Development of alkaline/ surfactant/polymer (ASP) flooding technology for recovery of Karazhanbas oil

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The tertiary oil recovery methods like alkaline, surfactant and polymer (ASP) flooding are very perspective in order to achieve the synergetic effect out of the different impacts which are caused by these chemicals, which affect oil and water filtration in the reservoir and increase oil recovery. In this communication, we consider the applicability of hydrophobically modified polyampholyte – poly(hexadecylaminocrotonate)betaine (PHDACB) as ASP flooding agent for recovery of oil from Karazhanbas oilfield. As “polysoap”, the aqueous solution of PHDACB dissolved in aqueous KOH was used. This system combines the advantages of alkaline, surfactant and polymer and exhibits the synergistic effect. The laboratory results showed that the ASP flooding considerably increases the oil recovery in addition to water flooding. In perspective, the ASP flooding may substitute the steam injection and other thermal enhanced oil recovery (EOR) technologies.

Keywords: ASP flooding; water flooding; enhanced oil recovery; oil reservoir.

Сілтілік/БӘЗ/ полимер (СБП) суландыру технологиясын Қаражанбас мұнайын өндіру үшін дамыту

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Мұнай бергіштікті артырудың үшіншілік әдісі ретінде өнімді қабатқа сумен бірге сілті, БӘЗ және полимер ерітінділерін қоса айдай қосымша мұнай өндіруге және синергетикалық әсерге жетуге мүмкіндік береді. Бұл мақалада Қаражанбас кен орнына АСП ерітіндісін қосып су айдау әдісі ретінде гидрофобты-модификацияланған полиамфолит – поли(гексадециламинокротонат)бетаин (ПГДАКБ) реагентін қолдану мүмкіншіліктері зерттеледі. Полимерлік сабын ретінде KOH ерітіндісінде ерітілген ПГДАКБ қолданылады. Бұл ерітінділер жүйесі өзінде сілті, БӘЗ және полимер агенттерінің артықшылықтарын біріктіріп, синергетикалық әсер көрсетеді. Зертханалық зерттеулер дәстүрлі су айдауға қарағанда, АСП ерітіндісін қосып су айдау айтарлықтай мұнайбергіштікті арттыратынын көрсетті. АСП ерітіндісін қосып су айдау, жылулық әдістерді баламалы түрде алмастыруға мүмкіншіліктері бар.

Түйін сөздер: АСП суландыру; суландыру; мұнай өндіруді жағарылу; мұнай қабат.

Разработка полимерного/ щелочного/ПАВ (АСП) заводнения для увеличения нефтеотдачи месторождения Каражанбас

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Третичные методы увеличения нефтеотдачи такие как щелочное, ПАВ и полимерное (АСП) заводнение являются очень перспективными так как позволяют достичь синергетического эффекта от применения данных реагентов, что приводит к увеличению нефтеотдачи. В этой статье изучена возможность применения гидрофобно-модифицированного полиамфолита – поли(гексадециламинокротонат)бетаина (ПГДАКБ) для АСП заводнения на месторождении Каражанбас. В качестве «полимерного мыла» используется водный раствор ПГДАКБ растворённого в растворе KOH. Данная система объединяет в себе преимущества щелочного, ПАВ и полимерного агентов и демонстрирует синергетический эффект. Лабораторные результаты показали, что АСП заводнение значительно увеличивает нефтеотдачу по сравнению с обычным заводением. АСП заводнение может стать альтернативной заменой тепловых методов увеличения нефтеотдачи.

Ключевые слова: АСП заводнение; заводнение; увеличение нефтеотдачи; нефтяной пласт.

