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THE EFFECT OF POLYELECTROLYTES OBTAINED ON THE BASIS OF ALLYL ALCOHOL AND ACRYLIC ACID DERIVATIVES ON THE STABILITY OF BENTONITE HYDRODISPERSION

Abstract. In connection with the increasing use of polyelectrolytic types of water-soluble polymers in various spheres of life, scientific and experimental work has become one of the most relevant problems of our time. In this regard, the needs for regulating the properties of polyelectrolytes are increasing. The properties of polyelectrolytes vary depending on the nature of its functional groups, ionization capacity. Therefore, the solution of these key problems from a scientific and practical point of view, that is, the regulation of the properties of polyelectrolytes in the target direction is carried out by converting a number of functional groups by polymeranalogical reaction with copolymerization of links-monomers differing in functional groups in different mole ratios. For this reason, allyl alcohol (AA), which had a strong non-ionizing hydrophilic functional group stable to the effect of the ionic strength of the external environment, pH and a tendency to react with dispersing systems, was copolymered in the optimal way determined in an aqueous medium with a high ability to enter into a chemical reaction, nitrylacrylic acid (NA) or acrylamide (AA) in different mole ratios. The results of the experiment showed that the yield and some chemical properties of copopolymerization products change depending on the mole ratio of the joints –monomers obtained for the reaction.

Keywords: allyl alcohol, nitrylacrylic acid, acrylamide, copolymerization, viscosity.

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Introduction. Due to the fact that polyelectrolytic types of water-soluble polymers are increasingly used in various fields of production, agriculture, and life, conducting scientific and experimental work aimed at obtaining new types of them, identifying areas of application has become one of the most relevant tasks of our time [1]. In this regard, the need for targeted regulation of polyelectrolytes' properties is increasing, depending on the direction of their application. Basically, the properties of polyelectrolytes vary depending on the nature, types, degree of hydrophilicity and ionization capacity of the active functional groups of the joints included in its composition [2]. Therefore, the solution of these key problems from a scientific and practical point of view, that is, the regulation of the properties of polyelectrolytes in the target direction is carried out by converting a number of functional groups by polymeranalogical reaction with copolymerization of links-monomers differing in functional groups in different mole ratios. For this reason, allyl alcohol (AA), which was resistant to the influence of the ionic force of the external environment, the pH index and had a strong tendency to interact with dispersed systems, was copolymerized in an optimal way, determined in an aqueous medium, with nitrilacrylic acid (NA) or acrylamide (AA), containing a functional group with a high ability to enter into a chemical reaction.

Materials and methods. Materials: Allyl alcohol for synthesis (sigma-aldrich). CAS No. 107-18-6, EC Number 203-470-7. Vapor pressure 24.3 hPa (20°C), Quality Level-200, form-liquid, autoignition temp-375°C, potency-64 mg/kg LD50, oral (Rat), expl. lim.-2.5-18 % (v/v), bp-97°C/1013 hPa, mp-129°C, transition temp-flash point 22°C, density-0.85 g/cm^3 at 20°C.

Acrylonitrile for synthesis (sigma-aldrich). Vapor pressure-124 hPa (20°C), quality Level-200, assay≥99% (GC), form-liquid, autoignition temp-480°C, potency-78 mg/kg LD50, oral (Rat), expl. Lim-2.8-28% (v/v), pH-6.0-7.5 (20°C, 50 g/L in H2O), bp-77.3°C/1013 hPa, mp-83.55°C.

Acrylamide for synthesis (sigma-aldrich). Vapor pressure-0.009 hPa (25°C), quality Level-200, assay≥99% (GC), form-solid, autoignition temp-424°C, potency-177 mg/kg LD50, oral (Rat),1141 mg/kg LD50, skin (Rabbit), pH-5.0-7.0 (20°C, 50 g/L in H2O), bp-125°C/33.3 hPa, mp-84°C, transition temp-flash point 138°C.

Methods: Ph meter (sigma-aldrich). Manufacturer/tradename-Oakton, measuring range-0-50°C, accuracy: 1°C (ATC), pH measuring range-0.00-14.99 pH unit, accuracy: 0.01 pH unit, resolution: 0.01 pH unit. Features toggle readout of pH and temperature. Waterproof with unique double junction electrode design that is ideal for most applications including tris buffers, organics, solutions with heavy metals, sulfides, and dirty water. Push-button three-point calibration, 4.01, 7.00, 10.00. Double-junction gel pH electrode. Powered by four 1.5V alkaline batteries.

