

Features of Synthesis of Anion Exchange Matrix “Polikon A” with Oxidated Ultrafine Additives on Lavsan Textile Bases

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Abstract—A comparative analysis of the studies on the influence of the textile structure of reinforcing fabric on the physicochemical and sorption characteristics of anion-exchange systems as a component of the “Polikon” mosaic materials is presented in this study. This study shows the promise of using polyester fibers as a reinforcing fiber base for the production of Polikon A membrane materials. The morphology, moisture capacity, static exchange capacity, and physical and mechanical characteristics of anion-exchange membrane systems were investigated. A modification of Polikon A anion-exchange matrices on lavsan fabric by oxidized ultrafine particles of silicon, iron and nickel is proposed.

Keywords: Polikon A, polyester filter dummy FL-4, textile lavsan, SEM, elemental energy dispersive analysis, DSC, wettability, moisture capacity, breaking stress at break, static exchange capacity

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INTRODUCTION

Over the past 60 years, ion-exchange membranes have evolved from a laboratory instrument into an industrial product with significant technical and commercial potential [1].

The creation of composite heterogeneous anion-exchange membranes with a mosaic structure and anion-exchange membranes, as their constituent element, promising for use in sorption and electro-membrane processes, especially for capacitive deionization of water, has been a very urgent task in the last decade [2, 3].

Due to the growing interest in reinforced polymer membranes based on thermosetting matrices and high-temperature fibers, obtained by low-stage and environmentally unstressed technologies, membranes synthesized by the method of polycondensation filling have come to the forefront [3, 4]. Earlier, we carried out a number of studies on various ion-exchange matrices reinforced with chemical fibers: polypropylene (PP), viscose (VF), polyacrylonitrile (PAN), phenol formaldehyde novolac (PFN), etc. [5, 6].

A bipolar membrane is known [7], which is obtained by joint hot pressing and simultaneous reinforcement of a sulfocationite membrane and a membrane based on benzyltrimethylammonium anionite. Sulfocationite membranes made on the basis of macroporous sulfocationite with a highly developed sur-

face used in hydrometallurgy, in particular as an ion exchange membrane, can be used for pH adjustment, and decomposition of salt systems into acid and alkali by electrodialysis.

A method for producing a bilayer membrane on the surface of heterogeneous ion-exchange membranes made of polyethylene and an ion polymer dispersed therein is described by applying a solution of sulfonated polytetrafluoroethylene in an organic solvent [8].

The application of membranes made of microfibers and nanofibers, or “felts,” is expanding; and they are used both in biological and industrial applications [9].

A search is constantly being made for new methods for increasing the mechanical stability and improving the electrochemical characteristics of ion-exchange membranes, for example, an asymmetric bipolar membrane consisting of a heterogeneous strongly basic ion-exchange membrane-substrate and a homogeneous film of sulfonated perfluorocarbon modifier formed on a preliminarily fat-free and activated surface of the membrane-substrate by treatment with concentrated acetic acid [10]. A two-layer combined membrane consisting of the first layer of an ion exchanger consisting of crushed cation exchange and anion exchange materials pressed with a binder, and the layer itself is covered with a reinforcing material is promising [11]. The second layer of the ion exchanger consists of either a cation exchange or anion exchange material, compressed with a binder. Moreover, the

first layer contains components in the ratio, wt %: cation exchange 5-85 and anion exchange material 85-5, and the rest is a polymer binder; and the second contains components in the following ratio, wt %: ion exchanger 65-90 and polymeric binder material 35-10. As the ion exchange material, any crushed ion exchange resin can be used. The resulting structure relates to semipermeable membranes and can be used in the purifying, concentrating, reagent-free softening of natural and industrial waters, the correction of acidity of electrolyte solutions of complex composition, the production of high-purity water, and the purification and separation of high molecular organic substances, for example, whey, proteins, amino acids, etc.

In [12], a hydrophilic composite microporous membrane made of thermoplastic resin is described, in which anion-exchange and cation-exchange groups are located on the outer surface or on the surface of the pores, the composite microporous membrane is obtained by graft polymerization of a microporous membrane substrate from a thermoplastic resin with an unsaturated monomer.