CHEMICAL BULLETIN
of Kazakh National University
http://bulletin.chemistry.kz/

УДК (622.276+541.64+678.744) http://dx.doi.org/10.15328/cb649

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1. Introduction

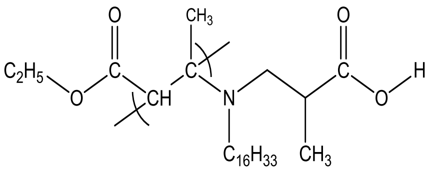
Nowadays, tertiary oil recovery methods are making their contribution in extracting more oil from mature oilfields. Alkali-Surfactant-Polymer (ASP) flooding as one of the perspective methods has been used for over 20 years throughout the world [1]. In ASP flooding, alkali, surfactant and polymer are injected into the reservoir simultaneously or as separated slugs. Because of the synergetic effect of alkali, surfactant and polymer, the microscopic and macroscopic volumetric sweep efficiency improvement is achieved [2]. Improvement of microscopic displacement is attributed to the reduction of oil-water interfacial tension (IFT) by surfactants that were added and by those which were generated in-situ as a result of alkali reaction with naturally occurring organic acids in the oil. In order to function properly, surfactants should be distributed between oil and water phases, this is regulated by pH value and ionic strength. Alkali can reduce surfactant adsorption and change ionic strength of the solution. Addition of polymer leads to the thickening of the aqueous phase, which leads to a more even distribution of the displacement front and thus improvement of macroscopic sweep efficiency [3,4].

ASP method already proved its effectiveness for displacement of discontinuous oil trapped after primary water flooding. China was one of the first oil producing countries which early recognized high potential of ASP method for oil recovery. In 1994, application of ASP chemical flooding on Daqing oilfield allowed increasing the average pilot area oil production rate by more than 2 times and decreasing water cut by 20% [3, 5]. Russian company Salym Petroleum Development proposes its own innovative ASP method, which is claimed to recover 90% of original oil in place (OOIP) [6], but other ASP field projects were mostly in Canada. Some of these projects allowed recovering 25% of the original oil in place incrementally. Despite of so high incremental recovery efficiency, large-scale projects started only after 2005 in China and Canada. The lack of ASP large-scale applications is related with the difficulties, which arise during the preparation of the injected solution and during the treatment of produced fluids. In addition, the understanding of the chemicals behavior inside a reservoir is not always clear [7]. Boost of oil production rate and decrease of water cut as a result of ASP flooding may come along with severe emulsification of produced fluids which will pose problems related with oil separation later on [3]. Nevertheless, ASP technology gains more attention from oil companies throughout the world. High potential of ASP method to increase oil recovery, possibility of solving the problems associated with oil-water separation after ASP flooding by simply choosing appropriate demulsifiers [8] and economic viability of the technology even at oil price of $30-$50 per barrel [9], all these reasons will lead to the shift in tertiary EOR methods towards application of ASP method for oil recovery improving from mature oilfields.

Application of ASP for improving heavy oil recovery may be more beneficial in comparison with thermal methods, which are dominant in recovering this oil, but may be not feasible due to the thin pay thickness of the reservoir [10] or in cases where application of these methods may pose geotechnical instability [11], economic restrictions or ecological problems [12]. World heavy oil reservoirs may exceed 4 trillion barrels. Thus, it is of great importance to rationalize reservoir management of these resources [13], and substitution of thermal EOR methods by ASP flooding for some oilfields may make production from these reservoirs more economically feasible.

2. Experiment

Hydrophobically modified polyampholyte – poly(hexadecylaminocrotonate)betaine (PHDACB) was synthesized by the procedure described in [14-16].



The structural unit of PHDACB was identified by Fourier NMR spectrometer Bruker 400 MHz (Bruker, Germany) in dimethylsulfoxide (DMSO). The average-number M_n and the average-weight M_w molecular mass of PHDACB measured in dimethylformamide (DMF) with the help of gel-permeable chromatograph "Malvern Viscotek 270 Dual Detector" (UK) were equal to $1.56 \cdot 10^6$ and $8.75 \cdot 10^6$ Dalton, respectively.

Samples of unconsolidated sand from Karazhanbas oilfield were densely packed into the cylindrical core holder (the length is 8.6 and the diameter is 4.3 cm) made from steel. Porosity of the models was measured by volume saturation method. Absolute air permeability of each sand pack was identified as well, all tested sand packs were characterized with the same air permeability of 6 Darcy. Brine and crude from Karazhanbas oilfield were used. Density and dynamic viscosity of oil at 30°C measured by Stabinger viscometer SVM 3000 were equal to 0.9257 g cm^{-3} and 300 mPa s, respectively. Salinity of brine was equal to 90 g L^{-1}. For evaluation of oil displacement parameters several pore volumes (1 pore volume was equal to 50 cm^3 of liquid) of chemical solutions were pumped through the sand packed tube with constant rate of injection 0.1 cm^3 min^{-1}. The PHDACB dissolved in aqueous solution of KOH was tested in the context of the efficiency of oil displacement against sodium dodecyl sulfate (SDS) and KOH solutions. All filtration processes were conducted by means of apparatus for core investigations UIC-C(2) (Russian Federation) (Figure 1).

