



Synthesis And Characterization Of Granular Ion Exchangers Based On Acrylonitrile Copolymers

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Abstract

This work presents the results of the synthesis of granular copolymers of acrylonitrile with hexahydro-1,3,5-triacrylyl triazine and their modification with organic amines, in particular diethylamine, as well as a study of the physicochemical characteristics and sorption properties of the obtained ion exchangers. The result of the study was the synthesis of granular ion exchangers with the necessary physicochemical properties based on acrylonitrile and divinylbenzene, N,N'-methylene-bis-acrylamide and hexahydro-1,3,5-triacrylyl triazine, the kinetics of this process was studied. The synthesized copolymers were modified with diethylamine, the physicochemical and ion-exchange properties of the obtained polymers were studied. It has been shown that acrylonitrile, its copolymers coated with divinylbenzene, N,N'-methylene-bis-acrylamide and hexahydro-1,3,5-triacrylyl triazine, as well as granular ion exchangers based on them, can be obtained. For the first time, copolymers of acrylonitrile and hexahydro-1,3,5-triacrylyl triazine with the necessary physicochemical characteristics were synthesized and, on their basis, conditions for obtaining weak anion-exchange resins on a complex basis were developed. The synthesized anion exchangers have complexing properties and can be used in the hydrometallurgy of non-ferrous and heavy metals, purification of waste water from toxic ions, separation and concentration of metal ions.

Key words: acrylonitrile; divinylbenzene; N,N'-methylene-bis-acrylamide; hexahydro-1,3,5-triacrylyl triazine; soluble copolymers; ion exchangers

Abbreviations:

CAGR - compound annual growth rate
GTT - hexahydro-1,3,5-triacrylyl-s-triazine;
AN - acrylonitrile;
DVB - divinylbenzene;
MBA - N,N'-methylene-bis-acrylamide;
DAC - 2,2'-azo-bis-isobutyronitrile;
DEA - diethylamine sulfate salt;
DMF - dimethylformamide;
SOC - sorption capacity

1- INTRODUCTION.

The global acrylonitrile market size was valued at USD 11.8 billion in 2019 and is anticipated to register a revenue-based CAGR of 4.3% from 2020 to 2027. The increasing demand for acrylic fibers

manufactured from acrylonitrile is expected to drive the market over the forecast period. Acrylonitrile is also one of the primary raw materials in the production of plastics and composites, which is further anticipated to propel its global demand [1]. For the synthesis of ion exchangers, the suspension copolymerization of acrylonitrile (AN) with crosslinking agents is widely used [2, 3]. Acrylonitrile ionites are obtained with crossing it with hexamethylenedimetalacrylamide, diallylfthalate, divinylbenzene (DVB), N,N'-methylene-bis-acrylamide (MBA), hexahydro-1,3,5-triacrylotriazine (GTT), etc [4-7]. In the literature, many are described synthesis and study of acrylonitrile copolymers with various crosslinking agents, aimed at obtaining ion exchangers for various cations and anions [2, 8-12],

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membranes for different substances [13-16], various hydrogels [17], polyelectrolytes [18], superabsorbents [19], materials for medical purposes [20-24], composite materials and etc [25, 26]. And the kinetics and mechanisms of the acrylonitrile reaction with different agents under conditions of radical and ion copolymerization are studied in detail and systematized [27-30].

The review of literature data shows that many work with acrylonitrile are devoted to obtaining fibrous sorbents, as working with directly with acrylonitrile is intensified with its high toxicity, and therefore many researchers prefer to work with a finished polyacrylonitrile products [12, 14, 15, 19, 29]. In practice, there is a high need for granular sorbents, since their physicochemical and performance characteristics make it possible to use in various sectors of the national economy.

