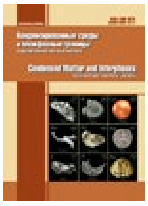


ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2023.25/11391

Sedimentation of bentonite suspensions under the influence of low molecular weight polymers based on amino ester salts

D. Yu. Vandyshev[1]✉, O. V. Sleptsova[1], V. Yu. Gazin[1], S. A. Malyutin[2], N. R. Malkin[2], Kh. S. Shikhaliev[1]

[1]*Voronezh State University,*
1 Universitetskaya pl., Voronezh 394018, Russian Federation

[2]*JSC Petrochem,*
14, Rabochaya st., Belgorod 308017, Russian Federation

Abstract

Among the available technologies for treating natural and wastewater from clay materials, coagulation/flocculation is the most common method due to its high efficiency, simplicity, and cost-effectiveness. Inorganic coagulants such as aluminum sulfate and ferric chloride, widely used as destabilizing agents for colloidal particles, have several significant drawbacks: low efficiency and toxicity. Organic reagents of both natural and synthetic origin are a good alternative.

This work is devoted to the evaluation of the flocculation action of new reagents, which are low molecular weight polymers based on amino ester salts on clay suspensions, as well as the selection of their optimal concentration, providing the maximum sedimentation rate.

Studies have shown that amino ester salts can be effectively used for the treatment of water-clay suspensions. An important factor is the nature of the anion used, which has a significant influence on the coagulation ability of esters. Thus, 40–50 % (wt.) aqueous solutions of amino ester chlorides added to clay suspensions in an amount not exceeding 0.1% (vol.) can be used to thicken clay suspensions. At the same time, aqueous solutions of amino ester bromides regardless of the concentration, introduced into bentonite suspensions of 0.1–0.4 % (vol.), contribute to improved sedimentation, reducing viscosity, and increasing filtration capacity. These results allow us to recommend the use of amino ester chlorides as a thickener in the preparation of drilling muds for strengthening the walls of wells during drilling, and bromides – for flocculation of bentonite suspensions in oil production.

Keywords: Flocculation, Coagulation, Amino esters, Sedimentation rate, Rheological properties, Bentonite, Drilling fluid

Funding source: The results were obtained as part of the work supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment to universities in the field of scientific activity for 2022-2024, project No. FZGU-2022-0003.

Acknowledgments: Research results were partially obtained on the equipment of the Collective Use Centre of Voronezh State University. URL: http://ckp.vsu.ru

For citation: Vandyshev D. Yu., Sleptsova O. V., Gazin V. Yu., Malyutin S. A., Malkin N. R., Shikhaliev Kh. S. Sedimentation of bentonite suspensions under the influence of low molecular weight polymers based on aminoether salts. *Condensed Matter and Interphases*. 20223;25(3): 424–434. https://doi.org/10.17308/kcmf.2023.25/11391

Для цитирования: Вандышев Д. Ю., Слепцова О. В., Газин В. Ю., Малютин С. А., Малкин Н. Р., Шихалиев Х. С. Седиментация бентонитовых суспензий под влиянием низкомолекулярных полимеров на основе солей аминоэфиров. *Конденсированные среды и межфазные границы*. 2023;25(3): 424–434. https://doi.org/10.17308/kcmf.2023.25/11391

✉ Dmitriy Yu. Vandyshev, e-mail: francy_2007@mail.ru

1. Introduction

Bentonite consists of clay minerals based on hydrous aluminosilicate such as montmorillonite, illite, quartz, pyrite, and other minerals [1, 2]. In water, bentonite clay is dispersed to a colloidal state in which the particles acquire a negative surface charge and consequently a negative zeta potential (ξ < -35 mV) due to the isomorphic substitution of aluminum ions for magnesium and iron ions (Mg^{2+} and Fe^{2+}) and silicon ions for Al^{3+} occurring in the octahedral and tetrahedral layers, respectively [3]. This explains the fact that when dispersed in water, bentonite forms a highly stable colloidal suspension, mutual repulsion of particles which prevents their aggregation and sedimentation [4–6].

Bentonite particles have a lamellar shape with a small average diameter (D_{50} < 5 μm), which causes a high surface area of the dispersed phase. At the same time, the value of the negative charge on different parts of the particle surface is not equal, the charge on the protruding curved areas depends on the pH of the dispersion medium. Therefore, the degree of flocculation of bentonite suspension and the structure of the formed precipitates strongly depends on the pH of the medium [5].

Bentonite has a number of useful properties such as non-toxicity, high ion exchange capacity, swelling ability, and large surface area with excess free surface energy [7]. It can be applied directly in its natural form or pre-treated by various chemical and physical activation methods [8]. The composition and desirable consumer properties of clay minerals have caused the popularity of bentonite as a raw material in the industrial sector [2]. However, its use in food, petroleum, wine, construction, and agriculture produces wastewater containing fine colloidal clay particles. The resulting colloidal suspensions require special treatment and separation of solid pollutants from water [9]. Direct discharge of stable colloidal suspension into water bodies is prohibited, as it causes a significant increase in turbidity and leads to serious problems for aquatic life [10]. Therefore, it is crucial to properly treat the generated wastewater before its discharge into water bodies [9, 11]. This issue is particularly acute in oil and gas production. Well formation in the oil and gas industry is accompanied by environmental pollution with drilling muds, their spent or waste part, drilling cuttings, etc. Waste drilling muds accumulate due to the duration of sedimentation of the drilled predominantly clayey rock during sedimentation in mud pits.

Various solid-liquid separation methods, including physical and chemical methods, are used to purify colloidal suspensions. There are several technologies such as electrocoagulation, membrane filtration, electroosmosis, and thermomechanical dewatering [12–15], but these methods are require a high expenditure of energy and finances [16]. Coagulation/flocculation is one of the most commonly used processes for water and wastewater treatment, especially for the separation of suspended colloidal particles. This method is highly efficient, economical, cheap, and non-energy consuming [17–20]. The key principle of coagulation and flocculation processes is to reduce the net negative charge of particles and to stimulate the van der Waals attraction forces between them [17]. Coagulation is aimed at destabilization of colloidal particles and formation of microaggregates, while flocculation is aimed at further agglomeration of particles and formation of larger floccules [17]. Thus, the formed aggregates are deposited by gravity, resulting in a relatively clear supernatant. Various chemicals including metal salts (coagulants) and polyelectrolytes (flocculants) are used to destabilize the colloidal suspension [20]. Aluminum sulfate as well as iron and aluminum chlorides are common coagulants, but their utilization is limited due to low removal efficiency, environmental and health concerns associated with the presence of residual metal in the supernatant, and the formation of toxic sludge [18]. Therefore, there is an ongoing search for environmentally friendly and economical alternative coagulants.

