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COPOLYMER BASED ON [(3-METHACRYLOYLAMINO)PROPYL] TRIMETHYLAMMONIUM CHLORIDE AS A FLOCCULANT FOR INDUSTRIAL WATER TREATMENT

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Abstract: The using of polymeric flocculants in the development of the oil industry in Kazakhstan is one of the innovative tasks. Therefore, the creation of new effective flocculants based on available industrial monomers with structure-forming is an urgent task. The mechanism of action of flocculants is based on the phenomenon of adsorption of flocculant molecules on the surface of colloidal particles, the formation of a network structure of flocculant molecules, and the adhesion of colloidal particles due to van der Waals and other forces. New polymeric flocculant with different molar composition was synthesized by radical copolymerization [(3-methacryloylamino)propyl]trimethylammonium chloride (TMAPMACh) with N,N-dimethyl-acrylamide (DMAA) at 333 K in the presence of ammonium persulfate, $(NH_4)_2S_2O_8$ as an initiator. The molar composition of the synthesized TMAPMACh-DMAA copolymer was determined by FTIR and NMR spectroscopy and conductometric titration with $AgNO_3$ solution. The flocculation properties of the copolymers were studied by measuring the sedimentation of dispersed particles of bentonite suspension in the presence of the flocculant. Sedimentation degree was determined by measuring the optical density of the suspension. It was found that TMAPMACh-DMAA copolymers had a flocculating effect and could be used for industrial wastewater treatment. Thermogravimetric analysis showed that this copolymer was thermally stable up to 270°C. Therefore, it can be used in deep well drilling to regulate the properties of drilling fluids.

Keywords: radical copolymerization; dimethylacrylamide; flocculants; sedimentation; industrial water treatment.

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1. Introduction

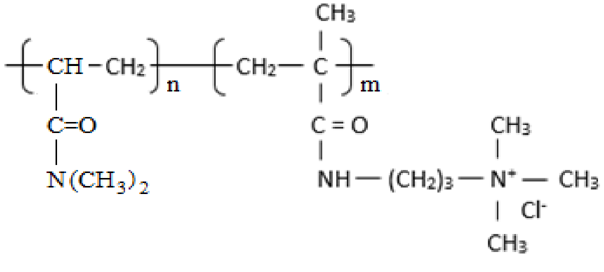
The using of a variety of new materials as industrial flocculants is limited by the complexity of the synthesis of primary raw materials and the high cost of the product itself or low efficiency of industrial wastewater treatment [1-3]. Currently, a large number of flocculants are known, among them quaternary ammonium compounds are often used [4, 5]. However, the flocculating activity of these compounds is not high. In this regard, the synthesis of new effective flocculants based on available industrial monomers and increasing their assortments (types) are an urgent task.

Polymer flocculants consist of chains of carbon atoms in a zigzag shape and are divided into groups according to their charge. Cationic flocculants also form additional chemical bonds, but now between positively charged polymer cations and negative anions on the surface of contaminant particles. In addition to the formation of additional bonds, positively charged cations neutralize the negative charge of suspended particles, which repels them from each other, which further activates the process of their association with the formation of floccules [6].

In this work, [(3-methacryloylamino)propyl]trimethyl ammonium chloride (TMAPMACh) and N,N-dimethylacrylamide (DMAA) are chosen as monomers for synthesis of flocculant. The DMAA monomer increases a hydrophobic property of the flocculant macromolecules and while the TMAPMACh monomer is charged positively, therefore synthesized copolymer TMAPMACh-DMAA are cationic flocculant.

2. Experimental

The copolymer TMAPMACh-DMAA was synthesized with the structural formula



were synthesized from a mixture of monomers with the molar composition [TMAPMACh]:[DMAA] = 20:80; 40:60, 50:50, 60:40 and 80:20 by radical copolymerization in the presence of an initiator ($(NH_4)_2S_2O_8$) by methodic used in [7, 8].

Bentonite clay was used for studying the flocculation properties of the TMAPMACh-DMAA copolymer. The clay was ground in a mill, then the powder was sieved with a hole diameter of no more than 0.2 mm, after that a 0.3 wt% solution of bentonite suspension was prepared and the suspension was left for 24 hours for the clay to swell completely [4, 8].

