



## Short communication

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## Influence of the particle size of sulfonated cation exchange resin on the physicochemical properties and surface morphology of MK-40 heterogeneous membranes

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### Abstract

The article presents the results of the study of the physicochemical properties and surface morphology of MK-40 heterogeneous membranes with a given particle size of sulfonated cation exchange resin within the ranges of  $< 20 \mu\text{m}$ ,  $32\text{--}40 \mu\text{m}$  and  $56\text{--}71 \mu\text{m}$  with the resin-polyethylene ratio of 65:35. The experimental membranes were manufactured at LLC Innovative Enterprise *Shchekinoazot* (Russia). A comparative analysis of the characteristics of the membranes showed that their main physicochemical properties change in accordance with the changes in surface parameters. With an increase in the particle size of the ion exchange resin, the moisture content and the thickness of the membranes decreased together with the surface macroporosity. What is more, the exchange capacity of the membranes did not depend on the particle size of the ion exchange resin.

Quantitative analysis of SEM images of swollen membranes revealed a number of peculiarities of their surface morphology. First, it was established that membranes with a size of resin particles within the range of  $56\text{--}71 \mu\text{m}$  had small ion-exchangers with a radius of  $R < 10 \mu\text{m}$  and no large ( $R > 20 \mu\text{m}$ ) ion-exchangers. Secondly, it was found that the fraction of the ion exchanger and the weighted average radius of the ion exchange resin particles decreased by 14% and 15% respectively with an increase in the preset dimensions of the ion exchanger. Thirdly, with an increase in the size of the resin particles, the surface macroporosity decreased by 7%, while the size of the macropores increased by more than 20%. To explain the revealed peculiarities of the surface morphology of MK-40 heterogeneous membranes with different particle sizes of sulfonated cation exchange resin, it is necessary to study the structure of their internal phase.

**Keywords:** Heterogeneous cation exchange membrane, Particle size of ion exchange resin, Surface morphology, Physicochemical properties

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## 1. Introduction

Currently, researchers and practitioners are focused on developing specialized membrane products that meet specific technological requirements, such as low membrane electrical resistance [1], specific selectivity [2], chemical and thermal stability [3], and/or scaling resistance [4]. The manufacture of new or the modification of existing commercial membranes for specific purposes is a complex interdisciplinary task since the parameters that determine their properties often act in opposite directions. For example, a high concentration of fixed ions in the membrane matrix results in a low electrical resistance, however, it also causes a high degree of swelling in combination with poor mechanical stability [1, 5]. In addition, one of the biggest challenges for the manufacture of heterogeneous membranes with an optimal combination of mechanical strength and electrochemical properties is the need for two continuous phases: ion exchange and inert phases. Continuous paths for ion transport are necessary for effective contact between ion exchange particles, while mechanical strength can be ensured by a continuous layer of binder material [6]. What is more, the deformation of the inert binder and ion exchange resin particles during swelling results in the formation of channels filled with the solution, which connect the ion-exchangers. To achieve high mechanical strength, ion exchange membranes can be reinforced with fabrics made of polymers such as nylon and polyester (Lavsan). This structure causes significant changes in the physicochemical properties of the membrane surface and volume on a micrometer scale. The presence of conductive (the ion-exchanger phase) and non-conductive (inert binder) sections and reinforcing fabric contributes to the development of electrical and geometric heterogeneity on the surface, which contributes to the development of electroconvection in electromembrane systems, the main mechanism for the overlimiting conductivity of membranes [7, 8].

The aim of the work is to study the influence of the particle size of the sulfonated cation exchange resin on the physicochemical properties and structural characteristics of the surface of the MK-40 heterogeneous membrane.

## 2. Experimental

In our study, we used experimental samples of the MK-40 heterogeneous cation exchange membrane with a preset size of particles of the ion exchange resin within the range of: < 20, 32–40, and 56–71  $\mu\text{m}$ . The samples were manufactured at the well-known Russian enterprise, LLC IE *Shchekinoazot*. The MK-40 membrane is a polymer composition of a strongly acidic cation exchanger KU-2-8, low-pressure L461N19 polyethylene, and a reinforcing fabric, Excelsior capron mesh, art. 56314. Fixed groups of MK-40 membranes are sulfonic acid groups,  $\text{SO}_3^-$ . The ratio of ion exchange resin and polyethylene in the composition of the experimental MK-40 membranes was traditional and was 65 wt. % to 35 wt. %. Particles of ion exchange resin of a certain size were selected using a complex of five sieves with a mesh diameter of 71, 32, and 20  $\mu\text{m}$ .

