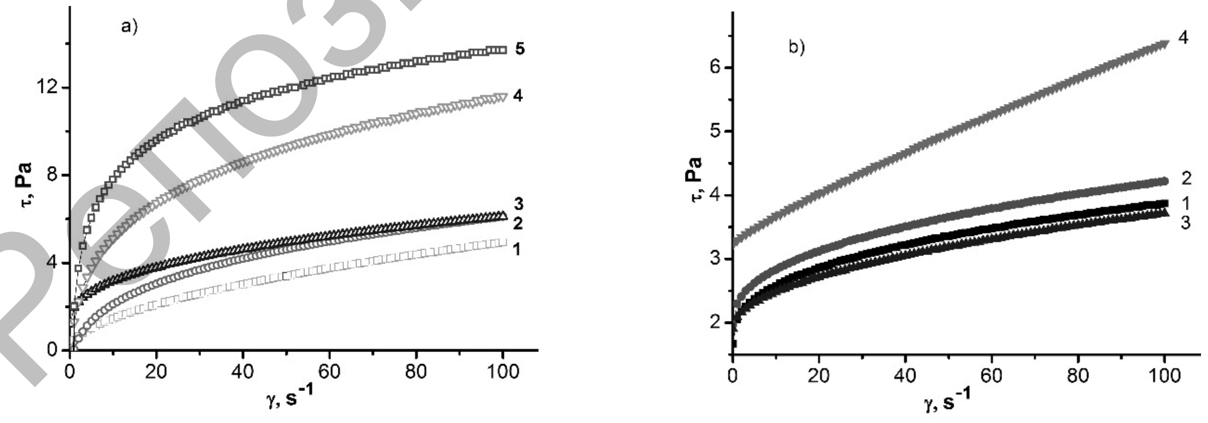

Figure 6. The shear stress-shear rate curves of 0.5 wt.% LAG (a) and 0.5 wt.% LAG-xanthan (2:1) solutions (b) at the ionic strength $\mu = 0.01$ adjusted by addition of NaCl (1), KCl (2), $MgCl_2$ (3), $CaCl_2$ (4) and oilfield water (5)

This sequence is in good agreement with the effectiveness of salts to enhance LAG gelation. It is seen that the effect of oilfield water is more substantial compared to solutions of individual salts. This may be due to combined effect of alkaline and alkaline earth metal ions with respect to coil-helix conformation of LAG.

In case of LAG-xanthan (2:1) mixture, the shear stress increases in the sequence: $CaCl_2 > KCl > NaCl > > MgCl_2$ (Fig. 6*b*). Changes in the rheological behavior of solutions during the transition from a LAG to LAG-xanthan mixture (decrease values τ_0, the transition from viscoelastic to the pseudoplastic flow), are apparently due to the formation of ternary complexes such as LAG-xanthan-Me^{2+}.

Influence of dispersed phase on the rheological behavior of LAG solutions [20]

Evaluation of the influence of bentonite on rheological characteristics of LAG solution is necessary for simulation of drilling mud ability to carry up the cuttings from the bottom hole of the well to the surface. Influence of dispersed phase on the rheological and conformational characteristics of 0.5 wt.% LAG solutions in the presence of bentonite was studied by rotational viscometry. The obtained results are summarized in Table 3. The values of correlation coefficient (R^2) show, that the model of Ostwald-de Waele good describes the rheological behavior of LAG solution and the colloid-dispersed systems LAG-bentonite excepting for 8 wt.% of bentonite concentration.