Copolymers of acrylonitrile with divinylbenzene have recently become one of the most widespread frameworks for the synthesis of ion exchangers [5]. Unlike other carcasses with a chemical composition, they differ in the degree of stickiness, the ability to control porosity and suitability for various chemical reactions. Improvement of methods for the synthesis of porous structural and known structural sorbents based on acrylonitrile is one of the urgent tasks today. The scientific novelty of the research is the development of conditions for obtaining weakly basic anion-exchange resins based on copolymers of acrylonitrile and hexahydro-1,3,5-triacrylyl triazine with specified physicochemical characteristics. The synthesized anion exchangers have complexing properties and can be used in the hydrometallurgy of non-ferrous and heavy metals, purification of waste water from toxic ions, separation and concentration of metal ions.

It is known that the physicochemical characteristics and sorption properties of modified polymer sorbents depend on the structure of the macrochain, the structure of the binding agent molecule, and the nature of the functional groups. In this regard, it is of great interest to study the process of copolymerization of acrylonitrile with a hexahydro-1,3,5-triacrylyl triazine binder containing three vinyl groups.

Copolymers of acrylonitrile with divinylbenzene are well documented in the literature. However, although the study of AN-MBA copolymerization is of theoretical and practical importance, the results of studying the kinetic aspects of this system are hardly covered in the scientific literature. During the study, the most important aspects of suspension copolymerization of MBA with acrylonitrile were studied.

This work presents the results of the synthesis of granular copolymers of acrylonitrile with hexahydro-1,3,5-triacrylyl triazine and their modification with organic amines, in particular diethylamine, as well as a study of the physicochemical characteristics and sorption properties of the obtained ion exchangers.

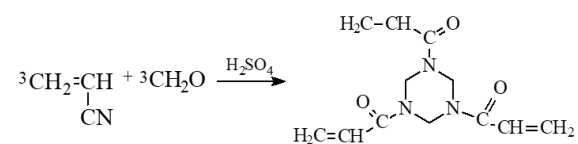
The subject and objects of research were chosen: the study of the kinetics of the synthesis of donor ion exchangers with the necessary physicochemical properties based on acrylonitrile and divinylbenzene, N,N'-methylene-bis-acrylamide and hexahydro-1,3,5-triacrylyl triazine, modification of the obtained copolymers with diethylamine and study of the physicochemical and ion-exchange properties of the obtained polymers. Investigation of the properties of acrylonitrile, its copolymers coated with divinylbenzene, N,N'-methylene-bis-acrylamide and hexahydro-1,3,5-triacrylyl triazine, and preparation of granular ion exchangers based on them.

EXPERIMENTAL PART.

Synthesis of hexahydro-1,3,5-triacrylyl triazine.

The synthesis of the precipitating agent hexahydro-1,3,5-triacrylyl-s-triazine (GTT) was carried out as follows: 150 ml of acrylonitrile (AN) and 15 ml of concentrated H₂SO₄ in a three-necked flask, equipped with a mechanical stirrer, reflux and dropping funnel. The mixture was heated to 70 °C and a suspension of 90 g of paraform and 350 ml of AN was added dropwise over 1 h without changing the temperature above 80 °C. At this time, the mixture was not heated. After adding the entire suspension, the reaction mixture is cooled and the resulting crystalline product is filtered from the ice-cooled solution. Then the crystals are washed with 500 ml of 1% NaOH solution, and then with distilled water. Dry weight of the product 148 g. The product was recrystallized from ethanol to obtain 129.5 g of hexahydro-1,3,5-triacrylyl triazine (product yield 52%).

It should be noted that hexahydro-1,3,5-triacrylyl-s-triazine polymerizes very easily even when boiled in alcohol or chloroform. A clear saturated solution of hexahydro-1,3,5-triacrylyl-s-triazine indicates the absence of polymer in the product. The reaction for obtaining a trifunctional monomer can be expressed as follows:



The formation of the coupling agent according to the above scheme was proved by obtaining the IR spectrum of the product. The IR spectrum of hexahydro-1,3,5-triacrylyl-s-triazine contains the following characteristic absorption bands. Absorption frequencies characteristic of stretching vibrations of the carbonyl group (-CO-) in the region of 1660 cm⁻¹, characteristic of stretching vibrations of the vinyl group (ν_c = c), C = C stretching vibrations of the methyl group at 1614 cm⁻¹, 2820 cm⁻¹ -2950 cm⁻¹ symmetric and asymmetric stretching vibrations (ν_s, ν_{as}), at 1000 cm⁻¹ the stretching vibrations of the -NCO- bond are clearly visible.