All experiments were conducted in the following sequence:

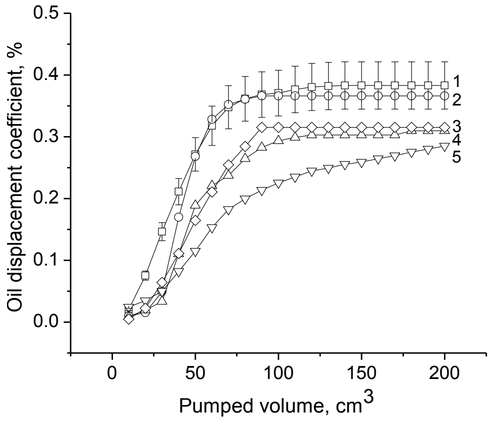
1. Determination of sand pack air permeability;
2. Saturation of sand pack with brine;
3. Brine displacement with oil, measurement of initial oil and connate brine saturation;
4. Simulation of water flooding process – oil displacement by brine, measurement of oil displacement coefficient;
5. Injection of ASP solution into the water flooded sand pack model with the constant registration of changing of oil displacement coefficient.

All experiments were conducted at 30°C, e.g. reservoir temperature of Karazhanbas oilfield.

3. Results and Discussion

Several experiments with varying concentrations of chemicals were conducted to investigate the oil displacement efficiency of the PHDACB dissolved in KOH aqueous solution. The results were compared with surfactant-only (SDS) and alkaline-only (KOH) flooding tests (Figure 2).

Figure 1 – UIC-C(2) apparatus for core investigations



Curves 1,3 — SDS with concentration of 0.5 (1) and 0.125% (3). Curves 2,4 – poly(alkylaminocrtonate)betaine with concentration of 0.5 (2) and 0.125% (4). Curve 5 — 0.5% of KOH; error bars given for the curve (1) are correct for all curves

Figure 2 – Effect of injection of various concentrations of alkali, SDS and PHDACB on oil displacement coefficient

Results of sand pack flooding experiments showed that the oil displacement coefficient reached 38 % in case of injection of 0.5% SDS solution, while injection of 0.5% solution of PHDACB dissolved in 0.5% aqueous KOH solution yielded up to 37% of oil displacement coefficient. Using 0.5% alkaline KOH solution resulted in 31% oil displacement coefficient after pumping of four pore volumes of alkaline solution through the model. Experiments showed that the displacement ability of SDS solution is higher than that of KOH solution though alkaline curve is characterized by upward trend at the end of the experiment, so application of SDS accelerates the displacement of oil in comparison with KOH. The aqueous solution of PHDACB dissolved in KOH was used as “polysoap” acting as polymer, surfactant and alkaline simultaneously. The effect of “polysoap” is in the same level of SDS.

The acid number of a crude oil is one of the most important parameters in alkali flooding and illustrates the amount of natural soap that can be produced by the addition of alkali. The acid number of Karazhanbas oil was equal to 0.54 mg g^{-1}. The EOR mechanism by alkaline flooding seems the penetration of the alkaline solution into the crude oil and the subsequent formation of water-in-oil (W/O) droplet flow that tend to reduce the mobility of the water phase and damp viscous fingering, leading to the improvement of sweep efficiency. The role of SDS in EOR is prescribed to significant lowering of the interfacial tension between the rock and oil forming oil-in-water (O/W) microemulsions. It is very interesting to clarify the EOR mechanism by hydrophobic polybetaines. In aqueous KOH, the macromolecules are negatively charged because of ionization of carboxylic groups. Therefore, they have a relatively low adsorption to sandstone and clays that are also negatively charged. It is expected that in aqueous KOH, the PHDACB is able to form the micellar or vesicular structures stabilized by intramolecular or intermolecular hydrophobic interactions of long alkyl chains (Figure 3). The micelles and vesicles in aqueous solution are preserved from precipitation by the presence of negatively charged carboxylate ions.