In recent years, the use of polyelectrolytes as flocculants has become a common practice due to their effectiveness in treating colloidal suspensions through a bridging mechanism [17]. Flocculation of fine colloidal particles with the employment of polyelectrolytes such as polyelectrolyte (PAA) can occur by various mechanisms including adsorption and binding of the polymer, charge neutralization, particle-surface complex formation, and depletion flocculation, or a combination of these mechanisms [6, 21–24]. Cationic polyacrylamide (CPAA) is most commonly used for destabilization and separation of stable colloidal drilling fluid suspension. The destabilization process with the help of CPAA is carried out due to the adsorption of cationic polymer chains due to the formation of hydrogen bonds between the particle surface and the primary amide functional groups of the polymer. Thus, charge neutralization becomes the main mechanism by which CPAA locally changes the charge of the particle surface [17]. The main characteristic of CPAA responsible for its function as a destabilizing agent is determined by the presence of a quaternary ammonium salt carrying a positive charge. The same is true for a cheap low molecular weight flocculant/coagulant, choline chloride (ChCl). It is also worth noting that ChCl exhibits its flocculating properties only at significantly high concentrations in relation to clay suspensions. Therefore, it is more often used as a thickener and stabilizer (coagulant property) in an individual form or as part of a mixture with inorganic and high molecular weight reagents [25–26]. However, it is important to note that the potential hazard of these reagents is determined by the content of monomers, residues of initial halogen derivatives of hydrocarbons involved in their synthesis, and other impurities. Therefore, their application requires additional purification stages. In this case, the search for simple in terms of synthesis methodology, environmentally safe and effective alternatives to traditional coagulants/flocculants becomes highly relevant.

From this point of view, amino esters are promising, the advantage of which is biodegradability and nontoxicity. This class of compounds has found wide application in the production of biologically active substances (BAS) [27], polyurethanes [28–30], catalysts and modifiers [31], emulsifiers of inverse emulsions [32–33], fabric softeners [34], and in the field of microelectronics [35–40]. However, their application for wastewater treatment, in particular, drilling muds, has not been previously considered.

In this regard, this work aimed to evaluate the flocculation action of new reagents, which are low molecular weight polymers based on amino ester salts, on clay suspensions, as well as the selection of their optimal concentration, providing the maximum sedimentation rate.

2. Experimental

The following raw materials and reagents were used in the work:

1) Bentonite clay with particle sizes in the range of 5–75 µm.

2) Flocculants/coagulants in the form of low molecular weight polymers based on hydrochlorides (AE-1) and hydrobromides (AE-2) of amino esters, which were synthesized at the Department of Organic Chemistry of Voronezh State University using reagents of "chemically pure" grade. The structure of the compounds was proved by a complex of physicochemical methods such as:

– ^{1}H NMR (spectra recorded on a Bruker DRX-500 instrument (500.13 MHz) in DMSO-d6 and an internal standard Me_4Si);

– HPLC-MS (spectra were recorded on Agilent Infinity 1260 chromatograph with Agilent 6230 TOF LC/MS interface. Separation conditions: mobile phase $MeCN/H_2O$ + 0.1% FA (formic acid), gradient elution, column – Poroshell 120 EC-C18 (4.6×50 mm, 2.7 µm), thermostat 23–28 °C, flow rate 0.3-0.4 ml/min. Ionisation – electrospray (capillary –3.5 kV; fragmentor +191 V; OctRF +66 V – positive polarity);

– To study sedimentation stability, we used a combined technique based on the works of A. A. Shkop. A. [41] and Averkina E. V. B. [42], which consisted of the following stages:

1. ***Preparation of bentonite suspension (BS).*** 100 ml of distilled water and clay stabilizer (ChCl), the concentration of which was 0.2 % (vol.), were placed in a 250 ml flask. 1.7 g of bentonitic clay was added to the obtained solution, the flask was tightly corked and stirred on a vibration table VB 1.1 (2 vibration frequencies 3000, 6000 min^{-1}, vibration amplitude controller, vibration arc, working table 185×135 mm) for uniform distribution of clay in the liquid volume due to dispersion of agglomerates. The resulting mixture was left to swell the clay particles for 24 hours. After soaking, the flask was shaken thoroughly to obtain stable BS.

2. ***Estimation of the deposition rate.*** The obtained BS was transferred into a 100 ml measuring cylinder (30 mm diameter and 230 mm height) and a certain amount (0.1–0.6 % (vol.)) of the test reagent solution (AE-1 or AE-2) with different concentrations of 40, 50, 60, 70 % (wt.)

was added. The range of reagent concentrations was selected based on the analysis of the available market of flocculants/coagulants close in chemical structure. After introducing a portion of the reagent, the contents of the cylinder were stirred by tilting it ten times slowly. The time interval during which the interface between the clarified liquid layer, presumably containing no clay particles, and the compacted suspension layer passes the path corresponding to the zone of free sedimentation of particles, was determined. According to the experimental data obtained, the flocculus sedimentation rate (*V*, mm/min) was calculated to the time of flocculus passage along this path. The primary results of the experiment were graphically represented as points in the coordinates "flocculus settling velocity *V* – the amount of reagent solution N". Each point represented the average value of the results of three or four experiments. The relative deviation of experimental data from the average value did not exceed 4.5 %.

To assess the flocculation quality of the BS (mechanical strength of the aggregates), after completion of the flocculation process and measurement of the sedimentation rate V_1, the sample was stirred again with a mechanical stirrer at 600 rpm for 40 s in a chemical beaker. The contents were then transferred back into the measuring cylinder and the sedimentation rate of suspended particles in the sample was determined (V_2, mm/min).

3) After each measurement of sedimentation rate, samples were taken to ***control the size of formed particles***. To qualitatively assess the size of the formed agglomerates, a Biomed-6 microscope equipped with a digital camera which was used at a magnification of 40 times. The microscope was equipped with an achromatic lens 40×0.65, halogen illuminator with smooth brightness control.

4) ***Viscosity measurements*** of the tested suspensions were carried out on an A&D SV-100A vibro viscometer. The principle of operation of the device was based on the dependence of power, which was used to excite the vibration of two thin sensor plates with a frequency of 30 Hz and a constant amplitude of about 1 mm, on the product of dynamic viscosity by suspension density (ν). The measurements were carried out at a constant temperature of 25 °C by a number of at least three repetitions. The instrument was standardized and calibrated with distilled water before each new measurement.