An original solution for the efficiency of maintaining increased mass transfer of salt anions is realized in a composite strongly base anion exchange membrane [13], consisting of three layers, the main layer of which is formed by a membrane-substrate containing 40% of polyethylene and 60% of strongly base anion exchange resin, which consists of a styrene-divinylbenzene copolymer with grafted trimethylammonium groups, and two other layers formed by poly-*N,N*-diallylmorpholinium and located on both side surfaces of the membrane-substrate. Under conditions of high-intensity electro dialysis, a membrane complex with long-term electrochemical stability is very important. Similar structures include a bilayer strongly base anion-exchange membrane [14], which consists of two layers, the first layer is a heterogeneous membrane-substrate containing 40% of polyethylene and 60% of strongly base anion exchange resin consisting of a styrene-divinylbenzene copolymer with grafted trimethylammonium groups, and the second layer is made of a water-insoluble copolymer of *N,N*-dimethyl-*N,N*-diallylammonium chloride and ethyl methacrylate.

Improved selectivity to the transport of counterions is achieved today by extended modification, for example, with ultrafine fillers, which is realized in a composite anion exchange membrane [15], which consists of a heterogeneous anion exchange membrane-substrate and a thin homogeneous cation exchange layer of sulfonated polytetrafluoroethylene deposited on its previously defatted surface, while the applied sulfonated polytetrafluoroethylene additionally contains not more than 3% carbon nanotubes.

In [16], anion-exchange composite membranes with an optimal thickness of ~ 40 μm , high tensile strength, and a hydrophilic surface are studied in com-

parison with the commercial analogue, the FAA-3-50 Fumatech anion-exchange membrane.

Hybrid membranes based on *N*-phosphorylated polybenzimidazole with different contents of silicon oxide (2–20 wt.%) were synthesized [17]. It was shown that hybrid membranes are characterized by high proton conductivity, and its maximum value is achieved with the introduction of 2–10 wt % dopant, while the introduction of silicon oxide helps to reduce gas permeability by ~ 1.5 times [18].

To improve the mechanodynamic properties and increase the level of resistance to hydrothermal aging, in [19], ion-exchange polymer matrix composites with a carbon fiber-based lateral structure were modified with in-situ synthesized graphite carbon nitride ($g\text{-C}_3\text{N}_4$).

This study is the continuation of comprehensive studies [2–6], for the first time, it proposes the use of Lavan fabric as a promising fibrous base, as well as the possibility of introducing ultrafine silicon, iron and nickel oxides into the composition of the created compositions, and the influence of the textile structure of the fiber base on the physical, chemical, and sorption characteristics of developed membranes is studied.

EXPERIMENTAL

“Polikon” materials were obtained by polycondensation filling of a fibrous matrix with a monomerization composition and further formation of an anionite matrix both on the fiber surface and in its structure [3–5]. The technological process consisted of preparation of raw materials, obtaining of monomerization compositions (epichlorohydrin + polyethylene polyamine) and their application onto a fibrous filler, synthesis, curing—forming of a spatial network of polymer matrices on the surface and in the volume of the system. The ratio of the polymer matrix to the fibrous base (Lavan and polyester filter dummy FL-4) in the finished membrane is 60 to 40%.

To study the kinetics and thermodynamics of the processes taking place, the method of differential scanning calorimetry was used on a DSC-500 instrument using DSK Tool interface software, which made it possible to identify the zones of maximum heat release and calculate the thermal effects and reaction rates. The experiment was carried out under the following conditions: medium—air, temperature range—from 25 to 140°C, and heating rate—8 K/min using a weight of 0.02 g. Calibration of the device was carried out using a reference tin. The accuracy of determination of ΔH is ± 10 cal/g.

