

Obtaining Ion Exchangers Based On Acrylonitrile By Granular Polymerization

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Abstract: Research on the improvement of methods for the synthesis of ion-exchange sorbents with a porous structure based on copolymers is relevant.

Keywords: granular, Polymers and materials, physicochemical characteristics and sorption properties.

The aim of this work is to obtain ion-exchange granular sorbents based on copolymers of acrylonitrile with a multifunctional crosslinking agent, hexahydro-1,3,5-triacrylyltriazine, by chemical transformations and to study their network structure.

Polymers and materials based on them occupy a very important place in our life, their production is increasing from year to year, new polymers are synthesized, new materials are invented. In this regard, the most important direction is the synthesis and study of the structure of ion-exchange materials with desired properties, which are widely used in various fields of the national economy and which is important in solving problems of ecology and environmental protection.

Therefore, obtaining ion exchangers based on acrylonitrile by granular polymerization in the presence of a crosslinking agent with subsequent chemical modification of functional groups is relevant.

Acrylonitrile copolymers with cross-linking agents of various structures have recently become the most common scaffolds for the synthesis of ion exchangers. They differ from scaffolds of other chemical compositions in the ability to control the degree of crosslinking and accessibility for various chemical reactions.

Such polymers - ion exchangers have long been used in various sorption technologies that require special mechanical and chemical resistance, when it is necessary to concentrate technological solutions to extract especially valuable components from them, to purify water supply sources, industrial waste water from toxic ions and environmentally hazardous compounds.

In this regard, studies on the improvement of methods for the synthesis of ion-exchange sorbents with a porous structure based on the above and other copolymers are relevant.

The aim of this work is to obtain ion-exchange granular sorbents based on copolymers of acrylonitrile with a multifunctional crosslinking agent, hexahydro-1,3,5-triacrylyltriazine, by chemical transformations and to study their network structure.

The physicochemical characteristics and sorption properties of the obtained copolymers depend on the structure of the macrochain, the nature of the functional groups of the obtained anion exchangers, etc. However, the network structure of copolymers of acrylonitrile with hexahydro-1,3,5-triacrylyltriazine remained uncharacterized.

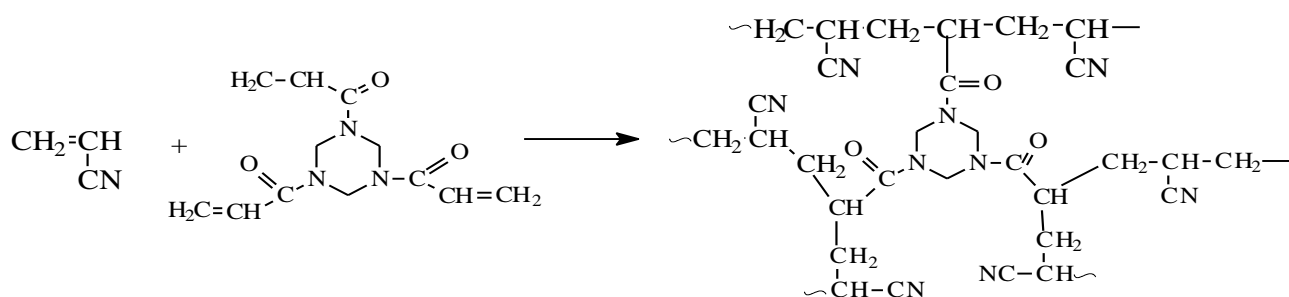
The copolymerization was carried out by the suspension method in the presence of dinitrile-azo-isobutyric acid as an initiator (up to 1 wt.% of the monomer mixture), stabilizer-water-soluble starch, at a temperature of 343 K in a saturated aqueous solution of NaCl (dispersion medium) obtained at room temperature. temperature, at a rotation speed of 450-500 rpm; reaction time up to 5 hours.

The ratio of monomers and pore-forming agent toluene, in which the initiator was dissolved, and the dispersion medium was 1:4 (water modulus). To obtain a porous structure, the inert solvent toluene was used in an amount of 30% by weight of the mixture of monomers. A 1% aqueous solution of starch was used as a protective colloid.

The required amount of the initiator, AN, GTT, stabilizer, blowing agent was introduced into the reactor, equipped with a mechanical stirrer, refrigerator and preliminarily placed in a thermostat with the initial temperature for copolymerization. After the completion of the reaction, the reactor was removed from the thermostat and the samples were decanted.