Table 3

Rheological parameters of 0.5 wt.% LAG solutions in the presence of bentonite at 25 ºC

$C_{bentonite}$, %	pH	Rheological parameters of Ostwald–de Waele equation					
		after 1 min of solution immobility			after 10 min of solution immobility		
		K, Pa·s	*n*	R^2	*K*, Pa·s	*n*	R^2
0	6.34	0.371	0.829	0.958	0.43	0.739	0.968
2	9.94	8.038	0.243	0.997	9.69	0.242	0.999
4	9.97	9.754	0.218	0.992	11.36	0.263	0.986
6	10.01	10.781	0.288	0.989	12.38	0.247	0.964
8	10.05	11.445	0.298	0.972	9.50	0.192	0.693

Rheological parameters of LAG/xanthan mixture were determined in presence of bentonite and KCl. As seen from Table 4, the rheological behavior of disperse systems obeys Ostwald-de-Waale' equation. The optimal values of *K* and *n* were obtained for the rations 1/1, 1/2 and 1/4. For the compositions 1/0, 2/1 and 4/1 the value of $n>0.3$, this worsens the flowing properties of the solutions [21].

Table 4

Rheological parameters of 0.5 wt.% LAG-xanthan mixtures in the presence of 1,5 wt.% bentonite and 1 wt.% KCl at 25 ºC

LAG/xanthan weight ratio	pH	Rheological parameters of Ostwald–de Waele' equation					
		after 1 min of solution immobility			after 10 min of solution immobility		
		K, Pa·s	*n*	R^2	*K*, Pa·s	*n*	R^2
1/0	9.9	4.482	0.238	0.968	3.273	0.322	0.960
1/1	9.2	2.780	0.268	0.978	3.293	0.226	0.994
1/2	9.7	2.731	0.235	0.998	1.779	0.499	0.978
1/4	9.1	3.123	0.206	0.994	3.719	0.161	0.986
2/1	9.2	2.301	0.335	0.830	2.303	0.279	0.887
4/1	9.1	1.357	0.344	0.949	1.539	0.331	0.958

Properties of Drilling Muds

On the basis of obtained results several drilling formulations were prepared by selecting the different concentration and composition of polysaccharides with and without addition of bentonite and/or KCl. The structural-mechanical, filtration and filter cake forming properties of these compositions are summarized in Table 5.

Table 5

Characteristics of drilling muds obtained on the basis of polysaccharides, bentonite and KCl

DM	Composition of DM*, wt.%					Characteristics of DM					
	LAG	Starch	Xanthan	Bentonite	KCl	pH	ρ, g/sm^3	η_{rel}, sec	WY, sm^3	δ, mm	SSS$_1$/SSS$_{10}$ dPa
1	0.4	3	0	1	3	10	1.04	41	4	0.2	2.7/3.3
2	0.4	3	0	2	1	10.1	1.04	40	3	0.4	3.1/4.2
3	0.4	3	0	1	0	10.2	1.04	40	4	0.5	3.0/4.5
4	0.34	0	0.1	1.75	0.05	9.8	1.02	36	5.6	0.5	2.5/2.9
5	0.25	0.75	0.1	0.5	0	11	1.01	29	10	0.2	0.6/0.6
6	0.17	0	0.33	0.5	3	9.4	1.02	30	10	0.5	1.6/1.6
7	0.17	0.5	0.33	1	3	9.6	1.03	35	10	0.6	3.0/7.0
8	0.17	1	0.33	0.5	3	9.5	1.02	30	10	0.5	1.7/1.6
9	0.15	0	0.45	3	3	9.8	1.03	39	10	0.5	3.5/2.8
10	0.13	0	0.37	1	2	9.7	1.01	41	10	0.5	2.8/2.7

Note: * The rest — water.

Analysis of the data shows that the samples 1–3 at LAG/corn starch ratio around of 1:7 possess good structural-mechanical and filtration characteristics. The thickness of filter cake may be increased by adding 2 wt.% of bentonite or deleting KCl from the mud composition.

The samples 4, 6, 9 and 10 exhibit good filter cake forming and filtration properties but not good thixotropic characteristics because SSS$_{10}$/SSS$_1$ < 1. This condition will decrease the efficiency of cuttings suspension by the drilling mud.