Synthesis of copolymers of acrylonitrile with divinylbenzene and N,N'-methylene-bis-acrylamide.

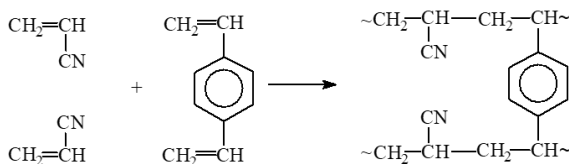
In the country, ion-exchange resins are actively used in thermal power plants, water treatment, food and pharmaceutical industries, etc. However, almost 100 % of the sorbents used are imported into our country. Therefore, the issue of industrial production of modern ion-exchange materials for various purposes and the production of new ion-exchangers with high performance characteristics is one of the most urgent tasks for replacing imported ones. Recently, ion exchangers based on acrylonitrile copolymers have been of great interest as an alternative to styrene-divinylbenzene sorbents. The reason divinylbenzene (DVB) was chosen as the coupling agent is because divinylbenzene rings provide copolymers with high levels of thermal stability and chemo-instability. An alternative DVB and a binding agent, N,N'-methylene-bis-acrylamide (MBA), can be easily synthesized from domestic reagents produced on an industrial scale at enterprises of the Republic of Uzbekistan.

In this study, copolymerization was carried out with the participation of an initiator 2,2'-azo-bis-isobutyronitrile (AIBN), which is insoluble in water, but well soluble in a mixture of monomers. DAC has the property of thermal homolytic decomposition in a monomer medium and can provide the required rate of decomposition to free radicals at temperatures of 323–343 K. A saturated aqueous solution of NaCl was used as a dispersion medium. This increases the ionic strength of the solution and also minimizes the solubility of acrylonitrile in water.

In suspension polymerization, there is an optimum bath modulus (volume ratio of monomer to aqueous phase) for each system. The amount of water practically does not affect the polymerization rate, but a significant decrease in the aqueous phase leads to a decrease in the stability of the dispersion. As the amount of water in the reaction mixture increases, the efficiency of the reactor decreases.

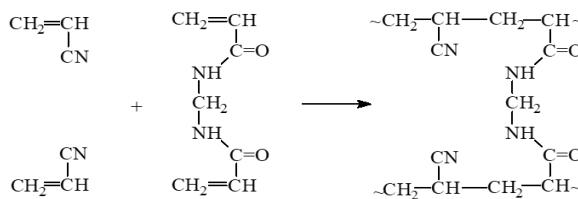
The experiments were carried out on water modules of reactions 1: 3, 1: 4 and 1: 5. The optimal water module was 1: 4, while the efficiency of the used reactor was maximum.

The reaction of copolymerization of AN and DVB and the approximate chemical structure of the copolymer AN-DVB can be represented by the following scheme:



The bond of the AN-MBA copolymer can be represented by a similar structure, except that the binding agent fragment becomes an MBA molecule

instead of a DVB molecule. The chemical structure of AN-MBA copolymer is as follows:



As a result of slurry copolymerization, the AN-DVB and AN-MBA copolymers consist of hard spherical grains, which very easily separate from the aqueous phase and settle to the bottom of the reactor.

RESULTS AND DISCUSSION.

Study of the kinetics of the suspension reaction of copolymerization of N,N'-methylene-bis-acrylamide with acrylonitrile. Copolymers of acrylonitrile with divinylbenzene are well documented in the literature. However, although the study of AN-MBA copolymerization is of theoretical and practical importance, the results of studying the kinetic aspects of this system are hardly covered in the scientific literature.

During the study, the most important aspects of suspension copolymerization of MBA with acrylonitrile were studied. It should be noted that the nature of copolymerization is important for the purposeful control of the physicochemical properties of the resulting product using various factors (reaction time, system temperature, the ratio of the starting monomers, etc.).