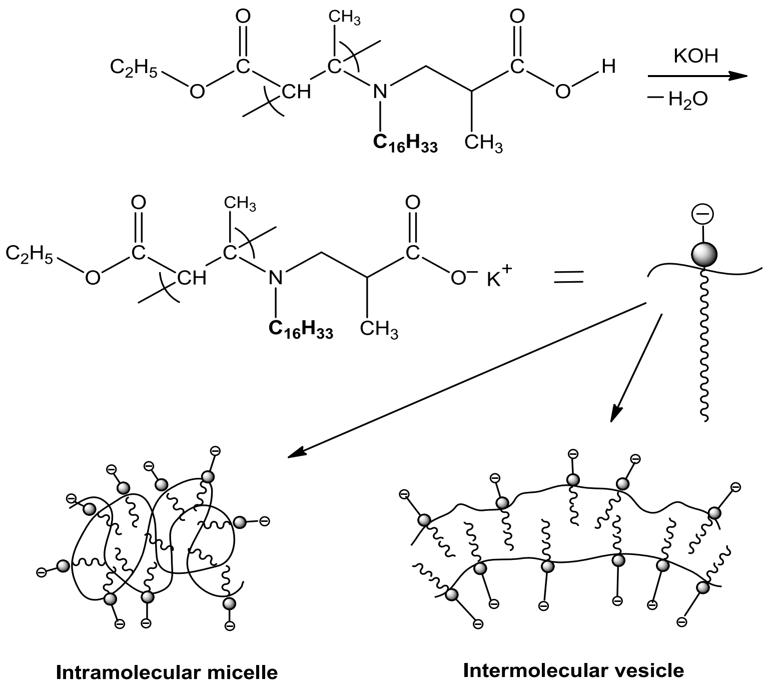


Figure 3 – Schematic representation of formation of intramolecular micelle and intermolecular vesicle structures of PHDACB in aqueous KOH solution.

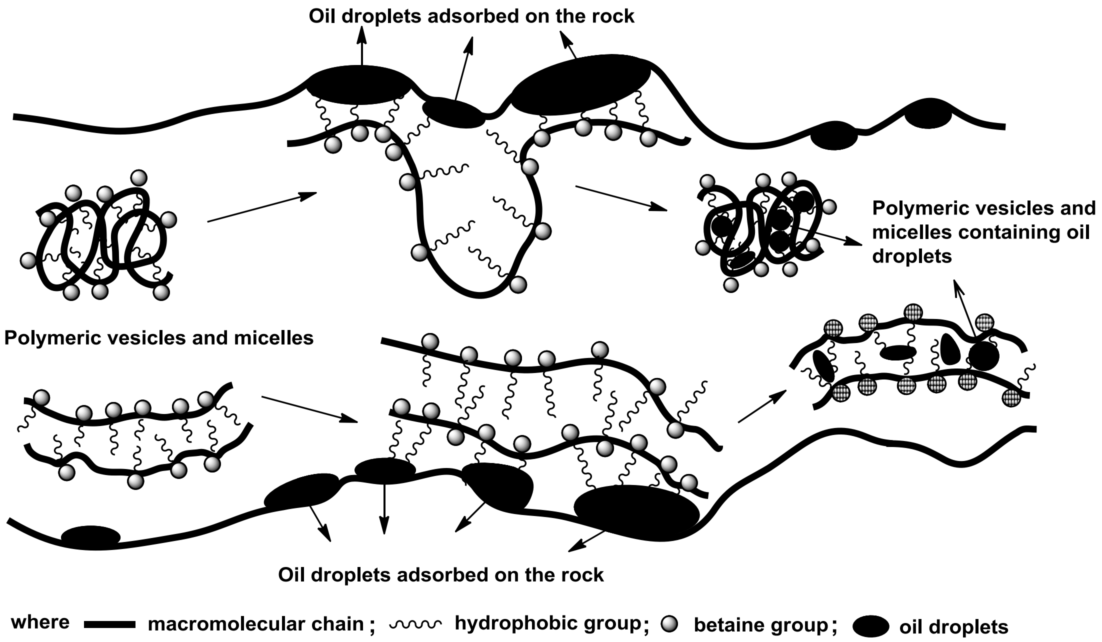


Figure 4 – The image of polymeric micellar flooding

Since in aqueous KOH the polymeric betaines can exist in the forms of micron- and nanosized micelles and vesicles consisting of hydrophobic core and hydrophilic edge [17], oil droplets adsorbed on the rock can imbibe into hydrophobic pockets forming O/W microemulsions. In the vicinity of rock/oil boundary, the long alkyl chains are probably inverted and dipped into oil environment, decrease the interfacial tension, entrap and sweep oil droplets then entrain along with the flowing aqueous phase (Figure 4). Partially unfolding of "polysoap" macromolecules near rock oil boundary may occur due to preferentially oil-wetness of hydrophobic groups and solvation of betaine parts by water.