The pycnometric method was used to determine the density of BS and the resulting systems. The obtained values were the average of three measurements performed at a constant temperature of 25 °C.

5) ***Determination of the acidity of the medium*** pH-meter "Ionometer I-160 MI" was used. Operating conditions of the device correspond to the values for devices of group 2 according to GOST 22261-94. The device complies with TU 4215-053-89650280-2009. Measurements were carried out at a constant temperature of 25 °C, the number of at least 3 repetitions.

3. Results and discussion

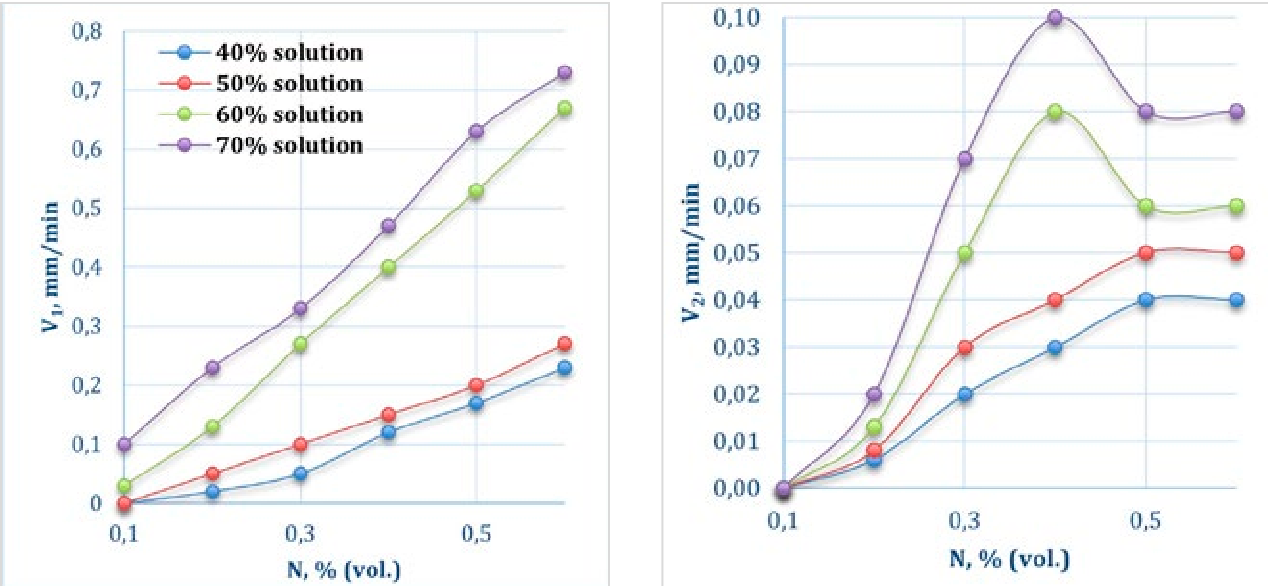
In order to select a flocculant/coagulant for BS with the best flocculation characteristics, the experiments were carried out in two stages.

The first stage consisted in comparison of sedimentation rates in free conditions of BS samples containing additives of reagents AE-1 and AE-2.

The second stage of the experiments included mechanical impact on the resulting systems, simulating the movement of the flocculated suspension from the thickening apparatus (settling tank) to the dewatering apparatus (centrifuge or filter press). The residual sedimentation velocity V_2 after mechanical action characterized the sedimentation ability of the BS, determined by the size of the aggregates formed, and hence the strength of the initial floccule. Identification of the optimal concentration of additives was carried out on the basis of the graphical plots obtained by analogy with the first stage.

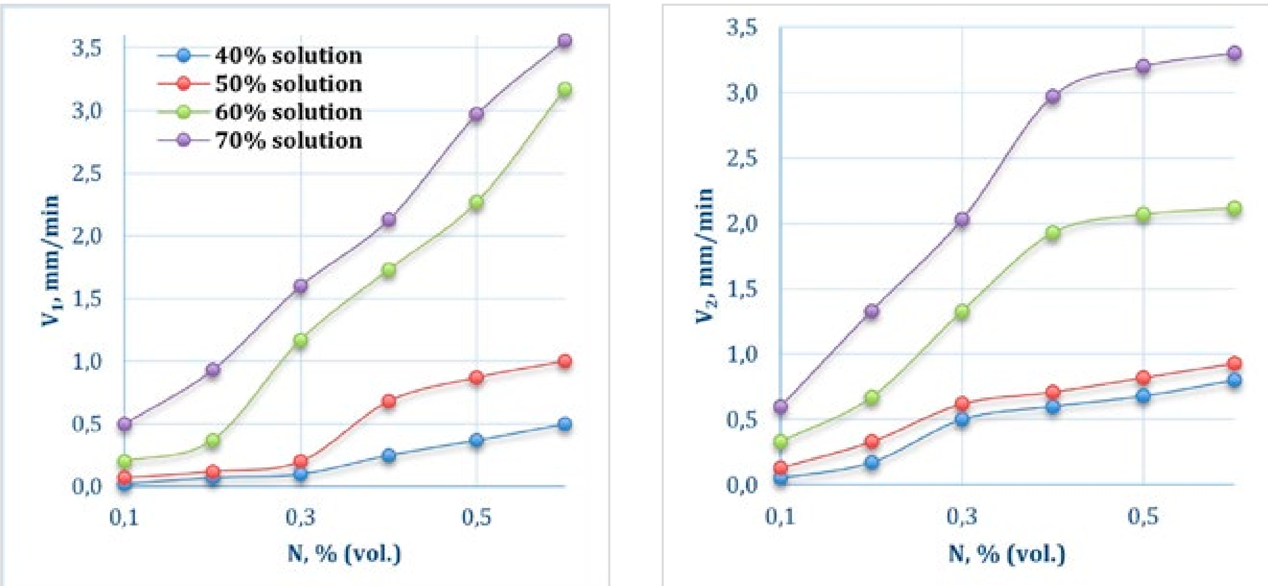
The structure, stability, purity of the BS filtrate, and water separation were visually assessed during each test. In addition, the viscosity, density of the suspension, pH of the dispersion medium, and the size of the aggregates formed were analyzed.