In fig. 1 shows the dependence of the copolymer yield on the reaction time. As can be seen from Fig. 1, the kinetic relationship is S-shaped, which indicates a spontaneous acceleration of the process. However, the product yield is practically independent of the composition of the monomer mixture obtained for the reaction, and a change in the amount of MBA in the mixture from 2.5 to 10 mol% does not lead to a large change.

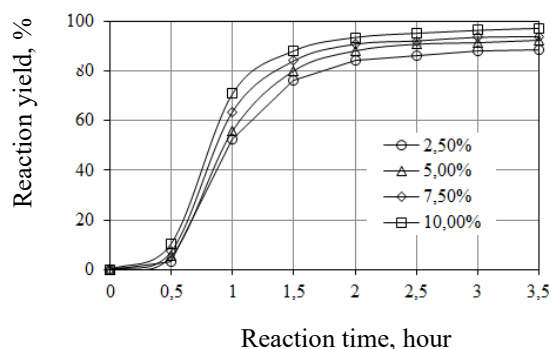


Fig. 1. Dependence of the yield of the copolymer AN-MBA on the reaction time. T = 343 K and [DAK] = 1 mass. %.

This indicates a high reactivity of MBA due to the presence of two unsaturated bonds in the studied system. A characteristic feature of the reaction is that

at all ratios of the initial mixture of monomers, a short induction period is observed, which is observed due to diffusion events during suspension polymerization.

The effect of the initiator concentration on the copolymer yield during copolymerization of AN with MBA was studied for 1 h at 343 K. The ratio of the mixture of monomers AN-MBA was 95.0: 5.0 mol%, the initiator concentration was 0.5-1.5 wt. was in the range of % (Fig. 2). As can be seen from Picture 2, the copolymer yield is 0.5-1.5 wt. From the concentration of the initiator, increases from 38.09 to 78.01% as the % range increases.

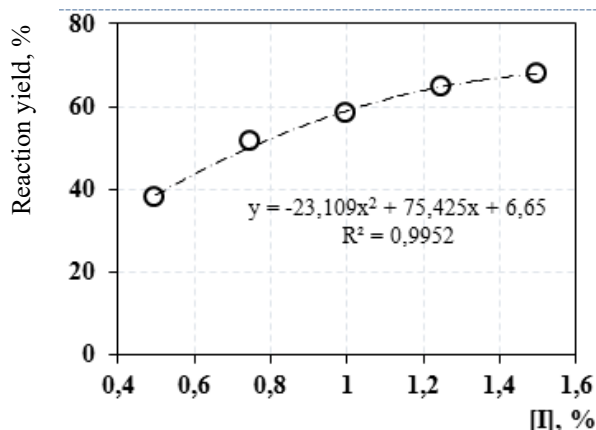


Fig. 2. Dependence of the yield of the copolymer AN-MBA on the concentration of the initiator. $\tau = 1$ hour

From the logarithmic dependence of the copolymerization rate on the DAC concentration (Fig. 3), the order of the reaction on the concentration of the initiator "n" was determined. The fact that the value of "n" is 0.62 indicates that the process under study is consistent with the laws of radical heterogeneous polymerization.

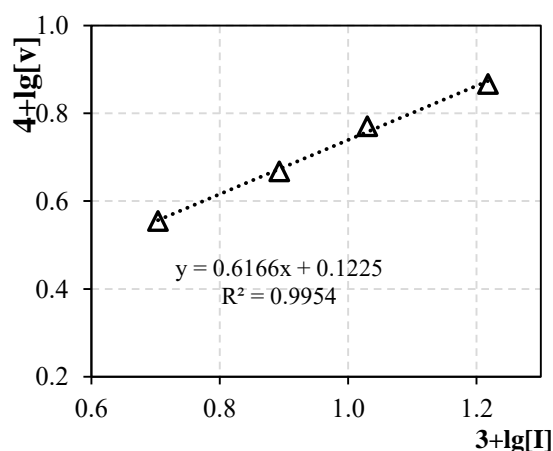


Fig. 3. Logarithmic dependence of the copolymerization rate on the concentration of AIBN.