Thus, hydrophobically modified polymeric betaines consisting of hydrophobic "tail" and hydrophilic "head" are perspective materials for heavy oil displacement due to combination the advantages of alkaline, surfactant and polymer and exhibiting the synergistic effect.

4. Conclusion

It was shown that application of chemical flooding methods for EOR from Karazhanbas viscous oilfield has potential to increase oil recovery on 38% in addition to conventional water flooding. Hydrophobically modified polyampholyte poly(alkylaminocrotonate) betaine was tested as polymeric soap in the context of the efficiency of oil displacement. It was shown that the "polysoap" has a high potential for EOR from viscous oil fields. It is expected that the ASP flooding for Karazhanbas oilfield can substitute the thermal oil recovery methods, which are not economically feasible.

Acknowledgements

This work was performed in the frame of the grant of the Ministry of Education and Science of the Republic of Kazakhstan 3397/GF4 "Development of the technology of obtaining hydrophobically-modified polymeric additives for inhibition of paraffin deposition and decreasing of pour point temperature of oil".

References (GOST)

1 Charest M. Alkaline-surfactant-polymer (ASP) flooding in Alberta small amounts of the right chemicals can make a big difference // Canadian Discovery Digest. – 2013. – Vol.1. – P.20-50.

2 Nuraje N., Gussenov I., Tatykhanova G., Akhmedzhanov T., Kudaibergenov S. Alkaline/surfactant/polymer (ASP) flooding // International Journal of Biology and Chemistry. – 2015. – Vol.8, Is.1. – P.30-42.

3 Olajire A. Review of ASP EOR (alkaline surfactant polymer enhanced oil recovery) technology in the petroleum industry: Prospects

and challenges // Energy. – 2014. – Vol.77. – P.963-982.
4 Sheng J.J. A comprehensive review of alkaline-surfactant-polymer (ASP) flooding // Asia-Pacific Journal of Chemical Engineering. – 2014. – Vol.9, Is.4. – P.471-489.
5 Youyi Zh., Qingfeng H., Weidong L., Desheng M., Guang-Zhi L. Recent progress and effects analysis of ASP flooding field tests // SPE Improved Oil Recovery Symposium. – April, Tulsa, Oklahoma, USA, 2012. – P.8.
6 Nikitina A Salym Petroleum: ASP technology as a solution of the problem of traditional resources depletion // Oil and Gas Vertical. – 2014. – Is.10. – P.24-36.
7 Sheng J.J. Enhanced Oil Recovery Field Case Studies. – Houston, Texas: Gulf Professional Publishing, 2013 – P.203-220.
8 Shubo D., Gang Y., Zhanpeng J., Ruiquan Zh., Yen P.T. Destabilization of oil droplets in produced water from ASP flooding // Colloids and Surfaces – 2005. – Vol.252. – P.113-119.
9 RPSEA Project #08123-02. Field demonstration of alkaline surfactant polymer floods in mature oil reservoirs brookshire dome, Texas, USA. URL: *http://research.engr.utexas.edu/sharma/sp-rpsea08123-02*
10 Yongge W., Mingzhe D., Ezeddin Sh. Study of Alkaline/Polymer Flooding for Heavy-Oil Recovery Using Channeled Sandpacks // SPE Reservoir Evaluation & Engineering. – 2011. – Vol.14, Is.3. – P.310-319.
11 Rahul K., Kishore K. M. ASP flooding of viscous oils. Proceeding of the SPE Annual Technical Conference and Exhibition. – Florence, Italy, 2010. – P.11.
12 Report “Solar enhanced oil recovery. An in-country value assessment for Oman” of GlassPoint Solar Inc. – January, 2014.
13 Ganesh C.T. Heavy oil reservoir management. Proceedings of the Latin American and Caribbean Petroleum Engineering Conference. – Rio de Janeiro, Brazil, 1997. – P.13.
14 Didukh A.G., Koizhaiganova R.B., Bimendina L.A., Kudaibergenov S.E. Synthesis and characterization of novel hydrophobically modified polybetaines as pour point depressants // Journal of Applied Polymer Science. – 2004. – Vol. 92. – P.1042-1048.
15 Aldyiarov T.K., Nasibullin M., Shakhvorostov A.V., Didukh A.G., Gabsattarova G.A., Kudaibergenov S.E. Novel effective pour point depressants for paraffinic oils // Oil and Gas. – 2015. – Is.5. – P.141-151.
16 Shakhvorostov A.V., Nurakhmetova Zh.A., Tatykhanova G.S., Nuraje N., Kudaibergenov S.E. Synthesis and characterization of hydrophobically modified polymeric betaines // Chemical Bulletin of Kazakh National University. – 2015. – Is.3. – P.79-88.
17 Seliverstova E.V., Ibrayev N.Kh., Shakhvorostov A.V., Nuraje N., Kudaibergenov S.E. Physicochemical properties of hydrophobically modified polymeric betaine on the water-air interface // Macromolecular Symposia. – 2016. - In Press.