Physicochemical properties of the studied samples were determined using standard testing methods for ion exchange membranes [9]. The total exchange capacity was determined under static conditions using acid-base titration. The total exchange capacity  $Q$  ( $\text{mmol/g}_{\text{dry}}$ ) was calculated taking into account the moisture content  $W$ . The moisture content  $W$  (%) in the membranes was determined by air-heat drying, the thickness  $l$  ( $\mu\text{m}$ ) was measured using a micrometer, and the density  $\rho$  ( $\text{g/cm}^3$ ) was measured using a pycnometer.

The surface morphology of the membranes was studied by scanning electron microscopy (SEM) using a JSM-6510 LV microscope (Japan). Since ion exchange membranes are swollen when activated, the study was carried out in a low vacuum mode using reflected electrons at an accelerating voltage of 20 kV. This SEM mode does not require preliminary drying of the sample and spraying a conductive layer on its surface [10]. The quantitative assessment of the fraction of ion exchange material ( $S$ , %) and porosity ( $P$ , %) on the surface of the membranes was carried out using an original software package [11]. The concept of a “pore” was understood as the space between the ion-exchanger and an inert binder (polyethylene). Taking into account the “size effect” of the inhomogeneous surface of heterogeneous membranes, to determine simultaneously the fraction and the radius of the

particles of the ion exchange resin ( $R$ ,  $\mu\text{m}$ ) and macropores ( $r$ ,  $\mu\text{m}$ ), the value of 500 was chosen as the optimal magnification ratio of the surface image [5].

### 3. Results and discussion

A comparison of the properties of the experimental MK-40 membranes with different particle sizes of ion exchange resin revealed the influence of the sizes of ion-exchanger particles on their physicochemical and structural properties (Table 1).

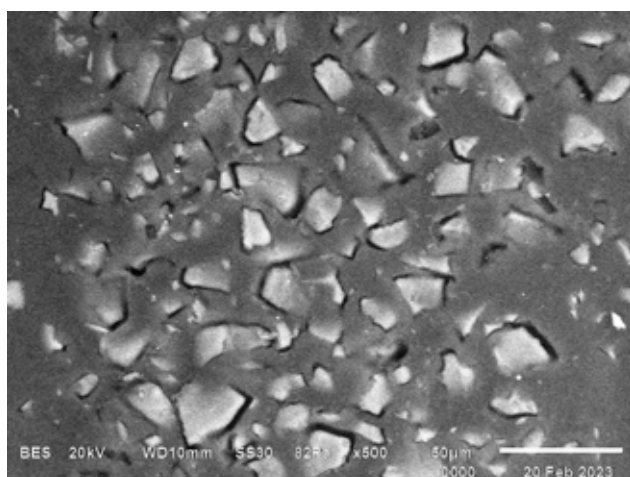
The surface structure of the studied heterogeneous cation exchange membranes was heterogeneous (Fig. 1). There were visible light areas of the conductive surface (ion-exchanger particles) and dark areas of inert polyethylene (non-conductive surface). A comparison of electron micrographs of the membrane surfaces with the minimum and maximum particle sizes of the ion exchange resin showed that with an increase in particle sizes, the fraction of the ion-exchanger  $S$  on the surface of the membranes in the swollen state decreased by 14% (Table 1). Quantitative analysis of the size of the ion

exchange resin particles on the surface revealed a difference in the values of the weighted average radius of slightly more than 15%.

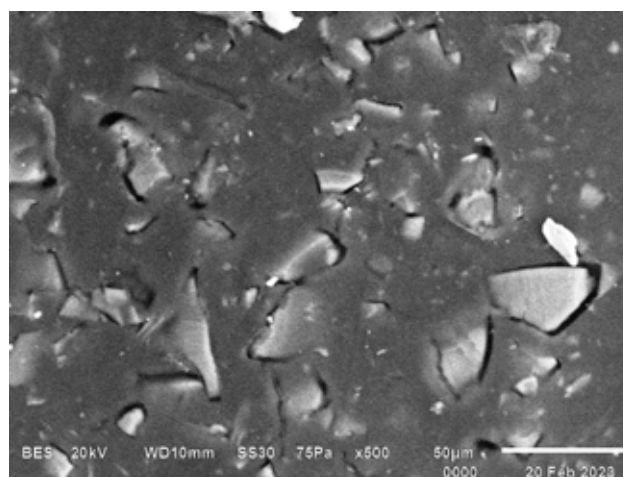
Histograms of the distribution of the fraction of resin particles of different radii  $S_R$  of the total phase area of the ion exchanger  $S_0$  on the surface of the experimental MK-40 membranes are shown in Fig. 2. For the MK-40 membrane with a minimum preset particle size of the ion-exchange resin, the maximum proportion (85%) were particles with a radius within the range from 1 to 10  $\mu\text{m}$ , 14% constituted particles with a radius of 11–13  $\mu\text{m}$ , the rest was resin particles with  $R < 1 \mu\text{m}$ . In the case of the membrane with the maximum preset particle size of the ion-exchange resin (from 56 to 71  $\mu\text{m}$ ) it was found that large particles were absent on their surface. Particles with a radius within the ranges from 1 to 10  $\mu\text{m}$  and from 11 to 16  $\mu\text{m}$  made up 70% and 28% of the total area of the ion exchange phase, respectively. It was revealed that with an increase in the particle size of the ion exchange resin, the surface macroporosity  $P$  (Table 1) tended to decrease by 7%. However, the value of the weighted average radius of macropores