The morphology and thickness of the samples were determined on an analytical complex based on a MIRA 2LMU scanning electron microscope. Microanalysis was carried out using the energy dispersive method using the INCA Energy 350 system. For the selected measurement modes and location of the sam-

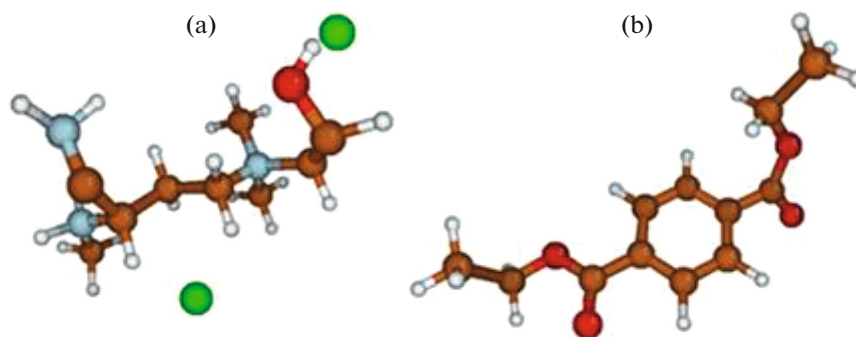


Fig. 1. Elementary optimized fragments of anionite matrix (a) and polyethylene terephthalate (b).

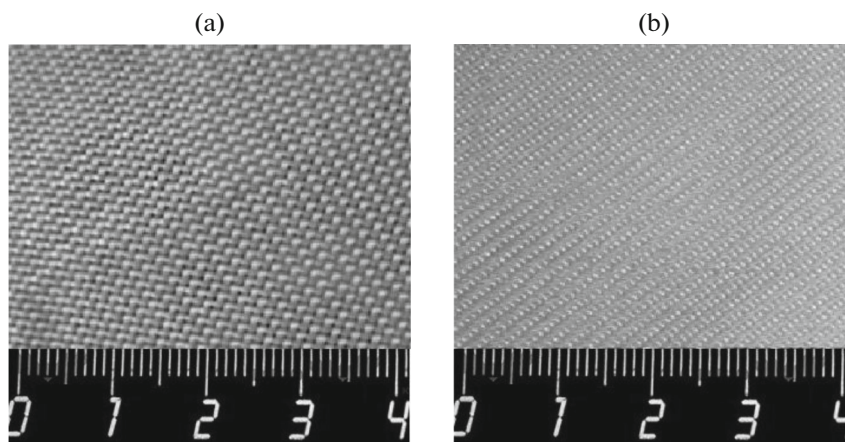


Fig. 2. Optical microscopy of polyester textile fabric (a) and polyester filter dummy FL-4 (b).

ple relative to the electron beam, the region of generation of characteristic X-ray radiation in depth is 1 μm .

The processes of tissue wetting by monomerization composition were studied using a K-8 cathetometer. The tensile tests were carried out on a Unimat 052 tensile testing machine at a clamp speed of 50 mm/min; the maximum load at break is recorded using a Physimeter 906 MC device.

In this study, we used ultrafine colloidal silicon oxide with a predominance of an amorphous phase and a specific surface area of $\sim 300 \text{ m}^2/\text{g}$ and ultrafine oxides of nickel (Ssp $\sim 9 \text{ m}^2/\text{g}$) and iron (Ssp $\sim 18 \text{ m}^2/\text{g}$) obtained by plasma technology by recondensation of ultrafine materials in the laboratory of the State Scientific Research Institute of Chemistry and Technology of Organoelement Compounds (GNIChTEOS) [20].

Elementary fragments of weakly basic epoxy-diane anion exchange resin and polyethylene terephthalate were developed the molecular model of which is shown in Fig. 1. The primary molecular models were optimized by MM2 force field methods to achieve convergent optimal geometry of macromolecules.

To predict the field performance data of the resulting structures, the sizes of elementary molecular fragments (length, width, height in \AA) are important,

which were determined for the fragments in Fig. 1a (6.01; 2.69; 7.51) and Fig. 1b (5.58; 3.42; 12.16), which, in turn, was used to estimate the theoretical value of the static exchange capacity the calculated value of which was $\sim 3.67 \text{ mEq/g}$.

RESULTS AND DISCUSSION

Taking into account the peculiarities of the polycondensation method for obtaining anion-exchange membrane materials, when the fibers of the reinforcing fabric and their textile structure are nanoreactors in which the formed anion-exchange matrix is synthesized and solidified, the first step was to assess the possibility and expediency of using the selected fibers to obtain membrane systems Polikon A, the influence of their textile structures on the physicochemical and sorption characteristics of the developed membranes.