According to the data obtained by measuring the sedimentation rate before mechanical action (Fig. 1a and 2a), additives AE-1 and AE-2 have a flocculation effect, causing the coagulation and sedimentation processes. The maximum sedimentation rate is observed when using 70 % (wt.) aqueous solution of the flocculating agent in the amount of 0.6 % (vol.) and is 0.73 mm/min for AE-1 and 3.56 mm/min for AE-2. On visual evaluation, agglomerate formation is noted for both additives, but when AE-2 is introduced into the BS, much larger aggregates are formed almost immediately and the supernatant becomes transparent. Over time, the flocculates formed almost completely settle to the bottom of the measuring cylinder. That is, the reagent AE-2 under equal conditions to a greater extent disrupts the aggregative and sedimentation stability of BS and, therefore, has a more pronounced flocculating effect, leading to accelerated sedimentation. At the introduction of AE-1 the formation of agglomerates is accompanied by the thickening of clay suspension, and the height of the clarified layer after the thickening



a b

Fig. 1 Dependence of flocculus sedimentation rate (V) on the amount (N) of injected solution of reagent AE-1 before (a) and after (b) mechanical impact



a b

Fig. 2. Dependence of flocculus sedimentation rate (V) on the amount (N) of injected AE-2 reagent solution before (a) and after (b) mechanical impact

of compacted layer of suspension practically does not change for several days. Probably, the reason of thickening is structure formation in the thickened layer of suspension, which is also based on coagulation and flocculation processes with the participation of the introduced reagent. Obviously, the mechanism of these processes at the introduction of investigated additives is somewhat different.

Of practical interest is the change in the sedimentation rate of flocculated clay after mechanical action on the suspension (Figs. 1b and 2b), which allows us to assess the strength of aggregates formed at the first stage of research. The residual sedimentation rate of BS samples containing AE-1 decreases significantly, almost by an order of magnitude (Fig. 1). The almost linear dependence of sedimentation rate on the amount of the introduced reagent is broken, which indicates the transition of sedimentation from free conditions to constricted conditions. Broken floccule visually acquires a shapeless appearance. In contrast to the first stage of tests, the clarified liquid after repeated sedimentation of the suspension becomes turbid, this is caused by the increase in the dispersibility of the system, subjected to mechanical influence, and the appearance of colloidal particles resistant to sedimentation due to their small size.

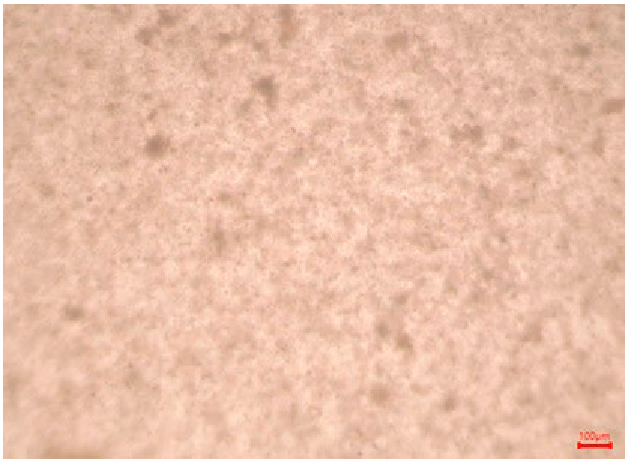
Mechanical impact on the flocculated BS sample containing AE-2 reagent practically does not change the rate of re-sedimentation of agglomerates. Only at high concentrations of AE-2 sedimentation rate ceases to depend on the amount of the introduced reagent, which may be due to the transition of the sedimentation process in the compacted layer in constricted conditions. It should be noted that for all BS with introduced AE-2 the liquid above the compacted layer remains transparent regardless of the mechanical influence.

The observed difference in the course of sedimentation processes in BS at the introduction of reagents AE-1 and AE-2 before and after mechanical action confirms assumptions about different mechanisms of coagulation-flocculation processes with the participation of these additives.

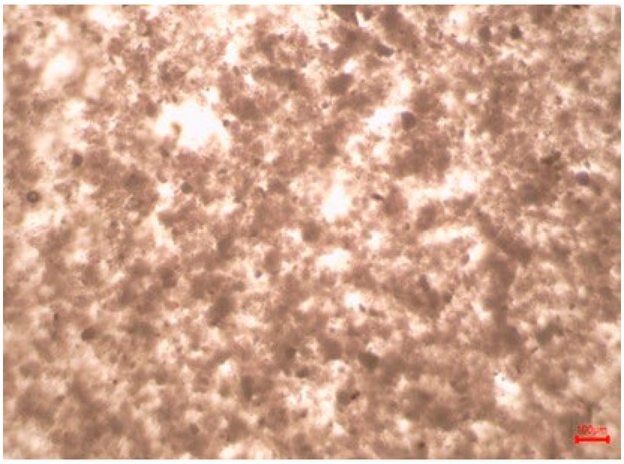
In addition to the observed regularities of macroscopic processes of particle deposition, we evaluated the dimensional characteristics of BS agglomerates using optical microscopy. The images obtained with 40× magnification (Fig. 3, 4) show that the introduction of reagents AE-1 and AE-2 into the BS causes coagulation process, i.e. clay particles sticking together to form agglomerates (images F1). When using the AE-1 additive, a structure with a more uniform distribution of agglomerates and inclusion of water in the structural grid is observed (Fig. 3). Probably, the introduction of the AE-1 additive leads to the formation of a coagulation structure with fragile contacts through the dispersion medium interlayers. Such contacts are easily destroyed by mechanical action, as shown by the F2 image (Fig. 3). The previously observed thickening effect and some sedimentation stability of the thickened layer of suspension are possible when AE-1 molecules are fixed on one particle and structured polyelectrolyte layers of amino ester in Cl-form are formed.

When AE-2 is used as a flocculation agent, the formation of larger and stronger aggregates that are not destroyed by mechanical action occurs (Fig. 4). Most likely, when AE-2 is used, the formation of some number of phase contacts occurs as a result of a decrease in the ionic-electrostatic stability factor provided by the negative surface charge of clay particles. The coagulated particles may also bind due to "bridging" fixation by the introduced AE-2 reagent, and the dispersion medium will be in a free state in the space between agglomerates.