**Table 1.** Physicochemical properties and structural characteristics of the surface of MK-40 membranes with different particle sizes of ion exchange resin

Resin particle sizes, $\mu\text{m}$	IEC, $\text{mmol/g}_{\text{dry}}$	$W$ , %	$\rho$ , $\text{g/cm}^3$	$l$ , $\mu\text{m}$	$S$ , %	$P$ , %	$R$ , $\mu\text{m}$	$r$ , $\mu\text{m}$
<20	$2.54 \pm 0.02$	$40.4 \pm 0.6$	$1.10 \pm 0.06$	$566 \pm 7$	$21 \pm 1$	$4.7 \pm 0.8$	$2.6 \pm 0.3$	$1.8 \pm 0.3$
32-40	$2.49 \pm 0.02$	$37.7 \pm 0.9$	$1.06 \pm 0.07$	$554 \pm 7$	$18 \pm 4$	$3.8 \pm 0.9$	$2.7 \pm 0.2$	$1.8 \pm 0.1$
56-71	$2.54 \pm 0.03$	$35.7 \pm 0.6$	$1.03 \pm 0.07$	$492 \pm 6$	$18 \pm 2$	$4.4 \pm 1.7$	$2.2 \pm 0.3$	$2.2 \pm 0.2$

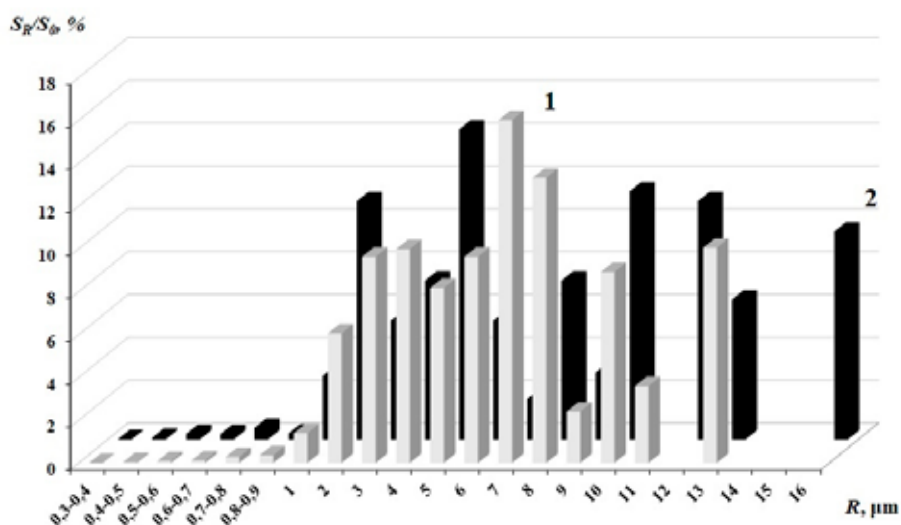


a



b

**Fig. 1.** SEM images of the surface of MK-40 sulfonated cation exchange membranes at a magnification of 500. The particle size of ion exchange resin is < 20  $\mu\text{m}$  (a), 56-71  $\mu\text{m}$  (b)