The best structural-mechanical, filtration and filter cake forming properties exhibit the sample 7 consisting of the mixture of LAG/corn starch /xanthan at the weight ratio 1:3:2 with total polysaccharide concentration 1 wt.%.

Conclusions

The rheological behavior of LAG and LAG/xanthan mixtures at a wide range of concentrations, temperatures, pH, salt content and dispersed phase can be described by Ostwald-de Waal or Herschel-Bulkley equations. In solutions of LAG — xanthan mixtures interpolymer complexes stabilized by hydrogen bonds are formed. The structural-mechanical, filter cake forming and filtration properties of drilling muds based on LAG-xanthan-corn starch mixture can be successfully controlled by changing of composition of polysaccharide mixture and concentration of bentonite and KCl. The developed drilling muds can be used for drilling of wells having unfavorable geological conditions.

Acknowledgements

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References

1 Kanesaka Sh. Binding effect of Cu^{2+} as a trigger on the sol-to-gel and the coil-to-helix transition processes of polysaccharide, gellan gum / Sh. Kanesaka, T. Watanabe, Sh. Matsukawa // Biomacromolecules. — 2004. — Vol. 5. — P. 863–868.

2 Mazen F. Conformational transition of native and modified gellan / F. Mazen, M. Milas, M. Rinaudo // International Journal Biological Macromolecules. — 1999. — Vol. 26. — P. 109–118.

3 Morris E. Gelation of gellan — a review / E. Morris, N. Katsuyoshi, M. Rinaudo // Food Hydrocolloids. — 2012. — Vol. 28. — P. 373–411.

4 Fukada H. Termodynamics and structural aspect of the gelling process in the gellan gum metal salt aqueous solutions / H. Fukada, K. Takahashi, S. Kitamura, Y. Yuguchi, H. Urakawa, K. Kajiwara // Journal of Thermal Analyss Calorimetry. — 2002. — Vol. 70. — P. 797–806.

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

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

7 Hans G. Gelation of Gellan Gum / G. Hans, S. Olav // Carbohydrate Polymers. — 1987. — Vol. 7. — P. 371–393.

8 Lin D. Critical behavior at sol-gel transition in gellan gum aqueous solutions with KCl and $CaCl_2$ of different concentrations / D. Lin, L. Xinxing, T. Zhen // Carbohydrate Polymers. — 2010. — Vol. 81. — P. 207–212.

9 Nickerson M. Rheological properties of gellan solutions: effect of calcium ions and temperature on pre-sol formation / M. Nickerson, A. Paulson, A. Speers // Food Hydrocolloids. — 2003. — Vol. 17. — P. 577–583.

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

11 Овчинников В.П. Буровые промывочные жидкости: учеб. пособие / В.П. Овчинников, Н.А. Аксенова. — Тюмень, 2008. — 309 с.

12 Минибаев В.В. Эффективность полисахаридных реагентов в буровых растворах различной степени минерализации среды / В.В. Минибаев, И.А. Ильин, С.В. Пестерев // Бурение и нефть. — 2009. — № 10. — С. 48–50.

13 Kudaibergenov S. Potential application of gellan for polymer flooding technology / S. Kudaibergenov, R. Ibragimov, I. Gusenov, G. Tatykhanova, Zh. Ibraeva, Zh. Adilov, et al. // International J. of Transport & Logistics. — 2012. — Vol. 4. — P. 47–51.

14 Kudaibergenov S. Laboratory test for enhanced oil recovery with gellan / S. Kudaibergenov, Zh. Adilov, N. Nuraje, A. Sagindykov, G. Tatykhanova, R. Ibragimov, et al. // International Journal of Biological and Chemical Sciences. — 2012. — Vol. 4. — P. 58–68.

15 Kudaibergenov S. Plugging behavior of gellan in porous saline media / S. Kudaibergenov, N. Nuraje, Zh. Adilov, D. Abilkhairov, R. Ibragimov, I. Gusenov, et al. // Journal of Applied Polymer Science. — 2015. — Vol. 132. — P. 41256.