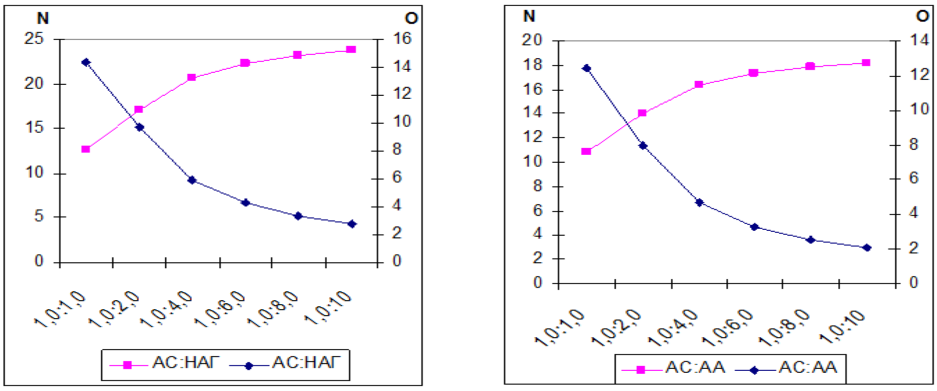
Viscosity (sigma-aldrich). Grade-certified reference material, quality Level-100, shelf life-limited shelf life, expiry date on the label, packaging-pkg of 18 × 500 mL, manufacturer/tradename-Paragon Scientific Ltd, application(s)-cleaning products, cosmetics, flavors and fragrances, food and beverages, personal care.

The regulation of the properties of polyelectrolytes in the target direction is carried out by converting a number of functional groups by polymeranalogical reaction with copolymerization of links-monomers differing in functional groups in different mole ratios. For this reason, allyl alcohol (aa), which was resistant to the influence of the ionic force of the external environment, the pH index and had a strong tendency to interact with dispersed systems, was copolymerized in an optimal way, determined in an aqueous medium, with nitrilacrylic acid (NAC) or acrylamide (AA), containing a functional group with a high ability to enter into a chemical reaction.

Preparation of copolymerization. Copolymerization preparation was prepared by adding a mole ratio of 1.0 Mol to 2.0 Mol of nitryl acrylamide (NA) or acrylamide (AA) to 1.0 Mol of allyl alcohol (AC). A polymeranalogical reaction was carried out to obtain a water-soluble polymer with polyelectrolytic properties from the resulting copolymerization products.

Research results and discussion. The yield of the copopolymerization product, formed mainly by an increase in allyl alcohol in the composition of the reaction mass, is somewhat decreasing. The optimal mole ratio for which the highest yield is formed begins when 2.0 moles of nitrylacrylacid (NA) or acrylamide (AA) per 1.0 moles of allyl alcohol (AC). With a change in the mole ratio of the reacting monomers, the chemical composition of the macromolecule of copolymerization products differs from each other. At the same time, the content of nitrogen,oxygen in the composition of the macromolecule of the copolymerization product also changes (Fig. 1a, b).

The results of the findings show that with an increase in the content of copolymerization products of nithyracryl or acrylamide, the nitrogen content increases and the oxygen content decreases. With an increase in allyl alcohol in the reaction mass, a decrease in the yield of copolymerization products and partial differences in the amount of nitrogen and oxygen found by theoretical and experimental methods occur due to the weak ability of the allyl alcohol link to form a radical and cause a faster break of the growing radical. Thus, as the content of the macromolecule of the copolymerization product formed by allyl alcohol increases, the viscosity (η) with the chemical property of their solution in water also changes somewhat . This is evidenced by the change in the specific (pmsh), given viscosity (pcelt), optical density (E), electrical conductivity (χ), and PH indicators of copolymerization products of acrylamide with allyl alcohol based on the concentration of the solution. That is, the fact that the polyelectrolytic properties of these copolymerization products are very weak can be seen from the small electrical conductivity.