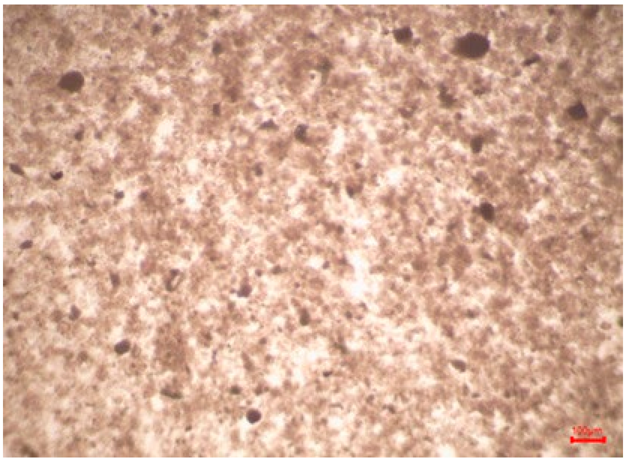
Viscometric studies confirmed the viscosity increase observed visually with increasing concentration of AE-1 (Fig. 5a) and viscosity decrease with increasing concentration of AE-2 in BS (Fig. 5b), associated with the formation of different structures during coagulation and flocculation processes involving the studied reagents. Obviously, the adsorption layers of polyelectrolytes based on hydrochlorides (AE-1) and hydrobromides (AE-2) of amino esters, in which Cl^- and Br^- act as counterions of the electric double layer, have a determining influence on these processes. Br^- has a larger ionic radius compared to Cl^-, the lower degree of hydration and higher adsorption capacity, and hence will preferentially reside in the dense adsorption part of the electrical double layer. This will lead to a decrease in the ξ-potential and, as



a

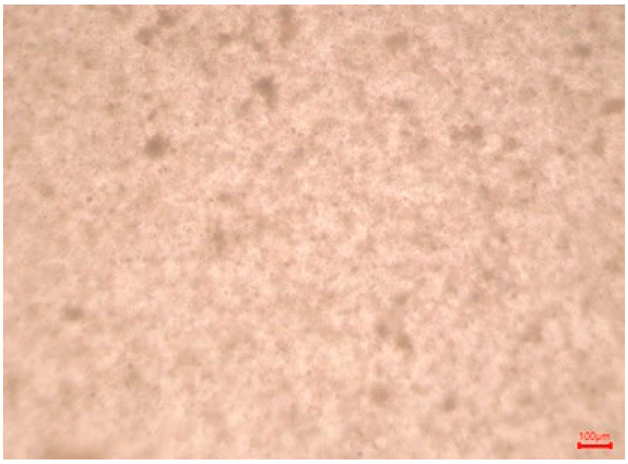


b

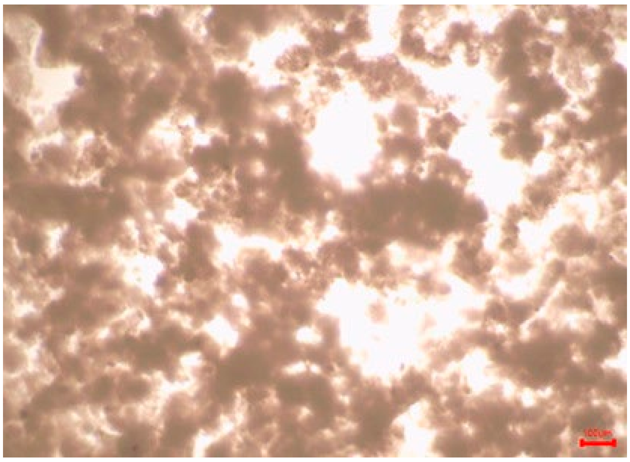


c

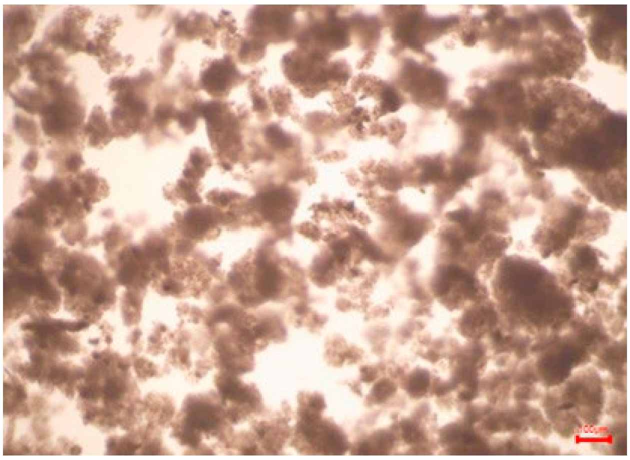
Fig. 3. View of the BS without additive (a), before (b) and after (c) mechanical action at introduction of 40 % (wt.) solution of AE-1 reagent in the amount of 0.1 % (vol.)



a



b



c

Fig. 4. View of the BS without additive (a), before (b) and after (c) mechanical action at introduction of 60 % (wt.) solution of reagent AE-2 in the amount of 0.4 % (vol.)

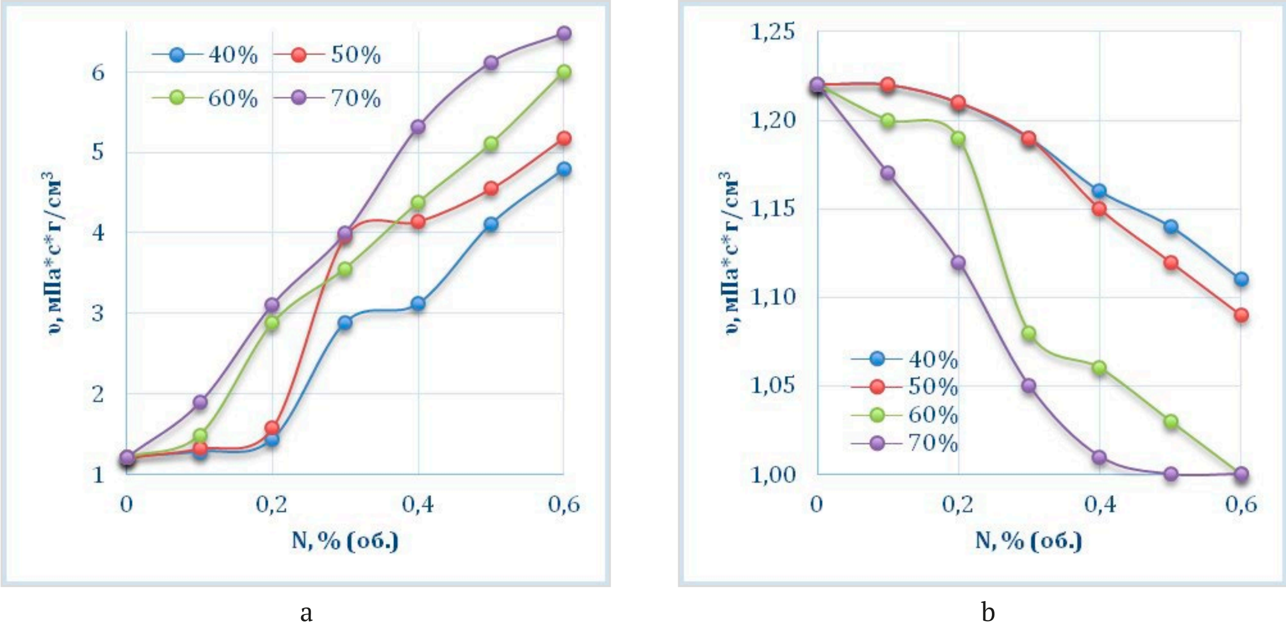


Fig. 5. Dependence of viscosity (υ) on the amount (N) of injected reagent solution AE-1 (a) and AE-2 (b)