16 Ping X. Xanthan gum production with pumping Static-mixing Loop Fermentor / X. Ping, L. Jianqun, J. Boying // Biotechnology Lett. — 1994. — Vol. 16. — P. 523–526.

17 Southwick J. Self-Association of xanthan in aqueous solvent-systems / J. Southwick, H. Lee, A. Jameson, J. Blackwell // Carbohydrate Research. — 1980. — Vol. 84. — P. 287–295.

18 Perez S. The molecular structures of starch components and their contribution to the architecture of starch granules / S. Perez, E. Bertoft // A comprehensive review. — 2010. — Vol. 89 — P. 389–413.

19 Дудля Н.А. Промывочные жидкости в бурении: учебник. / Н.А. Дудля, Г.Б. Хаиров, А.В. Третьяк, Я. Пинка. — Алматы: КБТУ, 2007. — 455 с.

20 Kudaibergenov S. Physico-Chemical and Rheological Properties of LAG in Aqueous-Salt Solutions and Oilfield Saline Water / S. Kudaibergenov, G. Tatykhanova, V. Sigitov, Zh. Nurakhmetova, E. Blagikh, I. Gussenov, et al. // Macromolecular Symp. — 2016. — Vol. 363. — P. 20–35.

21 Михеев В.Л. Технологические свойства буровых растворов / В.Л. Михеев. — М.: Недра, 1979. — 239 с.

22 Неверов А.Л. Буровые растворы с низким содержанием твердой фазы для бурения комплексами ССК на основе бентонитов Таганского месторождения / А.Л. Неверов, А.В. Гусев, А.В. Минеев, В.П. Рожков // Journal of Siberian Federal University. Engineering & Technologies. — 2013. — Vol. 6. — P. 95–106.

23 Будтов В.П. Физическая химия растворов полимеров / В.П. Будтов. — СПб.: Химия, 1992. — 384 с.

24 Matsukawa S. Structural change of polymer chains of gellan monitored by circular dichroism / S. Matsukawa, Z. Tang, T. Watanabe // Progress in Colloid and Polymer Science. — 1999. — Vol. 114. — P. 15–25.

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Анионды және ионды емес полисахаридтер негізінде бұрғылау ерітінділерін әзірлеу

Мақала анионды (геллан, ксантан) және ионды емес (крахмал) полисахаридтер негізінде жаңа бұрғылау ерітінділерін әзірлеуге арналған. Геллан, геллан–ксантан, геллан–жүгері крахмалы қоспаларының NaCl, KCl, $MgCl_2$, $CaCl_2$, бентонит қатысында және қатысынсыз вискозиметрлік, реологиялық және механикалық қасиеттері және ДСК нәтижелері көрсетілген. Температура, pH орта, тұздар және полисахаридтер концентрацияларының геллан, геллан–ксантан, геллан–крахмал қоспаларының реологиялық қасиеттері мен конформациялық ауысуларына әсері зерттелген. NaCl, KCl, $MgCl_2$, $CaCl_2$, бентонит қатысында және қатысынсыз әртүрлі температура, pH ортада 0.2–1.0 % геллан ерітінділерінің реологиялық қасиеттерін нақтырақ Оствальда-Де Ваале және Хершеля-Балкли теңдеулері сипаттайды. Гелланның шиыршық-шумақ конформациясына және золь-гель фазалық ауысуына температураның, тұздардың және pH ортаның әсері бұрғылау ерітінділерін жобалауда негізгі факторлар болып табылады. Модельді эксперименттер гелланның ксантан және крахмалмен қоспасы ұңғыма қабырғаларын тұрақтандыру және судың келуін тоқтатуда тиімді агент болып табылатынын көрсетті. KCl және бентонит қатысында геллан–крахмал және геллан–ксантан–крахмал қоспалары негізінде тиімді бұрғылау ерітінділері алынды. Бұл рецептер күрделі таулы-геологиялық жағдайларда ұңғымаларды бұрғылау үшін қолданылуы мүмкін.