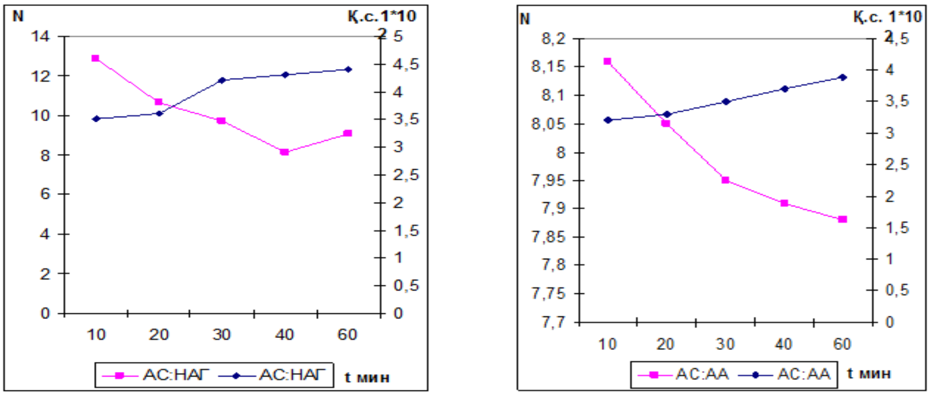


a) b)

Fig. 1. Changes in the content of nitrogen(N) and oxygen (O) in copolymerization products depending on the Mole ratio of compounds in the macromolecule (AC:NAG-a, AC:AA-B)

Therefore, a polymeranalogical reaction was carried out to obtain a water-soluble polymer with polyelectrolytic properties from the resulting copolymerization products. As a result, samples of polyelectrolyte containing a functional group that had different chemical properties were obtained on the basis of a product of copolymerization of nitrylacrylic acid or acrylamide with allyl alcohol. The composition of functional groups of these polyelectrolyte samples, the ratio of which varies depending on the time of the polymeranalogical reaction.This change in the functional groups of polyelectrolyte samples was explained by the quantitative values of the acid number (A.n) , nitrogen content (N%) determined by the method known from the literature of water-soluble polymers [3]. Basically, as the polymeranalogical reaction is carried out,the nitrogen content of the copolymerization product (N%) decreases, and the acid content (A.n) increases (Fig. 2a, b). At the same time, their polyelectrolytic properties differ to a certain extent from each other. It can be observed from the change in the quantitative values of the measured viscosity (pcelt) and electrical conductivity(χ) found by looking at the concentration of the solution.

These differences occur due to the gradual transition of the functional groups of nitrogen, nitrile, imide and amide in the composition of copolymerization products to the carboxide group with an increase in the time of the polymeranalogical reaction. The differences in the chemical properties of the obtained polyelectrolyte samples were also clarified by determining the effect on the stability of bentonite hydrodispersion.As can be seen from the results of the experiment, it is easy to see that the stability of bentonite hydrodispersion also depends on the concentration of solutions of added polyelectrolyte samples and the time of polymeranalogical reaction of these samples.

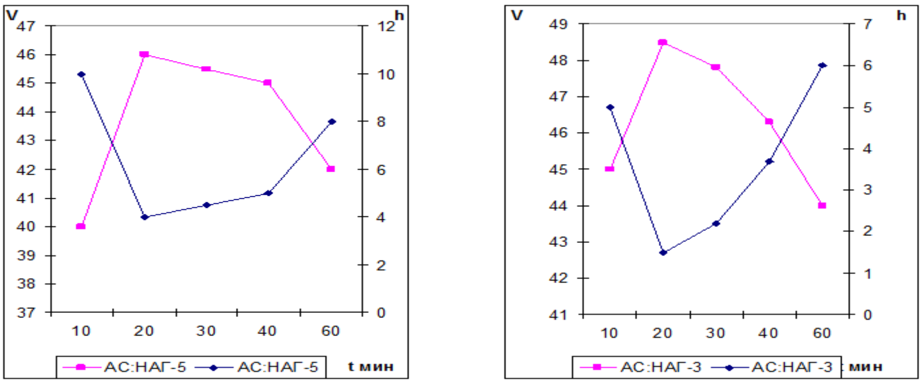


a) b)

Fig. 2. Changes in the nitrogen content (N) and acid number (A.n) of samples of copolymerization products in the ratio of 1.0:4.0 moles depending on the time of polymeranological reaction (AC: Nag-A, AC: AA-B)