These data are confirmed by the results of studying the effect of temperature in the range of 313-343 K

on the copolymerization of MBA with AN (Fig. 4). It has been found that the yield of the copolymer increases with increasing temperature.

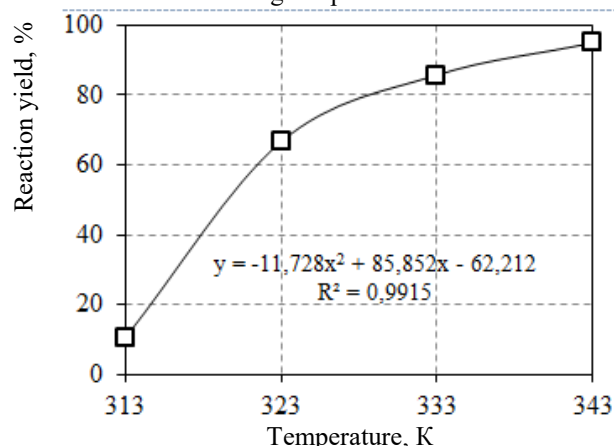


Fig. 4. Temperature dependence of the yield of the AN-MBA copolymer. $\tau = 1$ hour and $[DAC] = 1$ mass. %.

Based on the logarithmic dependence of the temperature value of the polymerization rate (Fig. 5), the value of the total activation energy of the process, calculated using the $E_{sum} = 2303 \cdot R \cdot \lg \alpha$, amounted to 65.65 kJ/mol, which corresponds to the usual laws of radical polymerization.

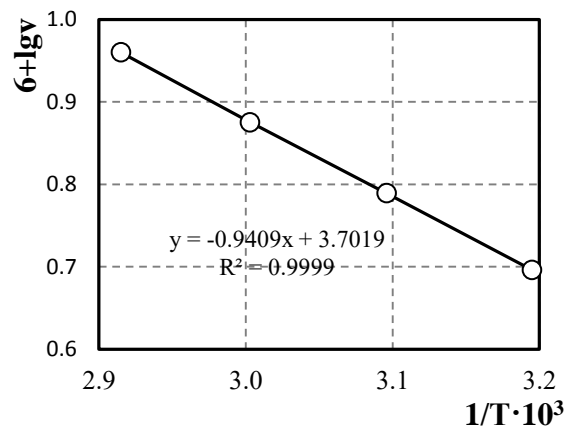


Fig. 5. Dependence of the copolymerization rate on the inverse reaction temperature. $\tau = 1$ hour and $[DAC] = 1$ mass. %.

Study of the process of suspension copolymerization of acrylonitrile with hexahydro-1,3,5-triacrylyltriazine.

Suspension polymerization of acrylonitrile with a binder hexahydro-1,3,5-triacrylyltriazine (GTT) in the presence of dinitrilazo-isoacid (1 wt% of the monomer mixture), the stabilizer is water-soluble starch (243 starch) in an aqueous saturated solution of NaCl). stirring speed 450-500 time/min, carried out by the suspension method for 5 hours at room temperature.

It is known that suspension copolymerization occurs under heterophase conditions. Copolymerization occurs in a monomer drop, which is soluble in its monomer and is formed in an aqueous organic solvent. The resulting granular copolymer is

insoluble in polyacrylonitrile solvents, indicating a bound structure.