The preliminary choice of Lavsan (Fig. 2a) and polyester filter dummy FL-4 (Fig. 1b) was based on the compliance of fibrous bases with the following criteria: do not swell, do not be destroyed in the synthesis and curing medium, and do not lose physical and mechanical properties under the technological parameters of the process [21, 22] (see Table 1). At the same time, the choice of a Lavsan fibrous base was

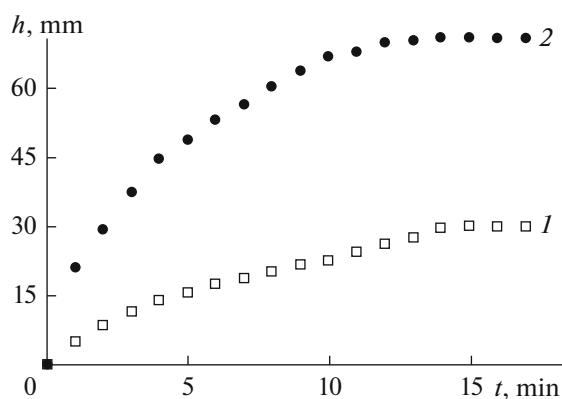


Fig. 3. Wettability kinetics by the monomerization composition of polyester textile fabric (1) and polyester filter dummy FL-4 (2).

based on the well-known properties of polyester threads: high strength, not changing over time, good handling properties, complete absence of “shape memory” and deformation, low capillarity, and resistance to microorganisms and mold.

To work out the technical methods and technological parameters of all processes, a further step in this direction was to study the influence of both the textile structure of fibers and ultrafine additives on the wetting process with the components of the anionite matrix, as well as on the kinetics and thermodynamics of the processes.

The conducted studies have shown a higher degree of wettability of the polyester filter dummy FL-4 (Fig. 3).

It is noted that a significant increase in the wettability indicators for the FL-4 fibrous base, namely, the wettability rate is ~2.9 times higher, and the amount of retained monomerization composition is 42% higher than that of Lavsan textile. There is also an earlier achievement (~11 min) of the wettability curve to the equilibrium state in comparison with Lavsan fabric

(~14 min), which is explained by the feature of its textile structure. According to its technical characteristics, the filter cloth was created to capture the smallest particles in the shortest possible time, to give it the above properties; in the process of its production, the fiber surface was smoothed. It is this feature of the textile structure, that explains the fact that the wettability curve for FL-4 comes earlier in comparison with Lavsan. The amount of retained MC was calculated according to the method corresponding to the applied method.

Based on the results of studies of the influence of the textile structure of the fiber on the wettability process, as well as the kinetics and thermodynamics of the processes, experimental batches of samples were developed, the properties of which are shown in Table 2.

Taking into account the better manufacturability, increased physical and mechanical characteristics with similar sorption properties, it was decided in the future to use Lavsan filter fabric FL-4 to obtain anion-exchange composite chemisorption fibrous materials Polikon-A. The characteristic morphological features of the Polikon A materials are presented in Fig. 4. Electron microscopy data indicate the uniform formation of a polymer matrix over the entire cross section of elementary fibers. It has been established that during polycondensation filling, a dense layer of an anionite matrix is formed on the selected fiber filler, its structural orientation is observed along the longitudinal axis of the fiber, while the impregnation processes uniformly go along the entire cross section of the fibers, which will further prevent separation of the materials obtained under intensive operating conditions. The chemical composition of Polikon A on the PL-4 Lavsan fabric was studied by the energy dispersive method. It was shown that carbon dominates the elemental composition (in weight %): 66.86 ± 4.61 ; oxygen, 14.09 ± 1.93 ; chlorine, 12.01 ± 0.94 ; and nitrogen, 7.04 ± 5.9 (Fig. 5).