It can be observed by the quantitative values of the sediment volume (Vml) and the released liquid (h), which change in the presence of solutions of polyelectrolyte samples of the same concentration of bentonite hydrodispersion. It is observed that the stability of bentonite hydrodispersion increases somewhat with a decrease in the amount of nitrogen, mainly due to an increase in the number of acids contained in the attached polyelectrolyte samples. It is not difficult to see that a polyelectrolyte sample with the highest stabilizing ability is formed when the polymeranological reaction time ranges from 15 to 25 minutes. The reason for this is that by the time of conducting a polymeranological reaction, the composition of the polyelectrolyte macromolecule formed mainly leads to a change in the functional groups of the carboxide, amide. Therefore, the increase in the carboxylic functional group along the macromolecule chain initially ensures that the conformational state of the macromolecule passes into a written form.

For this reason, bentonite has a positive effect on increasing their stability due to an increase in the ability to interact with hydrodispersion particles. It, in turn, increases the compatibility of the solid phase of bentonite hydrodispersion and the liquid medium. Due to this, the separation of a liquid medium from a solid phase slows down,that is, the stability of hydrodispersion reaches a high level (Fig. 3a, b).

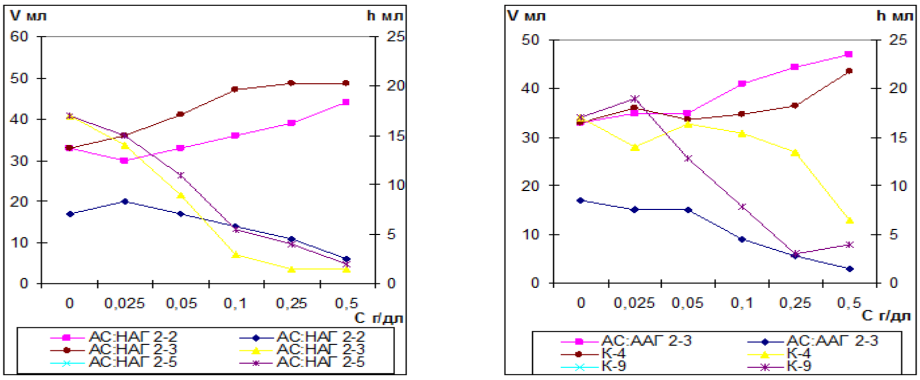


a) b)

Fig. 3. Change of bentonite hydrodispersion 0.25% in the presence of asnag-3,asnag-5 polyelectrolyte samples after one day of precipitation (V) and the volume of released liquid (H) by the time of polymeranological reaction (AC: nag-3-A, AC: nag-5-B)

It can be observed from the change in the quantitative values of the sediment volume and the height of the released liquid (h) in the presence of samples of polyelectrolyte asnag-3, ASNAG-5 of the same concentration of bentonite hydrodispersion.Such a change in the stability of bentonite hydrodispersion in the presence of polyelectrolyte samples as:Nag-3 as:Nag-5 is associated with an increase in the negative charge of the macromolecule of copolymerization products due to an increase in the density of the carboxylic functional group along the chain, which increases with an increase in the polymeranalogical reaction time.Because, as the density of a carboxylic functional group with sufficient dissociating ability of a negative charge increases along the macron chain, it becomes more difficult to form bonds by interacting with bentonite particles with a negative charge [4]. As a result, the hydrophilation of the surface part of small bentonite particles is somewhat reduced. For this reason, the process of stabilization of bentonite hydrodispersion is also not significantly ensured. Thus, as the time of a number of polymeranalogical reactions increases, the number of nitrile, imide, amide groups along the macro chain, which are stable under the influence of the external environment and have a good ability to form bonds with bentonite fine particles, and the increase in the carboxylic functional group increases the tendency of the macromolecule to go into a wrapped form due to increased conformational instability under the influence of the external environment [5].