The structure of the welded copolymer formed as a result of the interaction of the components can be described by the following scheme:

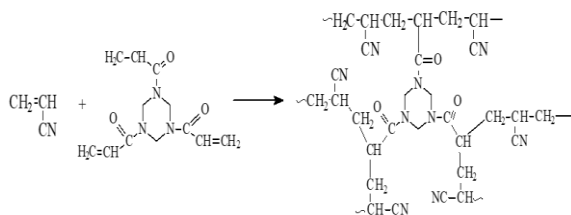


Table 1.
Influence of the amount of GTT on the copolymer yield

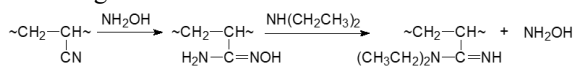
Components, wt%		Reaction time, hour.	[DAC], wt. %	Reaction temperature	Copolymer yield, %	Modified copolymer SOC si, mg-eq / g
AN	GTT					
97,5	2,5	5	1,0	70	28,6	3,85
97,0	3,0	5	1,0	70	47,3	3,36
95,0	5,0	5	1,0	70	60,5	2,52

Chemical modification of acrylonitrile copolymers with diethylamine.

The diethylamine sulfate (DEA) salt, neutralized to a slightly acidic medium, was used for chemical modifications. The reaction was carried out at 369–371 K for 5 h with the addition of 5 wt% DMF.

As a result of the interaction of the studied copolymers with DEA, it was noted that the maximum exchange rate of anion exchange resins did not exceed 0.3–0.5 meq / g, which indicates a very low rate of chemical change. Therefore, the catalytic effect of hydroxylamine was used in the amine reaction of previously observed fibrous polyacrylonitrile materials to increase the rate of conversion of cyanide groups into amide groups [31]. Granular copolymers of AN with MBA and HA with DVB were first treated with hydroxylamine and then reacted with DEA.

The reaction of chemical change of acrylonitrile bonds in the copolymer can be represented by the following scheme:



The previously introduced NH_2OH is released by reaction with DEA and amidine groups are formed. The presence of HA from the reaction medium after chemical changes was confirmed by a qualitative reaction with an aqueous solution of FeCl_3 . The anionites obtained by this method had an SOC of 5.2 (MBA with AN) and 7.0 (DVB with AN) meq / g, indicating that the chemical changes were at their maximum. Thus, the observed efficacy confirms that hydroxylamine has a catalytic effect on the amine reaction of granular soluble copolymers.

In pic. 6 shows the dependence of the SOC of anion exchanges on the concentration of DEA. The curves

Copolymers of hexahydro-1,3,5-triacrylyl-s-triazine with acrylonitrile are the first AN: GTT = 95: 5 monomers; 97: 3; and 97.5: 2.5% by weight. ratio.

The effect of the initial ratio of AN and GTT monomers on copolymerization is shown in Table 1. The data in Table 1 show that as the amount of GTT in the starting reaction mixture increases, the copolymer yield increases, indicating that the precipitating agent has a high reactivity in the test system.

in Picture 6 show that as the DEA concentration increases, the IEC SOC of the anion exchangers increases to 10% of the amine concentration. Higher concentrations lead to a decrease in the exchange capacity of the samples. At high DEA concentrations, the SOC value for both copolymers is practically the same.

The effect of temperature on anion exchange resins SOC was investigated in the range 323–388 K. The results are shown in Picture 7. As shown in Picture 7, samples based on copolymers AN:MBA and AN: DVB have a maximum SOC value of 368–370 K. Higher growth temperature leads to a significant decrease in the volume of exchange due to anionic groups formed as a result of hydrolysis.

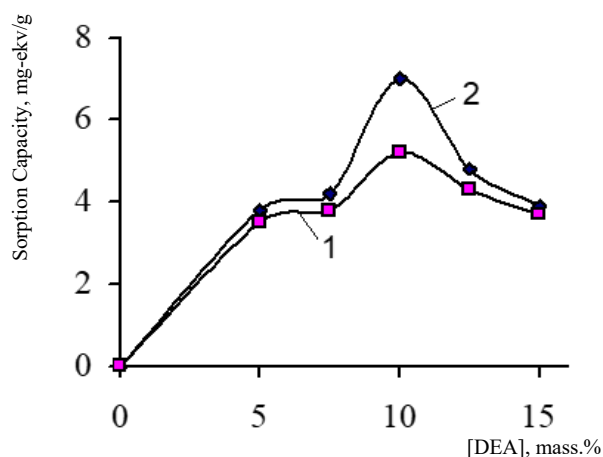


Fig. 6. Influence of DEA concentration on SOC of anion exchange resins based on AN: MBA (1) and AN: DVB (2) copolymers. VM = 1: 100, τ = 5 hours.