The duration of the suspension settling process depends on the settling speed of the particles. The degree of flocculation of dispersed phase particles, that is, the degree of purification of water from particles, was determined by the optical density (D) of the system. The optical density was measured at a wavelength of 546 nm on a i3 UV-VIS spectrophotometer. The relative error of measuring the optical density of suspensions did not exceed 2% [8, 9].

Flocculation of suspensions was carried out in graduated cylinders with a capacity of 40 ml. Copolymers with initial monomer concentrations of TMAPMACh-DMAA 78:22, 41:59 and 10:90 were selected for analysis with different concentration of copolymer in bentonite suspension [mg copolymer per g of bentonite]. The dosage of the flocculant solution varied from 0.1 ml to 1 ml per 40 ml of bentonite solution, where the polymer concentration was 0.1 wt. %. All flocculation experiments lasted 2 hours.

Flocculation efficiency (β) was determined using following equation:

$$\beta = (D_0 – D_i)\times 100\ \% / D_i \qquad (1)$$

were D_0 is the optical density of the suspension without flocculant; D_i is the optical density of the suspension after adding the flocculant.

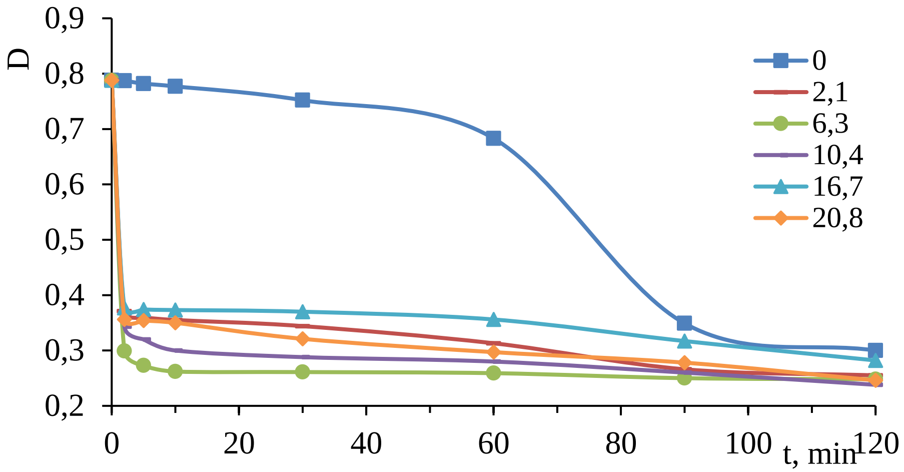
Thermal gravimetric analysis (TGA) was performed using a Pyris 1 – TGA Thermogravimetric Analyzer under nitrogen flow at a heating rate of 20^oC /min from 30 to 900^oC.

3. Results and discussion

Figures 1-4 show the results of a study of the influence of the TMAPMACh-DMAA copolymer on the flocculation rate of bentonite particles. It is seen that in a bentonite suspension without a flocculant, noticeable flocculation of particles begins after approximately 60 minutes. While, the presence of the TMAPMACh-DMAA copolymer, the particles’ flocculation begins instantly and the rate of particle sedimentation increases sharply. The degree of water purification from dispersed particles is also increasing. And the degree of water purification depends on the molar composition and concentration of the copolymer present in the suspension. For example, in the case of the TMAPMACh-DMAA copolymer with a molar composition of 78:28, the highest degree of water purification (68%) is achieved at a concentration of 6.3 mg CP/gB (Fig. 1), while in the presence of a copolymer with a composition of 41: 59 and 10:90, the highest degree of water purification (89% and 85%, respectively) from bentonite particles is achieved at a copolymer concentration of 2.1 mg CP/gB (Fig. 1 and 2).

The particle of the bentonite suspension is charged negatively and has an electrokinetic (zeta) potential −25 mV [4].