a consequence, a decrease in the aggregative stability of the BS as a result of the formation of rather strong aggregates - floccules. Therefore, amino ester bromide oligomers (reagent AE-2) have pronounced flocculating properties and can be used as flocculants of BS.

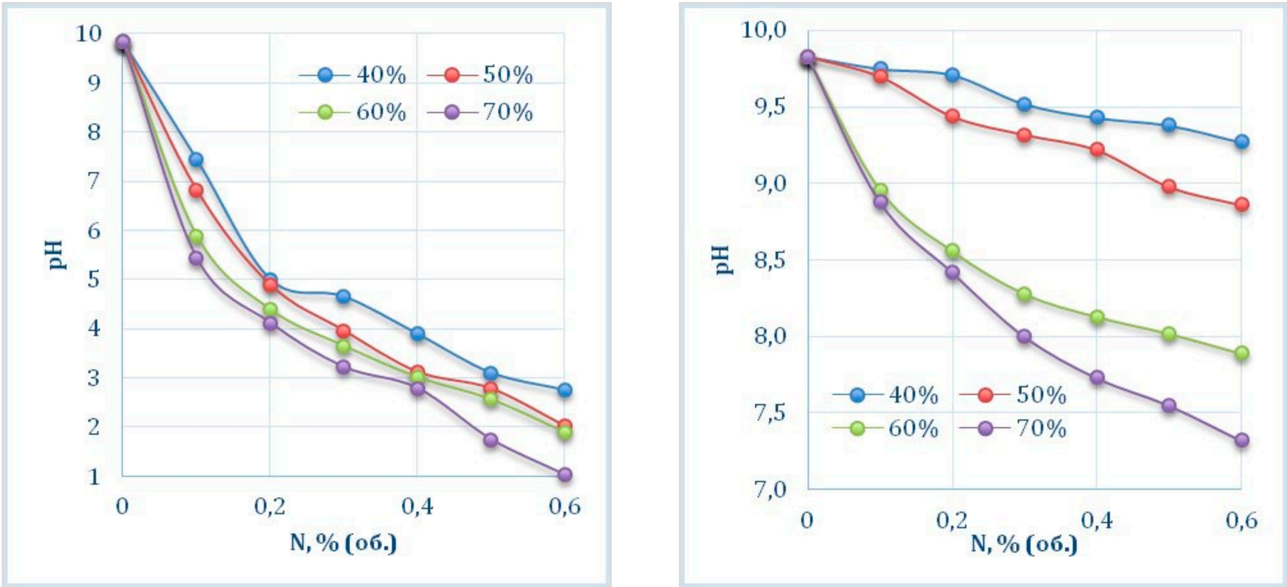
Cl^- ion of amino ester hydrochlorides (AE-1), which has higher mobility, participates mainly in the formation of the diffuse part of the electric double layer, providing a sufficiently high value of ξ-potential, and therefore will act as a stabilizer and thickener of the suspension. Anisometric (lamellar) clay particles at the introduction of AE-1 will be able to interact with their protruding parts through water layers, forming unstable coagulation contacts, easily destroyed as a result of mechanical impact. Formation of the coagulation structure (grid), as well as the participation of water molecules in this process (its binding), leads to the thickening of suspension and increasing its sedimentation stability. The ability of AE-1 to fulfill the function of a thickener can be used in the preparation of drilling muds to strengthen the borehole walls during drilling.

The use of AE-1 can be limited by hydrolysis of amino ester salts. For example, increasing the concentration of AE-1 in the BS leads to a significant decrease in the pH of the dispersion medium (Fig. 6a). This parameter limits the use of AE-1, and 40-50 % (wt.) aqueous solutions introduced in amounts not exceeding 0.1 % (vol.) are optimal as BS thickeners. For AE-2, a decrease in pH is also observed, but it is within acceptable limits (Fig. 6b).

It is also worth noting that regardless of the observed phenomena, the viscosity of the system, and pH, the density of BS was unchanged and was 1.023 g/cm^3. The change of physicochemical parameters after mechanical action on BS was not significant (within 10^{-3}).

4. Conclusions

As a result of the research, it is shown that the salts of amino esters obtained by us can be effectively used in the processes of water-clay suspension treatment. The nature of the used anion has a significant influence on the coagulating ability of esters: amino ester chlorides AE-1 can be used in the form of 40–50 % (wt.) aqueous solutions introduced in amounts not exceeding 0.1 % (vol.) for thickening of clay suspensions. At the same time, aqueous solutions of bromides of AE-2 amino esters introduced into bentonite suspensions in the amount of 0.1–0.4 % (vol.), regardless of the concentration, contribute to improved sedimentation. On this basis, we can conclude that the obtained results allow us to recommend to use of AE-1 as a thickener in preparation of drilling muds for strengthening of



а б

Fig. 6. Dependence of BS pH on the amount (N) of injected solution of reagent AE-1 (a) and AE-2 (b)

borehole walls during drilling, where AE-2 – for flocculation of bentonite suspensions during oil production. Both additives are characterized by low consumption, which makes them economically attractive for practical use.

Contribution of the authors

All authors made equivalent contributions to the publication.

Conflict of interest

The authors declare that they have no known financial conflicts of interest or personal relationships that could influence the work presented in this article.

Reference

1. Abu-Jdayil B. Rheology of sodium and calcium bentonite-water dispersions: Effect of electrolytes and aging time. *International Journal of Mineral Processing*. 2011;98(3-4): 208–213. https://doi.org/10.1016/j.minpro.2011.01.001

2. Karnland O. *Chemical and mineralogical characterization of the bentonite buffer for the acceptance control procedure in a KBS-3 repository*. Stockholm: Clay Technology AB; Technical Report, SKB-TR-10-60, 2010. 25 p.