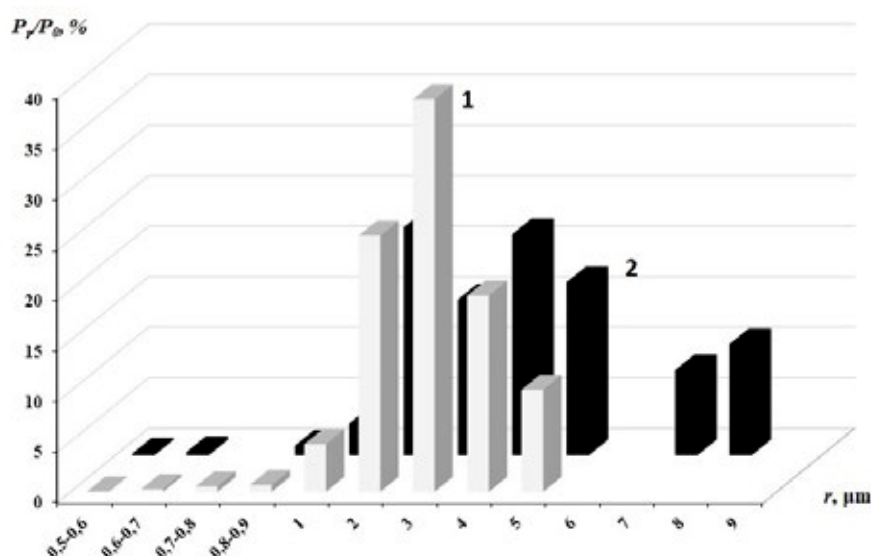


**Fig. 2.** Fractions of resin particles  $S_R$  of different radii  $R$  of the total area of the ion exchange phase  $S_0$  on the surface of the MK-40 membrane with the particle size of the ion exchange resin of  $< 20 \mu\text{m}$  (1) and  $56-71 \mu\text{m}$  (2)

increased by more than 20%. Histograms of the distribution of the macropore fractions along the radii on the surface of the experimental samples of the MK-40 membrane in the swollen state are shown in Fig. 3. For a membrane with a preset resin particle size of  $56-71 \mu\text{m}$ , a wider pore size variation interval was established, which was  $0.5-8 \mu\text{m}$  for swollen samples. What is more, the fraction of macropores in the range of  $1 < r < 5 \mu\text{m}$  and more than  $7 \mu\text{m}$  was 80 and 19%, respectively. For the MK-40 membrane with a minimum resin particle size, the maximum

fraction of macropores (97%) corresponded to sizes within the range of  $1 < r < 5 \mu\text{m}$ , while there were no macropores with  $r > 5 \mu\text{m}$ .

The obtained physicochemical characteristics of the studied membranes are given in Table 1. With an increase in the particle size of the ion exchange resin, the total exchange capacity did not change, and the moisture content, density, and thickness decreased by 12, 6, and 15%, respectively. The change in the basic physicochemical properties of the studied membranes with an increase in the particle size of



**Fig. 3.** Macropore fractions  $P_r$  of different radii  $r$  of their total area  $P_0$  on the surface of the MK-40 membrane with the particle size of the ion exchange resin of  $< 20 \mu\text{m}$  (1) and  $56-71 \mu\text{m}$  (2)

the ion exchange resin corresponded to a change in the structural characteristics of their surface. The moisture content ( $W$ ) and the thickness ( $l$ ) of the membranes fell with a decrease in their surface macroporosity and an increase in the particle size of the ion-exchanger. However, an inconsistent decrease in the density of membranes by 6% was also established. Typically, the change in the density and porosity of materials is of an antibatic nature. The exchange capacity ( $Q$ ) of the membranes did not depend significantly on the particle size of the ion exchange resin due to its equal content by weight per dry sample.

In previous studies [5] of Ralex sulfonated ion exchange membranes (MEGA a.s., Czech Republic), we established that the fraction and size of pores on their surface grew with an increase in the particle size of the ion exchange resin in the grinding. In the case of the studied experimental MK-40 membranes, an increase in the specified resin particle size resulted in a decrease in the macroporosity and an increase in the size of macropores.

#### 4. Conclusions

We studied the influence of the particle size of the sulfonated ion exchange resin on the physicochemical properties and structural characteristics of the surface of the MK-40 heterogeneous membrane. The change in the basic physicochemical properties of the studied membranes with an increase in the particle size of the ion exchange resin corresponded to a change in the structural characteristics of their surface.

However, a comparative analysis of the experimental results requires an explanation of the following facts established during the study: 1. a decrease in the weighted average radius of the ion exchanger sections on the surface of the membranes with an increase in the preset particle size of the ion exchange resin; 2. the presence of small ion-exchangers with a radius of  $R < 10 \mu\text{m}$  and the absence of large ion-exchangers with a radius of  $R < 20 \mu\text{m}$  in the samples of membranes with a particle size of 56–71  $\mu\text{m}$ ; 3. the symbatic nature of the change in the surface macroporosity and density of the membranes with an increase in the particle size of the ion-exchanger. To better understand and explain the identified changes in surface morphology and the physicochemical

properties of the membranes, it is necessary to further study their internal phase.

#### Contribution of the authors

The authors contributed equally to this article.

#### Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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