Кілт сөздер: коллоидтар, бұрғылау ерітінділері, геллан, интерполимерлі кешендер, тұтқырлық.

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Разработка буровых растворов на основе анионных и неионных полисахаридов

Статья посвящена разработке новых буровых растворов на основе анионных (геллан, ксантан) и неионогенных (крахмал) полисахаридов. Приведены результаты ДСК, вискозиметрические и реологические свойства геллана, смесей геллана–ксантана и геллан–кукурузного крахмала в отсутствии и присутствии NaCl, KCl, $MgCl_2$, $CaCl_2$ и бентонита. Изучены влияния температуры, pH среды, концентрации полисахаридов и солей на реологические характеристики и конформационные переходы смесей геллана, геллан–ксантан и геллан–крахмал. Более точное описание реологического поведения растворов геллана 0.2–1.0 мас.% при варьировании температуры, pH среды в присутствии NaCl, KCl, $MgCl_2$, $CaCl_2$ и бентонита описывают уравнения Оствальда-Де Ваале и Хершеля-Балкли. Влияние температуры, солей и pH на конформации спираль-клубок и золь-гель фазовые переходы геллана являются ключевыми факторами при проектировании буровых растворов. Модельные эксперименты показывают, что комбинации геллана с ксантаном и с крахмалом являются эффективными агентами для стабилизации стенок скважины и изолирования притока воды. Получены эффективные буровые растворы на основе смесей геллан–крахмал и геллан–ксантан–крахмал в присутствии бентонита и KCl. Сформулированные рецепты могут быть использованы для бурения скважин в сложных горно-геологических условиях.

Ключевые слова: коллоиды, буровые растворы, геллан, интерполимерные комплексы, вязкость

References

1 Kanesaka, Sh., Watanabe, T., & Matsukawa, Sh. (2004). Binding effect of Cu^{2+} as a trigger on the sol-to-gel and the coil-to-helix transition processes of polysaccharide, gellan gum. *Biomacromolecules*, *5*, 863–868.

2 Mazen, F., Milas, M., & Rinaudo, M. (1999). Conformational transition of native and modified gellan. *International Journal Biological Macromolecules*, *26*, 109–118.

3 Morris, E., Katsuyoshi, N., & Rinaudo, M. (2012). Gelation of gellan — a review. *Food Hydrocolloids*, *28*, 373–411.

4 Fukada, H., Takahashi, K., Kitamura, S., Yuguchi, Y., Urakawa, H., & Kajiwara, K. (2002). Termodynamics and structural aspect of the gelling process in the gellan gum/metal salt aqueous solutions. *Journal of Thermal Analyss Calorimetry*, *70*, 797–806.

5 Tuan-Chew, T., Wan-Teck, F., Min-Tze, L., & Azhar, M. (2014). Comparative assessment of rheological properties of gelatin or gellan in maize starch – egg white composite gels. *Journal of King Saud University, 4,* 311–322.

6 Ogawa, E., Matsuzawa, H., & Iwahashi, M. (2002). Conformational transition of gellan gum of sodium, lithium and potassium types in aqueous solutions. *Food Hydrocolloids*, *16*, 1–9.

7 Hans, G., & Olav, S. (1987). Gelation of Gellan Gum. *Carbohydrate Polymers*, *7*, 371–393.

8 Lin, D., Xinxing, L., & Zhen, T. (2010). Critical behavior at sol-gel transition in gellan gum aqueous solutions with KCl and $CaCl_2$ of different concentrations. *Carbohydrate Polymers, 81*, 207–212.

9 Nickerson, M.T., Paulson, A.T., & Speers, R.A. (2003). Rheological properties of gellan solutions: effect of calcium ions and temperature on pre-sol formation. *Food Hydrocolloids, 17*, 577–583.