In the paper [10] it was shown that the zeta potential of bentonite particles depended on the pH of media and electrolyte concentration. The increasing the acidity of 2–11 in demineralized water (DW) caused the changing of zeta potential from −21 to −33 mV. While in the tap water (TW) in this range of pH zeta potential of bentonite particles decreased from −13 to −18 mV.



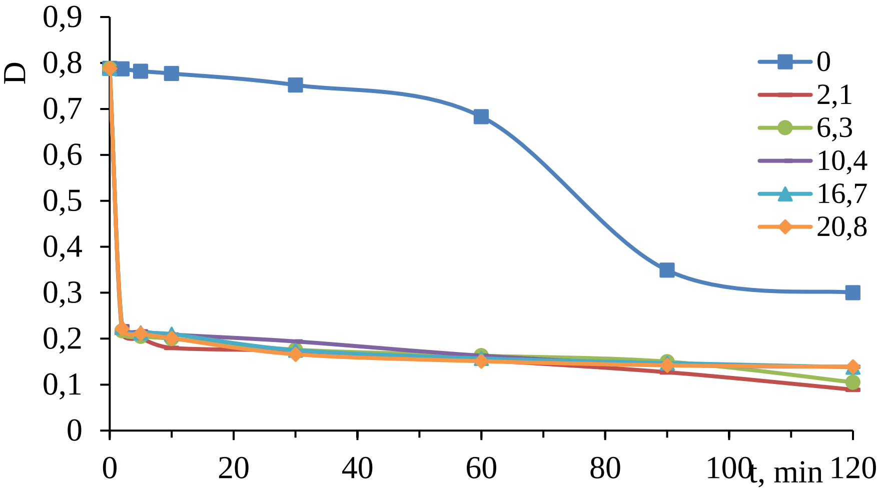
Concentration of the copolymer in the suspension (mg CP/gB):
1– 0; 2– 2.1; 3 – 6.3; 4 – 10.4; 5 – 16.7 and 6 – 20.8.

Figure 1 – Influence of the concentration of TMAPMACh-DMAA copolymer with composition [TMAPMACh]:[DMAA] = 78:22 on the rate of bentonite suspension flocculation.

It was also shown that at a sufficiently high chitosan concentration, the zeta potential of bentonite particles increased and reached a relatively constant value, but the bentonite colloids still exhibited negative zeta potentials over the entire chitosan concentration range (0–40 mg/L) in both DW and TW.

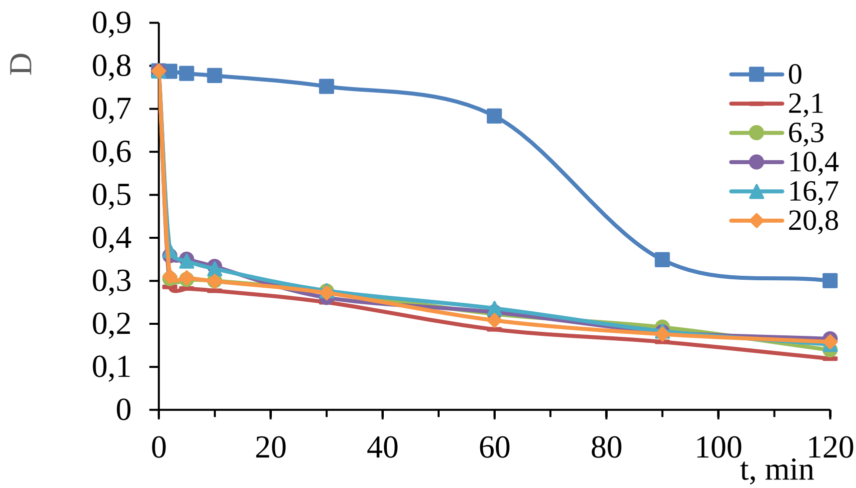
In the presence of flocculant the surface charge of the particles is decreased due to charge neutralization by adsorption of flocculant's macromolecules on the surface of particle through electrostatic mechanism. When the zeta potential reaches ±10 mV, the particles lose thermodynamic stability and any collision between particles leads to the formation of flocs (associations of particles). Large particles, under the influence of gravity, precipitate to the bottom of the dish, and water is purified from dispersed particles [4, 8-10].