Table 1. Technical characteristics of the considered fabrics

Characteristics of the fibrous base	Textile Lavsan	Polyester filter dummy FL-4
Surface density of the cloth, g/m ²	150 +/- 5	412 +/- 25
Number of threads per 10 cm on the base	134	220
Number of picks per 10 cm	82	160
Resistance to the action of solutions of mineral acids	++	+++

Table 2. Properties of Polikon A materials

Textile structure	Exchange capacity, mEq/g _{ob}	Moisture capacity, g H ₂ O/g _{ob}	Breaking stress at break, MPa
Textile Lavsan	2.1	0.36	22.1
FL-4	2.6	0.54	40.9

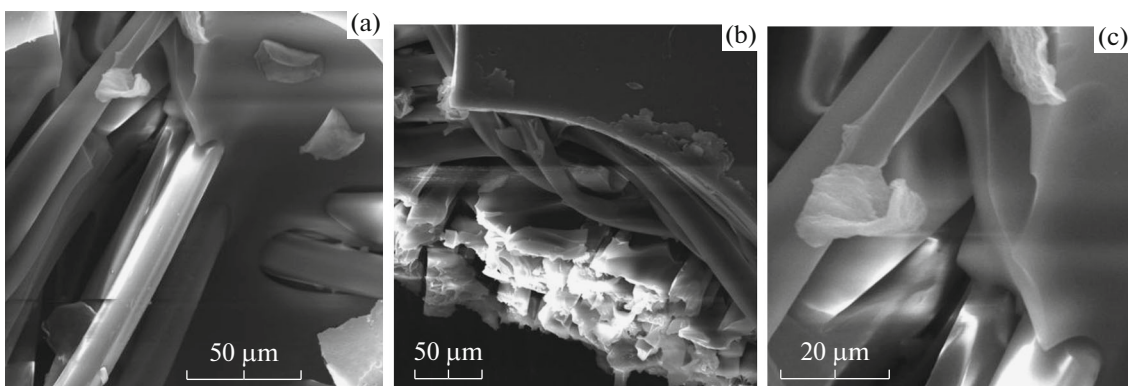


Fig. 4. Scanning electron microscopy of Polikon A materials on Lavsan fibrous base FL-4.

In order to avoid suffusion, as well as to give the anionite matrix of Polikon A a more uniform cross-linked structure, it was proposed to introduce oxidized ultrafine modifying additives Fe, Ni, and Si during the synthesis stage.

A study of the effect of ultrafine additives on the process of fabric wetting (Fig. 6) revealed insignificant differences (for nickel, 1.1 times and iron, 1.16 times) in terms of process speeds and the maximum held volume of the monomerization composition. The rate of impregnation with the introduction of ultrafine silicon oxide is ~ 0.8 times lower in the initial stage of the process compared to processes that occur in the absence of an additive. At the same time, a significant decrease in the maximum held impregnation composition was noted with a vertical method of fiber impregnation while reducing the overall process speed.

Based on the data obtained, adjustments were made to the technological process: the time of impregnation of the samples was increased and the position of the fibrous base was changed, which made it possible to achieve the necessary ratio of the fibrous reinforcing base; the polymer matrix.

The kinetics and thermodynamics of the processes involved in the synthesis and formation of the anionite matrix on the Lavsan fibrous base with the introduction of an additional heterophase system (Fig. 7) was studied by the method of differential scanning calorimetry and allowed to identify a number of features of the synthesis process and further structuring of the spatial architecture of the matrix.

Studies have shown that in the presence of ultrafine additives, the synthesis and curing process proceeds at a faster rate (for Si, 1.3; for Fe, 1.54; for Ni, 1.56 times). An increase in the heat effect of the curing reaction, as well as the active participation of ultra-dispersed additives, in the process of structure formation of ion-exchange matrices of Polikon A materials with the formation of a more branched cross-linked structure is noticeable.

It is noted that the presence of silicon colloidal oxide qualitatively changes the course of exothermic polycondensation processes, which manifests in the absence of a second neoclassical crystallization peak characteristic of the Lavsan fibrous base. The addition of silicon colloidal oxide leads both to a decrease in the rate of impregnation and to a change in the dynamics of exothermic polycondensation processes, which is probably due to the surface properties of ultrafine particles. As shown by our studies of the IR spectra and elemental composition of ultrafine particles, the surface shell of Si particles has a disordered amorphous-