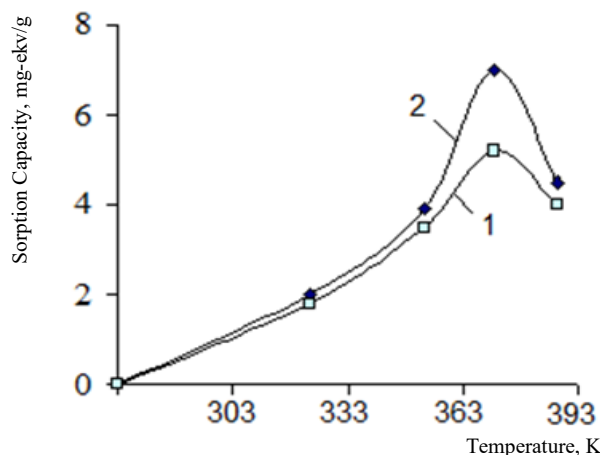


Fig. 7. Anion exchange resins AN: MBA (1) and AN: MBA (2) are temperature dependent VM = 1: 100, τ = 5 hours

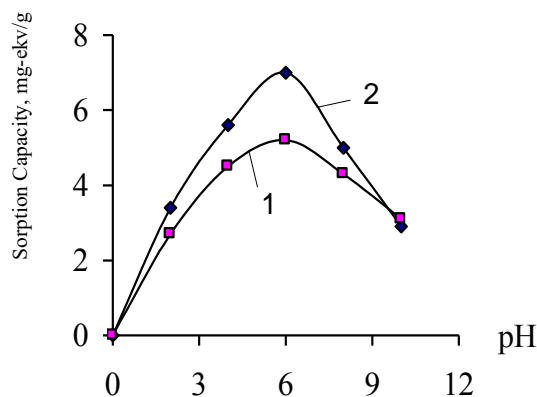


Fig. 9. Dependence on pH of anion exchange resins. 1-AN: MBA and 2-AN: DVB; T = 368 K, BM = 1: 100.

To study the effect of the reaction time on the exchange volume of the obtained anion exchangers, the modification process was carried out for 2-6 hours.

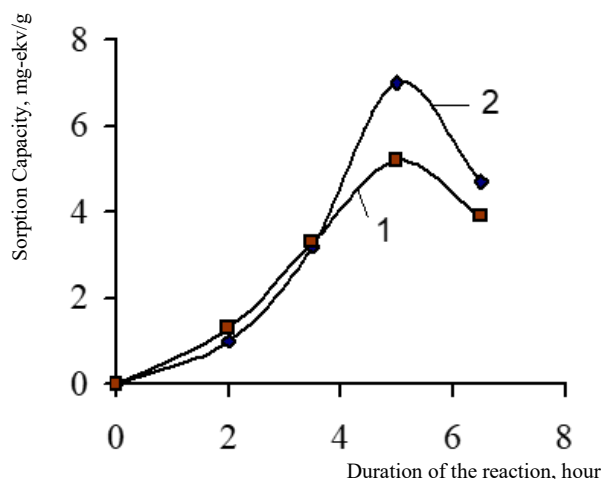


Fig. 8. Influence of the duration of the diethylation reaction on anion exchange resins. 1-AN: MBA and 2-AN: DVB; T = 368 K, BM = 1: 100.

The results obtained are shown in Picture 8. As can be seen from Pic. 8, as the reaction time increases, the exchange volume of the anion exchangers increases to 7.0 mEq / g as a result of a 5-hour reaction. When the reaction time exceeds 5 hours, the SOC value drops sharply, and as a result of the 6-hour reaction, the exchange rate decreases to 5.2 and 7.0 mEq / g, respectively, for AN:MBA and AN:DVB. copolymers. The results obtained show once again that the nitrile amination reaction continues until the formation of carboxyl groups.