As can be seen from Figures 1-4, in our case the efficiency of water purification from bentonite particles depends on the molar composition and concentration of the TMAPMACh-DMAA copolymer. For this case, the optimal molar composition and concentration of the TMAPMACh-DMAA copolymer added to the bentonite suspension are [TMAPMACh]:[DMAA] = 41:59 and 2.1 mg of copolymer per gram of bentonite respectively (Fig. 4).



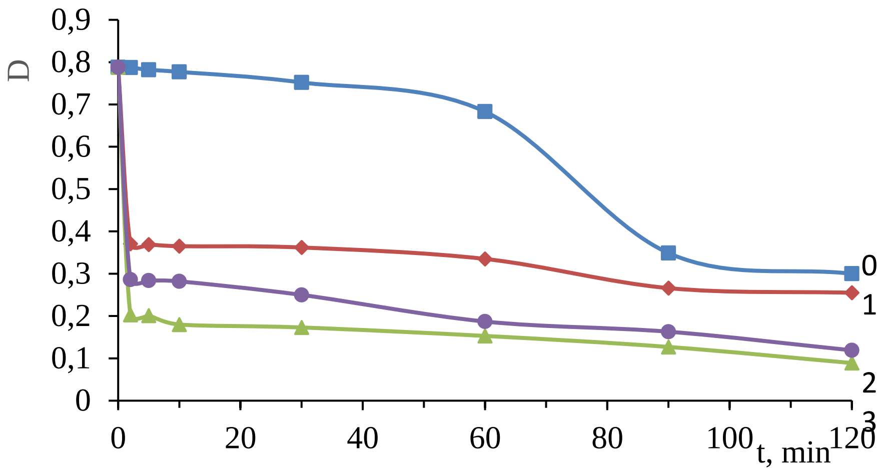
Concentration of the copolymer in the suspension (mg CP/gB):
1– 0; 2 – 2.1; 3 – 6.3; 4 – 10.4; 5 – 16.7 and 6 – 20.9.

Figure 2 – Influence of the concentration of TMAPMACh-DMAA copolymer with composition [TMAPMACh]:[DMAA] = 41:59 on bentonite suspension flocculation.



Concentration of the copolymer in the suspension (mg CP/gB):
1 – 0; 2 – 2.1; 3 – 6.3; 4 – 10.4; 5 – 16.7 and 6 – 20.9.

Figure 3 – Influence of the concentration of TMAPMACh-DMAA copolymer with composition [TMAPMACh]:[DMAA] = 10:90 on the rate of bentonite suspension flocculation.



Concentration of the copolymer in the suspension: 2.1 mg CP/gB
Molar composition of the copolymer [TMAPMACh]:[DMAA]:
1 – 78:22; 2 – 10:90 and 3 – 41:59;
0 – flocculation of the bentonite suspension without copolymer.

Figure 4 – Influence of the molar composition of TMAPMACh-DMAA copolymer on the rate of bentonite suspension flocculation.

For the application of polymeric surfactants in the oil producing industry, it is necessary to know their resistance to high temperatures. Therefore, in this work, the thermal stability of the TMAPMACh–DMAA copolymer was investigated. The copolymer's thermal weight loss curves are shown in Figure 5. As can be seen, at a heating rate of 20°C/min in the temperature range of 30–900°C, the process leads to differential weight loss curves with several peaks, indicating the complexity of thermal degradation. The process of heating the copolymer can be divided into several stages. In the temperature range of 30–227°C, the copolymer weight loss is 13.8%. This weight loss can be attributed to the weight of residual water and other organic solvents that were used for precipitation from the reaction medium and purification of the synthesized copolymer. Further, in the temperature range of 227–370°C, the copolymer weight loss is 26.6%. In this temperature range, a partial rupture of the lateral quaternary amine bonds and thermal oxidation of the group apparently occurs. If we look at the structural formula of the copolymer, the mass fraction of the quaternary amine group is approximately 43%.