3. Duman O., Tunç S. Electrokinetic and rheological properties of Na-bentonite in some electrolyte solutions. *Microporous Mesoporous Materials*. 2009;117(1-2): 331–338. https://doi.org/10.1016/j.micromeso.2008.07.007

4. Tchobanoglous G., Burton F. L., Stensel H. D. *Wastewater engineering: treatment and reuse*. Metcalf & Eddy Inc., McGraw-Hill Education, Boston; 2003. 1819 p.

5. Shaikh S. M. R., Nasser M. S., Hussein I. A., Benamor A. Investigation of the effect of polyelectrolyte structure and type on the electrokinetics and flocculation behavior of bentonite dispersions. *Chemical Engineering Journal*. 2017;311: 265–276. https://doi.org/10.1016/j.cej.2016.11.098

6. Zhang B., Su H., Gu X., X. Huang. Wang H. Effect of structure and charge of polysaccharide flocculants on their flocculation performance for bentonite suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2013;436: 443–449. https://doi.org/10.1016/j.colsurfa.2013.07.017

7. Carlson L. *Bentonite Mineralogy*. *Working Report*. POSIVA OY, Finland. 2004. 189 p.

8. Karimi L., Salem A. The role of bentonite particle size distribution on kinetic of cation exchange capacity. *Journal of Industrial and Engineering Chemistry*. 2011;17(1): 90–95. https://doi.org/10.1016/j.jiec.2010.12.002

9. Nasser M. S., Twaiq F. A., Onaizi S. A. Effect of polyelectrolytes on the degree of flocculation of papermaking suspensions. *Separation and Purification Technology*. 2013;103: 43–52. https://doi.org/10.1016/j.seppur.2012.10.024

10. Yousefi S. A., Nasser M. S., Hussein I. A., Benamor A., El-Naas M. H. Influence of polyelectrolyte structure and type on the degree of flocculation and rheological behavior of industrial MBR sludge. *Separation and Purification Technology*, 2020;233: 116001. https://doi.org/10.1016/j.seppur.2019.116001

11. Chatterjee T., Chatterjee S., Woo S. H. Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer. *Chemical Engineering Journal*. 2009;148(2-3): 414–419. https://doi.org/10.1016/j.cej.2008.09.016

12. Ghernaout D., Ghernaout B., Boucherit A. Effect of pH on electrocoagulation of bentonite suspensions in batch using iron electrodes. *Journal of Dispersion Science and Technology*. 2008;29(9): 1272–1275. https://doi.org/10.1080/01932690701857483

13. Hilal N., Ogunbiyi O. O., Al-Abri M. Neural network modeling for separation of bentonite in tubular ceramic membranes. *Desalination*. 2008;228(1-3): 175–182. https://doi.org/10.1016/j.desal.2007.10.006

14. Ju S., Weber M. E. Mujumdar A. S. Electroosmotic dewatering of bentonite suspensions. *Separations Technology*. 1991;1(4): 214–221. https://doi.org/10.1016/0956-9618(91)80016-s

15. Mahmoud A., Fernandez A., Chituchi T. M., Arlabosse P. Thermally assisted mechanical dewatering (TAMD) of suspensions of fine particles: Analysis of the influence of the operating conditions using the response surface methodology. *Chemosphere*. 2008;72(11): 1765–1773. https://doi.org/10.1016/j.chemosphere.2008.04.075

16. Shaikh S. M. R., Nasser M. S., Magzoub M., Benamor A., Hussein I. A., El-Naas M. H. Qiblawey H. Effect of electrolytes on electrokinetics and flocculation behavior of bentonite-polyacrylamide dispersions. *Applied Clay Science*. 2018;158: 46–54. https://doi.org/10.1016/j.clay.2018.03.017

17. Shaikh S. M. R., Nasser M. S., Hussein I., Benamor A., Onaizi S. A., Qiblawey H. Influence of polyelectrolytes and other polymer complexes on the flocculation and rheological behaviors of clay minerals: A comprehensive review. *Separation and Purification Technology*. 2017;187: 137–161. https://doi.org/10.1016/j.seppur.2017.06.050

18. Lee C. S., Robinson J., Chong M. F. A review on application of flocculants in wastewater treatment. *Process Safety and Environmental Protection,* 2014;92(6): 489–508. https://doi.org/10.1016/j.psep.2014.04.010

19. Lin J. L., Huang C., Chin C. J. M., Pan J. R. Coagulation dynamics of fractal flocs induced by enmeshment and electrostatic patch mechanisms. *Water Research*. 2008;42(17): 4457–4466. https://doi.org/10.1016/j.watres.2008.07.043

20. Barbot E., Dussouillez P., Bottero J. Y., Moulin P. Coagulation of bentonite suspension by polyelectrolytes or ferric chloride: Floc breakage and reformation. *Chemical Engineering Journal*. 2010;156(1): 83–91. https://doi.org/10.1016/j.cej.2009.10.001

21. Daifa M., Shmoeli E., Domb A. J. Enhanced flocculation activity of polyacrylamide-based flocculant for purification of industrial wastewater. *Polymers for Advanced Technologies*. 2019;30: 2636–2646. https://doi.org/10.1002/pat.4730

22. Ma J., Shi J., Ding L., ... Fu K. Removal of emulsified oil from water using hydrophobic modified cationic polyacrylamide flocculants synthesized from low-pressure UV initiation. *Separation and Purification Technology*. 2018;197: 407–417. https://doi.org/10.1016/j.seppur.2018.01.036

23. Liu T., Ding E., Xue F. Polyacrylamide and poly(N.N-dimethylacrylamide) grafted cellulose nanocrystals as efficient flocculants for kaolin suspension. *International Journal of Biological Macromolecules*. 2017;103: 1107–1112. https://doi.org/10.1016/j.ijbiomac.2017.05.098

24. Nasser M. S., James A. E. The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions. *Separation and Purification Technology*. 2006;52: 241–252. https://doi.org/10.1016/j.seppur.2006.04.005

25. Smith E. L., Abbott A. P., Ryder K. S. Deep eutectic solvents (DESs) and their 186 applications. *Chemical Reviews*. 2014;114(21): 11060–11082. https://doi.org/10.1021/cr300162p