References

1 Charest M (2013) Can Disc Dig 1:19-52.
2 Nuraje N, Gussenov I, Tatykhanova G, Akhmedzhanov T, Kudaibergenov S (2015) Int J Biol Chem 1(30):173-188.
3 Olajire AA (2014) Energy 77:963-982. *http://dx.doi.org/10.1016/j.energy.2014.09.005*
4 Sheng JJ (2014) Asia-Pacific Journal of Chemical Engineering 9:471-489. *http://dx.doi.org/10.1002/apj.1824*
5 Youyi Z, Qingfeng H, Weidong L, Desheng M, Guang-Zhi L (2012) Recent Progress and Effects Analysis of ASP Flooding Field Tests. SPE Improved Oil Recovery Symposium, 14-18 April, Tulsa, Oklahoma, USA. *http://dx.doi.org/10.2118/151285-MS*
6 Nikitina A (2014) Oil and Gas Vertical [Neftegazovaya vertical] 10:24-36. (In Russian)
7 Sheng J (2013) Enhanced oil recovery field case studies. Gulf Professional Publishing, Houston, Texas, USA. P.203-220. ISBN: 978-0-12-386545-8
8 Deng S, Yu G, Jiang Z, Zhang R, Peng Y (2014) Colloid Surface 252:113-119. http://dx.doi.org/10.1016/j.colsurfa.2004.09.033
9 RPSEA Project #08123-02 (2014) Field demonstration of alkaline surfactant polymer floods in mature oil reservoirs brookshire dome, Texas, USA. *http://research.engr.utexas.edu/sharma/sp-rpsea08123-02*
10 Yongge W, Mingzhe D, Ezeddin S (2011) SPE Reservoir Evaluation & Engineering 14:1-10. *http://dx.doi.org/10.2118/137460-PA*
11 Rahul K, Kishore M (2010) ASP flooding of viscous oils. Proceeding of the SPE Annual Technical Conference and Exhibition, 19-22 September, Florence, Italy. *http://dx.doi.org/10.2118/135265-MS*
12 (2014) Report “Solar enhanced oil recovery. An in-country value assessment for Oman” of GlassPoint Solar Inc. – January, 2014.
13 Ganesh CT (1997) Heavy oil reservoir management. Proceedings of the Latin American and Caribbean Petroleum Engineering Conference, Rio de Janeiro, Brazil. *http://dx.doi.org/10.2118/39233-MS*
14 Didukh AG, Koizhaiganova RB, Bimendina LA, Kudaibergenov SE (2004) J Appl Polym Sci 92:1042-1048. *http://dx.doi.org/10.1002/app.20075*
15 Aldyiarov TK, Nasibullin M, Shakhvorostov AV, Didukh AG, Gabsattarova GA, Kudaibergenov SE (2015) Oil & Gas [Neft i Gaz] 5(89): 141-151. (In Russian)
16 Shakhvorostov AV, Nurakhmetova ZhA, Tatykhanova GS, Nuraje N, Kudaibergenov SE (2015) Chemical Bulletin of Kazakh National University 3(79):79-88. *http://dx.doi.org/10.15328/cb645*
17 Seliverstova EV, Ibrayev NKh, Shakhvorostov AV, Nuraje N, Kudaibergenov SE (2016) Macromolecular Symposia (In Press)