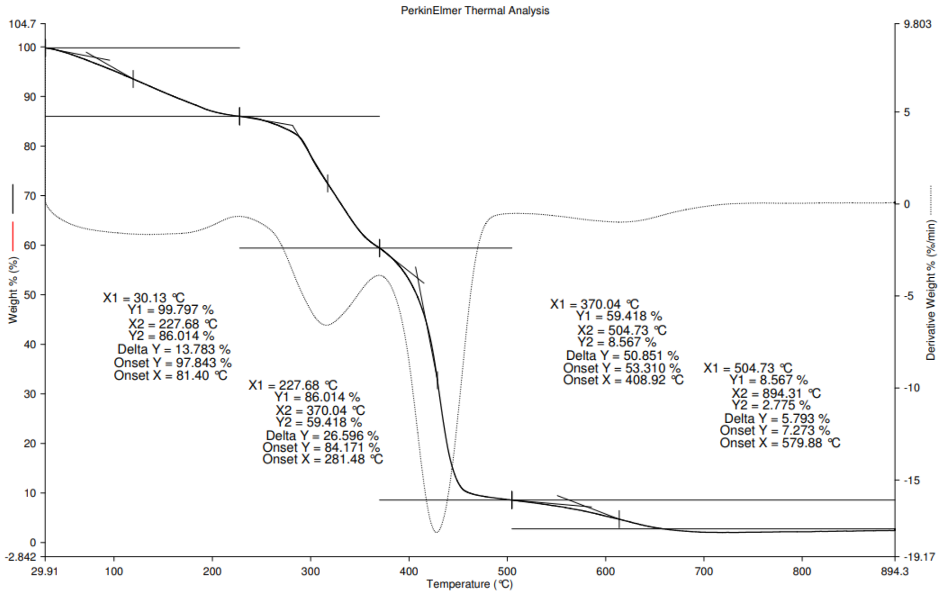


Figure 5 – Thermogravimetric analysis (TGA) curves of the copolymer TMAPMACh-DMAA

Further, in the temperature range of 370–504 °C, the maximum loss of copolymer mass (50.8%) is observed. In this range, in our opinion, there is a complete rupture of carbon-carbon, amide and amine bonds and oxidation of the atoms that make up the copolymer with the formation of nitrogen, carbon, chlorine and hydrogen oxides. In the temperature range of 504–894 °C, a small residual loss of copolymer mass (2.8%) occurs. Thus, taking into account the above, it can be concluded that the synthesized TMAPMACh–DMAA copolymer is thermally stable up to 227 °C. Consequently, it can be used as a component of drilling fluids to regulate the rheological properties and other parameters of the latter.

4. Conclusion

1. A new TMAPMACh-DMAA copolymer with different molar composition was synthesized by radical copolymerization in the presence of ammonium persulfate as an initiator.

2. The molar composition of the synthesized TMAPMACh-DMAA copolymer was determined by FTIR- and ^{1}N NMR-spectroscopy and conductometric titration method.

3. The flocculation properties of the TMAPMACh-DMAA copolymers were determined. The optimal molar composition and concentration of the copolymer added to the bentonite suspension were [TMAPMACh]:[DMAA] = 41:59 and 2.1 mg of copolymer per gram of bentonite, respectively.

4. It has been established that the TMAPMACh-DMAA copolymer is thermally stable up to 270°C, and therefore can be used as a component of drilling fluid in deep well drilling.

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СОПОЛИМЕР НА ОСНОВЕ [(3-МЕТАКРИЛОИЛАМИНО)-ПРОПИЛ]ТРИМЕТИЛАММОНИЙХЛОРИДА КАК ФЛОКУЛЯНТ ДЛЯ ОЧИСТКИ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД

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Резюме: Использование полимерных флокулянтов в развитии нефтяной промышленности Казахстана является одной из инновационных задач. Поэтому создание новых эффективных флокулянтов, обладающих структурообразующими свойствами на основе доступных промышленных мономеров является актуальной задачей. Механизм действия флокулянтов основан на явлении адсорбции макромолекул флокулянта на поверхности дисперсных (коллоидных) частиц, образования сетчатой структуры молекул флокулянта и слипание коллоидных частиц за счет ван-дер-Ваальсовых и других сил. Методом радикальной сополимеризации [(3-метакрилоиламино)пропил]триметиламмоний хлорида (ТМАПМАХ) с N,N-диметилакриламидом (ДМАА) при 333 К в присутствии инициатора (персульфата аммония, $(NH_4)_2S_2O_8$) синтезирован новый полимерный флокулянт с различным мольным составом. Мольный состав синтезированного сополимера ТМАПМАХ-ДМАА определен методами ИК- и ЯМР-спектроскопии и кондуктометрического титрования раствором $AgNO_3$. Флокулирующие свойства сополимеров изучены путем исследования седиментации дисперсных частиц суспензии бентонита в присутствии флокулянта. Степень седиментации определена путем измерения оптической плотности суспензии. Установлено, что сополимеры ТМАПМАХ-ДМАА обладают флокулирующими действиями и могут быть использованы для очистки промышленных сточных вод. Термогравиметрический анализ показал, что данный сополимер термически устойчив до 270ºС. Поэтому он может быть применен в глубинном бурении скважин для регулирования сойств буровых растворов.

Ключевые слова: радикальная сополимеризация; диметилакриламид; флокулянты; седиментация; очистка промышленных сточных вод.

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ӨНДІРІСТІК АҒЫН СУЛАРДЫ ТАЗАРТУҒА АРНАЛҒАН ФЛОКУЛЯНТ РЕТІНДЕ ҚОЛДАНУҒА БОЛАТЫН [(3-МЕТАКРИЛОИЛАМИНО)ПРОПИЛ]ҮШМЕТИЛАММОНИЙ ХЛОРИДІ НЕГІЗДЕГІ СОПОЛИМЕРЛЕР

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Түйіндеме. Қазақстанның мұнай өнеркәсібін дамытуда полимерлік флокулянттарды қолдану инновациялық міндеттердің бірі болып табылады. Сондықтан қол жетімді өнеркәсіптік мономерлер негізінде бойында құрылымтүзгіштік қасиеті бар жаңа тиімді флокулянттарды жасау маңызды мәселе болып табылады. Флокулянттардың әсер ету механизмі флокулянт макромолекулаларының дисперстік (коллоидтық) бөлшектердің бетіне адсорбциялану құбылысына, флокулянт макромолекулаларының желілік құрылымының түзілуіне және ван-дер-Ваальс және басқа да күштердің әсерінен коллоидтық бөлшектердің адгезиясына негізделген. [(3-метакрилоиламино)пропил]-үшметиламмоний хлоридінің (ТМАПМАХ) N,N-диметилакриламидпен (ДМАА) 333 К температурада инициатор (аммоний персульфаты, $(NH_4)_2S_2O_8$) қатысында радикалдық сополимерлеу әдісі арқылы мольдік құрамы әртүрлі жаңа полимерлік флокулянт синтезделді. Синтезделген ТМАПМАХ - ДМАА сополимерінің мольдік құрамы ИҚ- және ЯМР-спектроскопиясы және $AgNO_3$ ерітіндісімен кондуктометриялық титрлеу арқылы анықталды. Сополимерлердің флокуляциялық қасиеттері флокулянт қатысында бентонит суспензиясының дисперстік бөлшектерінің шөгуін зерттеу арқылы анықталды. Суспензияның оптикалық тығыздығын өлшеу арқылы бөлшектердің седиментациялану дәрежесі анықталды. ТМАПМАХ - ДМАА сополимерлерінің бойында флокуляциялық қасиеттің бар екендігі, олай болса оларды өндірістік ағынды суларды тазарту үшін қолдануға болатындығы анықталды. Термогравиметриялық талдау жұмыстары бұл сополимердің 270°С-қа дейін термиялық тұрақты екендігін көрсетті. Сондықтан оны терең ұңғымаларды бұрғылау барысында бұрғылау ерітінділерінің қасиеттерін реттеу мақсатында қолдануға болады.

Түйінді сөздер: радикалдық сополимеризация; диметилакриламид; флокулянттар; седиментация; өндірістік ағын суларды тазалау.

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