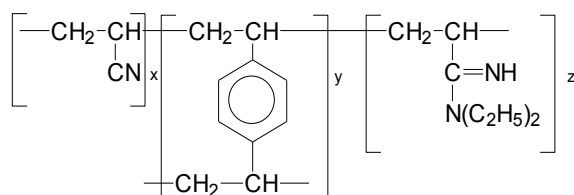
Experiments were carried out in the pH range 3–10 to determine the effect of ambient pH on the amine of AN: MBA and AN: DVB copolymers. The results obtained are shown in Figure 9. From the data presented in Figure 9, it can be seen that the optimal medium for anion exchange resin with DEA is a weakly acidic medium (pH = 5.5–6.5).

Developed ion exchange copolymers are investigated with an IR spectroscopic method. In the IR spectrum, stretching vibrations associated with the $-\text{CH}_2$ bond in the region of 2937 cm^{-1} , stretching vibrations associated with the $\text{C}\equiv\text{N}$ group in a field of 2242 cm^{-1} , and stretching vibrations associated with the CN bond in the field of 1651 cm^{-1} , 1452 cm^{-1} . In the region $-\text{CH}_2-$ bending vibrations associated with the bond are observed, in the region of 1361 cm^{-1} , stretching vibrations associated with the C-H (ring) bond are observed.

Figure 11 shows the results of potentiometric titration of AN: MBA: DEA (1) and AN: DVB: DEA (2) anions.

The direction of the curves indicates the formation of ion exchangers with weakly basic groups. The dissociation constants ($\text{pK} = 5.15$ and 5.30 ; $m = 1.44$ and 1.56) also confirm this.

Based on the data of IR spectroscopic and potentiometric titration of ion exchangers, the structure of the sorbent polymers can be represented by the following approximate scheme:



where: $z \gg x$.

CONFLICTS OF INTEREST.

There are no conflicts to declare.

CONCLUSIONS.

According to the results of the study, the following conclusions were made: Laws of suspension copolymerization of acrylonitrile with binders N,N'-methylene-bis-acrylamide, divinylbenzene and

hexahydro-1,3,5-triacrylyl triazine for the modification of acrylonitrile copolymers of donor sorbents. The possibility of obtaining granular copolymers with different physicochemical properties, depending on the amount of the binder and the reaction conditions, has been shown. It was found that increasing the amount of binder to 5% leads to a decrease in the SOC of copolymers modified with diethylamine.

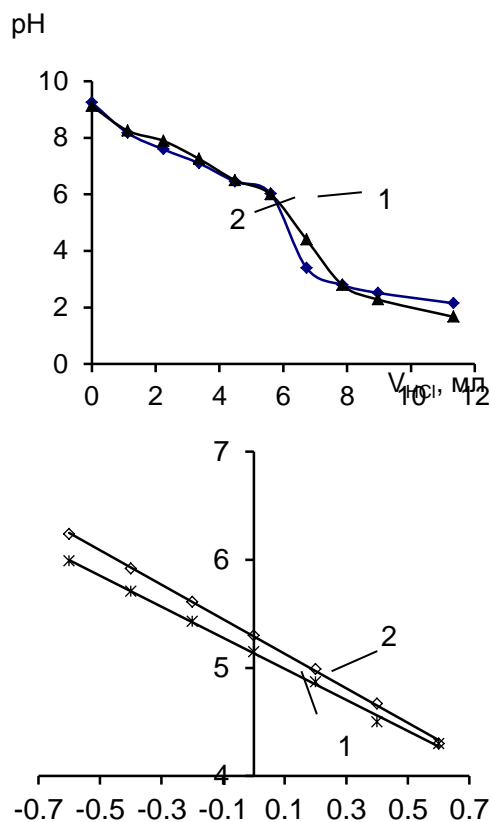


Fig 10. Results of potentiometric titration of AN: MBA: DEA (1) and AN: DVB: DEA (2) anions with 0.1 n HCl) integral titration curve; b) Titration results, expressed in the coordinates of the Henderson-Hasselbach equation.

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