Therefore, the hydrophilizing property of the surface part of bentonite particles of the polyelectrolyte macromolecule is also weakened. This, in turn, leads to a significant decrease in the ability of polyelectrolyte samples with a high polymeranalogical reaction time to regulate the stability of bentonite hydrodispersion. It is shown by the change in the volume of sediment and the height of the released liquid (h), determining the separation of the solid phase of bentonite hydrodispersion from the system in the presence of polyelectrolyte samples that differ in the time of the polymeranalogical ReAction (Figure-3A, B). Basically, as the stability of bentonite hydrodispersion increases, the height of the liquid separating from the solid phase of the system decreases. The decrease in the process of separation of the liquid medium from each other with the solid phase of bentonite hydrodispersion is associated with an increase in its stability. The regulation of the stability of bentonite hydrodispersion affects to some extent not only the composition of the functional groups of polyelectrolyte samples, but also the concentration of their solutions. For this purpose, changes in the stability of bentonite hydrodispersion in the presence of different concentrations of solutions of asnag2-3 asnag2-5 and ASAAG2-3 polyelectrolyte samples obtained by polymeranalogical reaction of copolymerized products in the optimal mole ratio were studied. The results of the experiment show that the stability of bentonite hydrodispersion varies per unit of time depending on the volume of the solid phase and the height of the liquid. Changes in the numerical values of these measurements showed that the separation of the two phases occurs rapidly, since the stability of the bentonite hydrodispersion is insufficient without the addition of polyelectrolytes. The process of separation of the phases of the dispersion system initially proceeds at an accelerated pace, even with a small concentration of added polyelectrolyte solutions. This is due to the fact that during periods of low concentration of polyelectrolytes, the process of Flocculation in the system takes precedence [6]. This is due to the fact that individual types of macromolecules are enlarged, forming a relationship with small particles of the dispersion phase. As a result, the separation of large and hydrophobized units from the system is accelerated [7]. As a result , at these concentrations, the optical density (E) of the liquid on the surface of the precipitate is also lower, that is, the degree of transparency is higher, in the same series with the acceleration of the separation of the dispersion phase from the liquid medium. With an increase in the concentration of added polyelectrolyte samples, the separation of the dispersion phase and the dispersion medium from each other gradually decreases,and the process of complete separation from a certain concentration stops (Fig. 4 a, b).



a) b)

Fig. 4. Change in bentonite hydrodispersion after a day depending on the concentration of the added polyelectrolyte solution of the precipitate(V) and the volume of the released liquid (h)

In this interval, the dispersion moves to the highest level of optical density (D), along with the fact that the height of the released liquid (h) in the surface part of the phase has the lowest numerical value. This is due to the increased stability of the system. However, the ability of bentonite hydrodispersion to high stability and the concentration required for it are closely related to the chemical composition of the functional group of polyelectrolyte samples. The ability to ensure maximum stability is shown by the samples ASNAG2-3 and ASNAG2-5 obtained in an optimal way (Fig.4a). In comparison, differences in the ability to regulate the stability of bentonite hydrodispersion occur due to the presence of a nitrile and hydroxide functional group in the macromolecule of ASNAG2-3 ASNAG2-5 polyelectrolyte samples compared to ASNAG2-3, K-4 polyelectrolyte. It is not difficult to see that these identified patterns are observed even when the regulation of the stability of bentonite hydrodispersion in the presence of studied polyelectrolyte samples is studied by changes in the relative filtration rate (Urel). In addition, when analyzing the numerical values of the optical density (e), viscosity (η), electrical conductivity (χ), pH of the filtered liquid medium, it makes it possible to make an assumption that the interaction of fine bentonite particles with the macromolecule of polyelectrolyte samples occurs by a homogeneous mechanism. This is due to the fact that the functional groups of the studied polyelectrolyte samples are homogeneous in nature and chemical composition, although they differ slightly in their ratio. Thus, through the conducted research, new polyelectrolyte samples used in the regulation of the stability of bentonite hydrodispersion were obtained, and by comparing its stabilizing properties, it was found that their effectiveness is 2-2.5 times higher than that of K-4,K-9 polyelectrolytes, which are currently produced in industrial conditions and widely used in practice, and the causal effects of its occurrence were explained by the method of examination of the results presented in the work.

Conclusion. The stability of bentonite hydro-dispersion of polyelectrolytes obtained on the basis of allyl alcohol and acrylic acid derivatives has been successfully synthesized by copolymerization. The results of the experiment showed that the yield and some chemical properties of copopolymerization products change depending on the mole ratio of the joints –monomers obtained for the reaction. It can be clearly seen that the copolymerization product of nitrylacrylic acid with allyl alcohol is insoluble in water. The yield of the copopolymerization product, formed mainly by an increase in allyl alcohol in the composition of the reaction mass, is somewhat decreasing. The regulation of the properties of polyelectrolytes in the target direction was carried out by converting a number of functional groups by copolymerization of binder-monomers that differ in different mole ratios in functional groups by means of a polymeranalogical reaction. As a result, samples of polyelectrolyte with a functional group with various chemical properties were obtained based on the product of copolymerization of nitrylacrylic acid or acrylamide with allyl alcohol.