As is known, suspension copolymerization takes place under heterophasic conditions. Copolymerization takes place in monomer drops, and the resulting copolymer is insoluble in its own monomer and water-organic medium. The granular copolymer does not dissolve in polyacrylonitrile solvents, which indicates the presence of a crosslinked structure.

The structure of the resulting copolymer between the reacting components can be schematically illustrated as follows:



Thus, a copolymer was obtained with the starting components: AN:GTT=97.5: 2.5; 97:3; 95:5 mass%.

The density of copolymers was determined by the pycnometric method. To determine the density of the copolymer, the density of water at 293K was studied for comparison with the density of the copolymer at the same temperature. After weighing a dry pycnometer with an error of not more than 0.0002 g, it was filled to the mark with water, closed with a glass stopper, and immersed in a water bath at a temperature of 293 K for 30 min. After that, the water level in the pycnometer was accurately set to the mark.

Having closed the cork and thoroughly wiped the pycnometer from the outside, the second weighing was performed. After that, water was poured out of the pycnometer, dried, cooled in a desiccator, and several pieces of the test copolymer were placed. After closing the lid, the third weighing was carried out. Next, the water level in the pycnometer was brought to the mark, closed and immersed in a water bath with 293K for 30 min. Then the water level was brought to the mark, the water was carefully taken from the outside and the fourth weighing was carried out.

The density of the copolymer can be determined by the formula:

$$\rho = \frac{m_2 - m_0}{(m_1 - m_0) - (m_3 - m_2)} \quad \text{где}$$

m_0 - mass of the pycnometer, g;

m_1 - weight of the pycnometer with water, g;

m_2 - weight of the pycnometer with copolymer, g;

m_3 - weight of the pycnometer with water and copolymer, g;

A weighed portion of the sample was placed in a weighing bottle containing 5 cm³ of the corresponding liquid. The flask was hermetically sealed, placed in a centrifuge, kept for 5 minutes at a speed of 3000 rpm, then removed from the centrifuge, the flask was freed from the sample with tweezers, excess solvent was removed with filter paper and weighed on a balance with an accuracy of the 4th decimal place.

After weighing, the swollen sample was again placed in a bottle with solvent. The actions were repeated after 5, 10 and 15 minutes. and further excerpts.

The measurements were stopped when the difference in the masses of the last three measurements did not exceed 3 mg.

The degree of swelling for each time value was calculated using the following formula:

$$\alpha_{(\tau)} = \frac{m_{(\tau)} - m_0}{m_0}$$

Where:

$\alpha_{(\tau)}$ - degree of sample swelling for a fixed time value;

$m_{(\tau)}$ - the mass of the swollen sample for a fixed time value;

m_0 - mass of the original substance.

The swelling coefficient q_{2m} was calculated using the following formula:

$$q_{2m} = \frac{g_{2m} - g_2}{g_2} \cdot \frac{\rho_2}{\rho_0} + 1;$$

Where:

g_2 - weight of dry cross-linked polymer;

g_{2m} - weighed swollen cross-linked polymer;

ρ_2 and ρ_0 - polymer and solvent densities, respectively.

Index m shows that this parameter is measured in the state of equilibrium swelling. The degree of swelling of the samples was studied by centrifugation.

Calculation of grid parameters

The number average molecular weight of chain segments between crosslinking sites (MC) and the concentration of chains in the copolymer (nC), which characterize the density of crosslinking, were calculated using the equation proposed in [39]:

$$M_C = \frac{\rho_2 V_1 \left[(q_{2m} + 1)^{-1} - \frac{1}{2} (q_{2m} + 1)^{-1} \right]}{\ln \left(\frac{1}{q_{2m} + 1} \right) - (q_{2m} + 1)^{-1} - \chi_1 (q_{2m} + 1)^{-2}}$$

Where:

ρ_2 - polymer density;

q_{2m} - swelling constant;

V_1 - molar volume of solvent; χ_1 - the Huggins parameter (for the polyacryloniryl-DMF system it is assumed to be 0.29).

The network parameters were calculated using the found values of the number average molecular weight (MW) of the active chain and the density of the polymer according to the following formula:

$$n_c = \frac{N_C}{N_A} = \frac{\rho_2}{M_C} = \frac{v_C}{V_C} = \frac{1}{V_2}$$

Where:

v_C - number of moles of active chains in the sample, mol;

n_c - the number of moles of active chains per unit volume of the crosslinked copolymer, mol/cm³;

N_C - concentration of active chains per unit volume of the crosslinked polymer (cm³)-1;

N_A - Avogadro's number;

$\overline{V_C}$ - effective molar volume of the active chain, cm³/mol;

V_2 - polymer volume, cm³

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