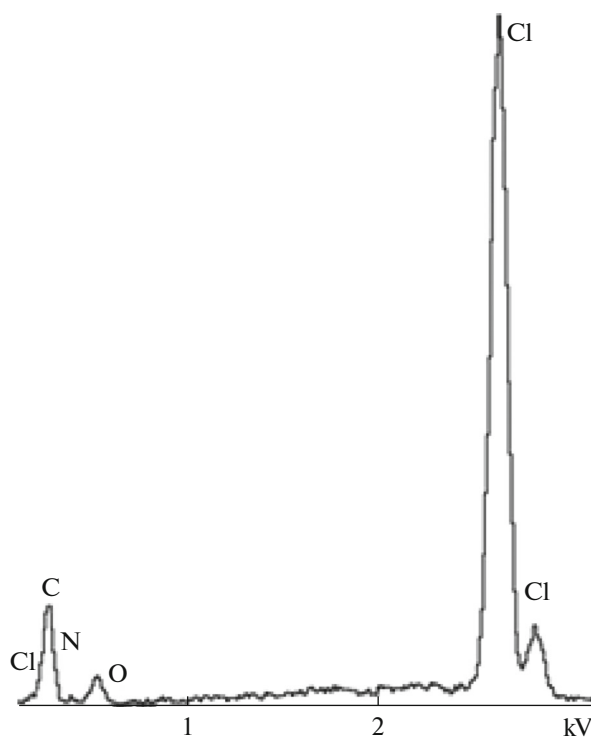


Fig. 5. Elemental analysis of the Polikon A membrane.

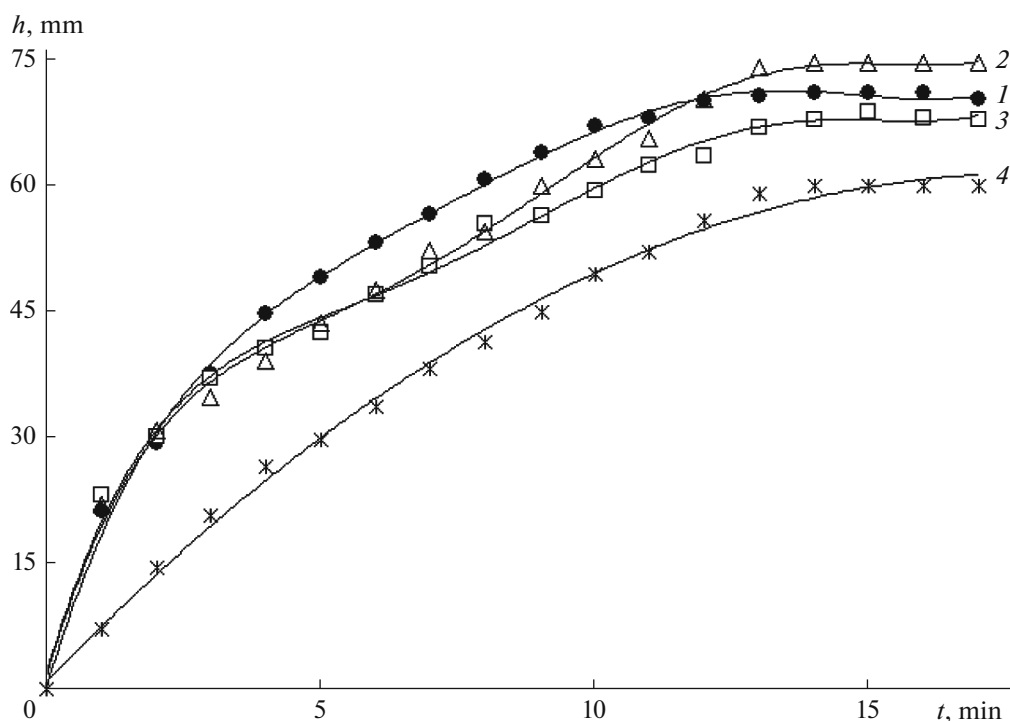


Fig. 6. Kinetics of wettability by the monomerization composition of the fibrous base FL-4 (1), in the presence of ultrafine oxides: (2) Fe, (3) Ni, (4) Si.