26. Zhang Q., De Oliveira Vigier K., Royer S., Jérôme F. Deep eutectic solvents: Syntheses. properties and applications. *Chemical Society Reviews*. 2012;41(21): 7108–7146. https://doi.org/10.1039/c2cs35178a

27. Shomurodov A., Makhsumov A., Ismailov B., Obidov S. B. N-diethanoloiloamino-(butin-2-il)-sorbinate and its physico-chemical properties. *Universum: Chemistry & Biology*. 2021;6(84): 20–24. (In Russ., abstract in Eng.). https://doi.org/10.32743/UniChem.2021.84.6.11856

28. Davletbaeva I. M., Dulmaev S. E., Sazonov O. O., Gumerov A. M., Ibragimov R. G., Davletbaev R. S., Valiullin L. R. Polyurethanes based on modified amino ethers of boric acid. *Polymer Science, Series B*. 2020;62(4): 375–384. https://doi.org/10.1134/S156009042004003X

29. Nizamov A. A., Myasnikov G. V., Davletbaev R. S.,... Davletbaeva, I. M. Polyurethane gel electrolytes based on phthalic anhydride-modified amino ethers of ortho-phosphoric acid. *Herald of Technological University*. 2022;25(8): 121–125. (In Russ., abstract in Eng.). https://doi.org/10.55421/1998-7072_2022_25_8_121

30. Sazonov O. O., Zakirov I. N., Davletbaev R. S., Korobkina A. A., Sidorova M. I., Davletbaeva I. M. Thermal sensitive vapor permeable polyurethanes based on amino esters of ortho-phosphoric acid. *Herald of Technological University*. 2021;22(1): 37–40. (In Russ., abstract in Eng.). Available at: https://elibrary.ru/item.asp?id=44548999

31. Davletbaev R. S., Emelina O. Yu., Davletbaeva I. M., Gumerov A. M. Complexes of amino esters of

boric acid as modifiers of polydimethylsiloxanes. *Vestnik Kazanskogo tekhnologicheskogo universiteta*. 2012;10: 120–122. (In Russ., abstract in Eng.). Available at:https://elibrary.ru/item.asp?id=17788724

32. Tokunov V. I., Kheifets I. B. Hydrophobic-emulsion drilling fluids*. Moscow: Nedra Publ. 1983. 167 p.

33. *Drilling completion and workover fluids: Oil and gas technologies*. 2008;11 (Appendix). 63 p. 34.

34. Case R. O., Tawney K. J., Jefwerth J. L. *Quaternized MDEA complex esters with a high content of complex monoester mixed with quaternized complex ethers*. Patent RF, no. 2006100036/04. Publ. 06.27.2006, bull. no. 18. (In Russ.) Available at: https://patents.google.com/patent/RU2006100036A/en

35. Kuznetsova N. A., Chaltseva T. V., Norkina R. N., … Koroleva N. A. *Negative photoresist for "explosive" photolithography*. Patent RF, no. 2017103195. Publ. 22.03.2018, bull. no. 9. Available at: https://patents.google.com/patent/RU2648048C1/en

36. Lemaire P. C., Oldham C. J., Parsons G. N. Rapid visible color change and physical swelling during water exposure in triethanolamine-metalcone films formed by molecular layer deposition. *Journal of Vacuum Science & Technology A: Vacuum. Surfaces. and Films*. 2016;34(1): 01A134. https://doi.org/10.1116/1.4937222

37. Dutta S., Karak N. Synthesis. Characterization of poly(urethane amide) resins from nahar seed oil for surface coating applications. *Progress in Organic Coatings*. 2005;53(2): 147–152. https://doi.org/10.1016/j.porgcoat.2005.02.003

38. Ashraf S. M., Ahmad S., Riaz U. Development of novel conducting composites of linseed-oil-based poly(urethane amide) with nanostructured poly(1-naphthylamine). *Polymer International*. 2007;56(9): 1173–1181. http://dx.doi.org/10.1002/pi.2265

38. Yadav S., Zafar F., Hasnat A., Ahmad S. Poly (urethane fatty amide) resin from linseed oil – a renewable resource. *Progress in Organic Coatings*. 2009;64(1): 27–32. https://doi.org/10.1016/j.porgcoat.2008.07.006

39. Lee C. S., Ooi. T. L., Chuah C. H., Ahmad S. Rigid polyurethane foam production from palm oil-based epoxidized diethanolamides. *Journal of the American Oil Chemists' Society*. 2007;84: 1161–1167. https://doi.org/10.1007/s11746-007-1150-5

40. Palanisamy A., Rao. B. S., Mehazabeen S. Diethanolamides of castor oil as polyols for the development of water-blown polyurethane foam. *Journal of Polymers and the Environment*. 2011;19: 698–705. https://doi.org/10.1007/s10924-011-0316-2

41. Shkop A., Tseitlin M., Shestopalov O. Exploring the ways to intensify the dewatering process of polydisperse suspensions. *Eastern-European Journal of Enterprise Technologies*. 2016;6(10 (84)): 35–40. https://doi.org/10.15587/1729-4061.2016.86085

42. Averkina E., Shakirova E., Butakova L. Influence of flocculant reagents on the parameters of clay suspensions. *Earth Sciences and Subsoil Use*. 2020;43(2); 230–241. https://doi.org/10.21285/2686-9993-2020-43-2-230-241

Information about the authors

Dmitriy Yu. Vandyshev, Cand. Sci. (Chem.), Associate Professor of the Department of Organic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0001-8606-458X
francy_2007@mail.ru

Olga V. Sleptsova, Cand. Sci. (Chem.), Associate Professor of the Department of High Molecular Compounds and Colloidal Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0009-0006-7467-275X
slepts@gmail.com

Vladislav Yu. Gazin, Master's student of the 2nd year of the Department of Organic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0009-0009-4000-6638
gazin2000@gmail.com

Stanislav A. Malyutin, Cand. Sci. (Tech.), General Director of JSC Petrochem (Belgorod, Russian Federation).

https://orcid.org/0009-0006-0572-8545
malyutin@petrohim.ru

Naum R. Malkin, Chief Technologist of JSC Petrochem (Belgorod, Russian Federation).

https://orcid.org/0009-0006-9744-3044
n.malkin@petrohim.ru

Khidmet S. Shikhaliev, Dr. Sci. (Chem.), Professor, Head of the Department of Organic Chemistry, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-6576-0305
shikh1961@yandex.ru

Received 27.01.2023; approved after reviewing 07.03.2023; accepted for publication 15.04.2023; published online 25.09.2023.

Translated by Dmitriy Vandyshev