10 Camelin, I., Lacroix, C., Paquin, C., Prevost, H., Cachon, R., & Divies, C. (1993). Effect of chelatants on gellan gel rheological properties and setting temperature for immobilization of living bifidobacteria. *Biotechnology Progress*, *9*, 291–297.

11 Ovchinnikov, V.P., & Aksenova, N. A. (2008). *Burovye promyvochnye zhidkosti [Drilling Fluids]*. Tumen [in Russian].

12 Minibaev, V.V., Ilyin, I.A., & Pesterev, S.V. (2009). Effektivnost polisakharidnykh reagentov v burovykh rastvorakh razlichnoi stepeni miniralizatsii sredy [The efficiency of polysaccharide reagents in drilling fluids with different degree of mineralization of the environment]. *Burenie i neft — Drilling and Oil, 10*, 48–50 [in Russian].

13 Kudaibergenov, S., Ibragimov, R., Gusenov, I., Tatykhanova, G., Ibraeva, Zh., & Adilov, Zh. et al. (2012). Potential application of gellan for polymer flooding technology. *International J. of Transport & Logistics*, *4*, 47– 51.

14 Kudaibergenov, S., Adilov, Zh., Nuraje, N., Sagindykov, A., Tatykhanova, G., & Ibragimov, R. et al. (2012). Laboratory test for enhanced oil recovery with gellan. *International Journal of Biological and Chemical Sciences, 4,* 58–68.

15 Kudaibergenov, S., Nuraje, N., Adilov, Zh., Abilkhairov, D., Ibragimov, R., Gusenov, I. et al. (2015). Plugging behavior of gellan in porous saline media. *Journal of Applied Polymer Science, 132*, 41256.

16 Ping, X., Jianqun, L., & Boying, J. (1994). Xanthan gum production with pumping Static-mixing Loop Fermentor. *Biotechnology Lett.*, *16,* 523–526.

17 Southwick, J., Lee, H., Jameson, A., & Blackwell, J. (1980). Self-Association of xanthan in aqeous solvent-systems. *Carbohydrate Research*, *84*, 287–295.

18 Perez, S., & Bertoft, E. (2010). The molecular structures of starch components and their contribution to the architecture of starch granules. *A comprehensive review, 89*, 389–413.

19 Dudley, N.A., Khairov, G.B., Tretyak, A.V., & Pinka, Ya. (2007). *Promyvochnye zhidkosti v burenii [Washing liquid in drilling]*. Almaty: KBTU [in Russian].

20 Kudaibergenov, S., Tatykhanova, G., Sigitov, V., Nurakhmetova, Zh., Blagikh, E., & Gussenov, I. et al. (2016). Physico-Chemical and Rheological Properties of LAG in Aqueous-Salt Solutions and Oilfield Saline Water. *Macromolecular Symp*, 363, 20–35.

21 Mikheev, V.L. (1979). *Tekhnolohicheskie svoistva burovykh rastvorov [Technological properties of drilling fluids]*. Moscow: Nedra [in Russian].

22 Neverov, A.L., Gusev, A.V., Mineev, A.V., & Rozhkov, V.P. (2013). Burovye rastvory s nizkim soderzhaniem tverdoy fazy dlia bureniia kompleksami SSK na osnove bentonitov Tahanskoho mestorozhdeniia [Drilling muds with low content of the solid phase for drilling complexes ssk on the basis of bentonites tagansky deposits]. *Journal of Siberian Federal University*. *Engineering & Technologies*, *6*, 95–106 [in Russian].

23 Budtov, V.P. (1992). *Fizicheskaia khimiia rastvorov polimerov [Physical chemistry of polymer solutions]*. Saint Petersburg: Khimiia [in Russian].

24 Matsukawa, S., Tang, Z., & Watanabe, T. (1999). Structural change of polymer chains of gellan monitored by circular dichroism. *Progress in Colloid and Polymer Science, 114*, 15–25.