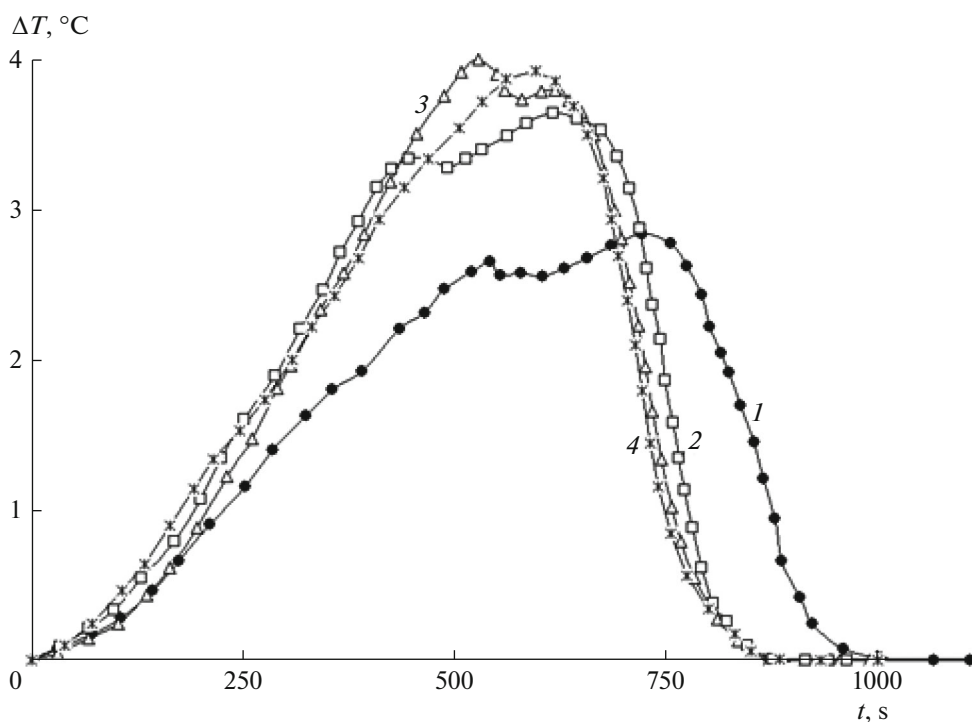


Fig. 7. Data of differential scanning calorimetry of the process of formation of anion-exchange matrices based on Lavsan fibrous base FL-4. (1) In the presence of ultrafine oxides: (2) Fe, (3) Ni, (4) Si.

porous structure with a large number of hydroxyl groups.

In Table 3, the influence of the choice of a fibrous base on the sorption characteristics of anion-exchange

membrane materials is studied. A comparative analysis of the experimental data showed that the Polikon A anion-exchange membrane systems based on FL-4 Lavsan have sorption characteristics 20% higher than for

Table 3. Characteristics of Polikon A anion exchange materials [2–6]

Polikon A on various fibrous bases	Exchange capacity, mEq/g _{ob}	Moisture capacity, g H ₂ O/g _{ob}
FL-4	2.6	0.54
PFN	2.0	0.64
PAN	2.0	0.55
Viscose	1.8	0.43
PP	1.5	0.35

materials based on PAN, PFN, polypropylene, and viscose fillers.

CONCLUSIONS

The studies conducted are aimed at expanding the nomenclature horizons of solutions to the fundamental problem of creating composite heterogeneous anionic-cation-exchange membranes of a mosaic structure and anion-exchange membranes as their constituent element. A polyester fiber base is a promising basis, which, on the one hand, has extreme wick, and on the other hand, it is highly hydrophobic and has a tendency to extreme antibacterial properties, as well as manufacturability. FL-4 is more effective when used as a reinforcing base for Polikon A membrane materials in comparison with textile Lavsans, which have a moisture capacity of ~0.54 g H₂O/g_{ob} and reach breaking stress values of ~40.9 MPa at break. The theoretical level of static exchange capacity of ~3.67 was determined, which agrees quite well with the experiment of 2.6 mEq/g_{ob}.

The influence of both the textile structure of fibers and ultrafine additives on the kinetics and thermodynamics of the synthesis process and further structuring of the spatial architecture of the matrix is studied. Studies have shown that during polycondensation filling, a dense layer of anionite matrix is formed on the fibrous filler, its structural orientation is observed along the longitudinal axis of the fiber. The introduction of ultrafine additives makes it possible to activate the promising properties of Lavsans fibers with simultaneous production of a multilevel monolithic structure of an anionite matrix. It is noted that the presence of silicon colloidal oxide qualitatively changes the staging of exothermic polycondensation processes, which is manifested in the absence of a second crystallization peak characteristic of Polikon A materials on a Lavsans fibrous base.

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