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АЛЛИЛ СПИРТІ МЕН АКРИЛ ҚЫШҚЫЛЫНЫҢ ТУЫНДЫЛАРЫ НЕГІЗІНДЕ АЛЫНҒАН ПОЛИЭЛЕКТРОЛИТТЕРДІҢ БЕНТОНИТ ГИДРОДИСПЕРСИЯСЫНЫҢ ТҰРАҚТЫЛЫҒЫНА ӘСЕРІ

Аңдатпа. Суда еритін полимерлердің полиэлектролиттік түрлерін өмірдің әртүрлі салаларында қолданудың артуына байланысты ғылыми-тәжірибелік жұмыстар біздің заманымыздың өзекті мәселелерінің біріне айналды. Осыған байланысты полиэлектролиттердің қасиеттерін реттеу қажеттілігі артып келеді. Полиэлектролиттердің қасиеттері оның функционалдық топтарының сипатына, иондану қабілетіне байланысты өзгеріп отырады. Сондықтан, осы негізгі мәселелерді ғылыми-практикалық тұрғыдан шешу, яғни полиэлектролиттердің қасиеттерін мақсатты бағытта реттеу полимераналогиялық реакция арқылы бірқатар функционалдық топтарды түрлендіру арқылы жүзеге асырылады. Функционалдық топтарда әртүрлі мольдік қатынаста ерекшеленетін байланыстырушы-мономерлердің сополимерленуі жүзеге асырылды. Осы себепті сыртқы ортаның иондық беріктігінің, рн-ның және дисперсиялық жүйелермен әрекеттесу үрдісінің әсеріне тұрақты күшті иондfestбайтын гидрофильді функционалдық тобы бар аллил спирті (АА) сополимерленген. Химиялық реакцияға, нитрилакрил қышқылына (NA) немесе акриламидке (АА) әртүрлі мольдік қатынаста түсу қабілеті жоғары сулы ортада оңтайлы түрде анықталады. Тәжірибе нәтижелері көрсеткендей, сопополимерлену өнімдерінің шығымдылығы мен кейбір химиялық қасиеттері реакция үшін алынған буын –мономерлердің мольдік қатынасына байланысты өзгереді.

Тірек сөздер: аллил спирті, нитрилді акрил қышқылы, акриламид, сополимерлену, тұтқырлық.

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ВЛИЯНИЕ ПОЛИЭЛЕКТРОЛИТОВ, ПОЛУЧЕННЫХ НА ОСНОВЕ ПРОИЗВОДНЫХ АЛЛИЛОВОГО СПИРТА И АКРИЛОВОЙ КИСЛОТЫ, НА СТАБИЛЬНОСТЬ ГИДРОДИСПЕРГИРОВАНИЯ БЕНТОНИТА

Аннотация. В связи с ростом использования полиэлектролитных форм водорастворимых полимеров в различных сферах жизни научно-практические работы стали одной из актуальных проблем современности. В связи с этим возрастает необходимость регулирования свойств полиэлектролитов. Свойства полиэлектролитов различаются в зависимости от характера их функциональных групп, способности к ионизации. Поэтому научно-практическое решение этих основных задач, то есть целенаправленная регуляция свойств полиэлектролитов, осуществляется путем преобразования ряда функциональных групп посредством полимераналогической реакции. В функциональных группах осуществлялась сополимеризация связывающих мономеров, различающихся в различных родильных отношениях. По этой причине сополимеризуется аллиловый спирт (АА) с сильной неионизирующей гидрофильной функциональной группой, устойчивой к влиянию ионной силы внешней среды, рн и тенденции взаимодействия с дисперсионными системами. Способность вступать в химическую реакцию, нитрилакриловую кислоту (NA) или акриламид (АА) в различных мольных соотношениях оптимально определяется в водной среде с высоким содержанием молей. Результаты эксперимента показали, что выходы и некоторые химические свойства продуктов сополимеризации изменяются в зависимости от Молевого соотношения соединений – мономеров, полученных для реакции.

Ключевые слова: аллиловый спирт, нитрилакриловая кислота, акриламид, сополимеризация, вязкость.