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ION TRANSPORT IN ORGANIC AND INORGANIC MEMBRENES

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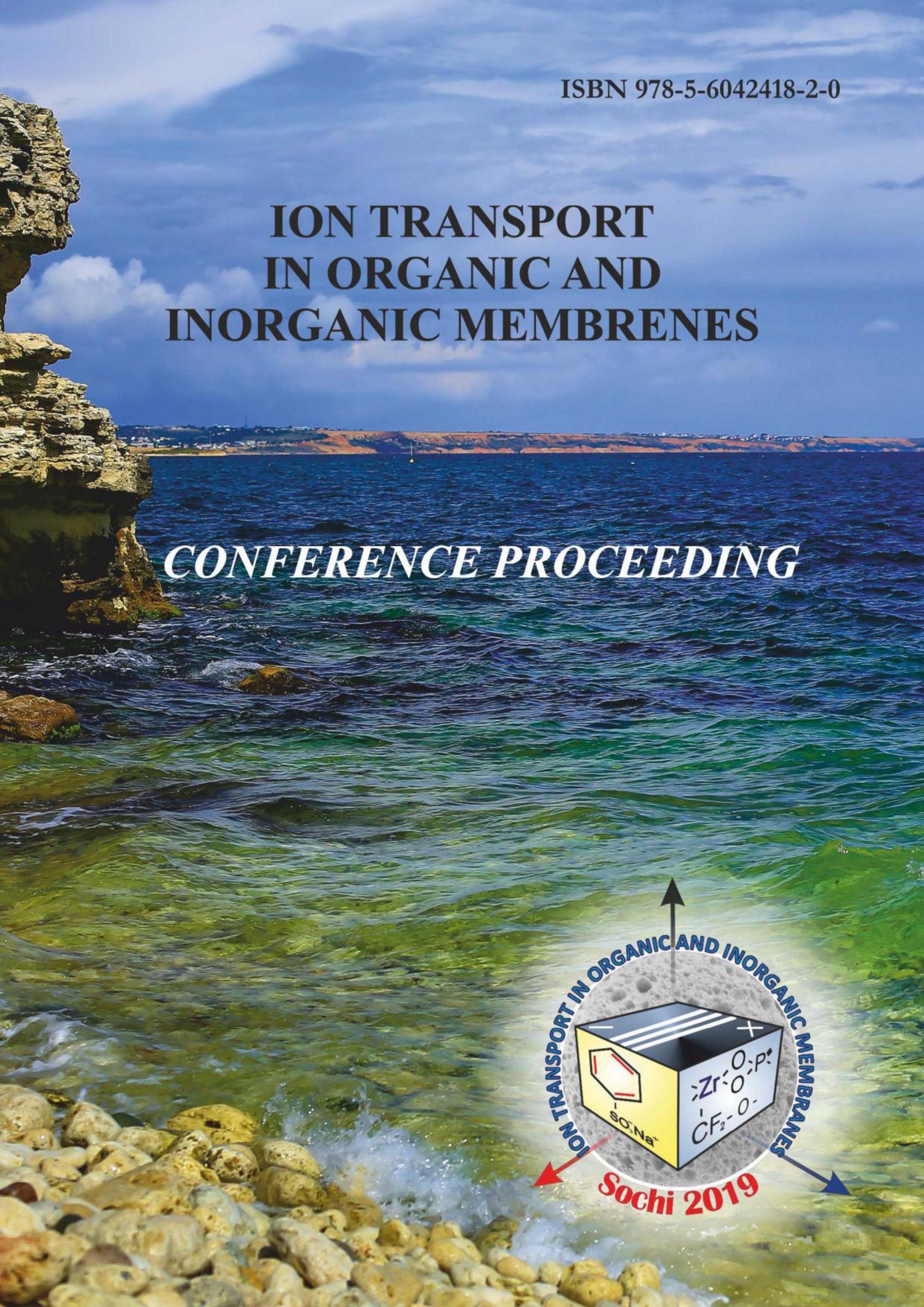

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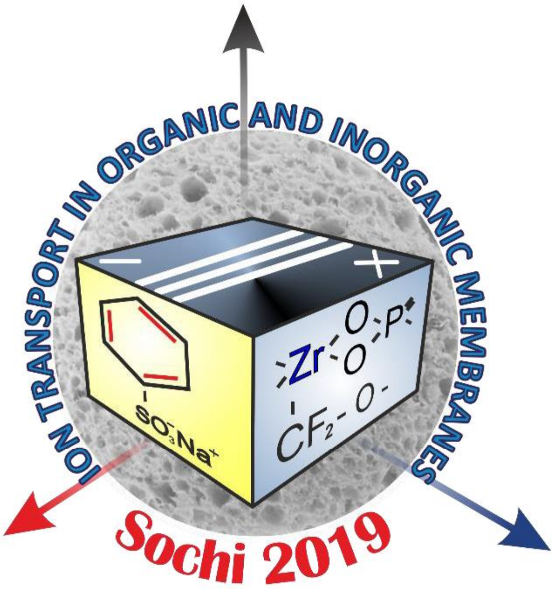

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«MEMBRANE TECHNOLOGY»
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TRANSPORT CHARACTERISTICS OF POROUS GLASS MEMBRANES IN ELECTROLYTE SOLUTIONS

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Introduction

Recently, much attention has been paid to the study of the physical properties of various materials introduced into porous matrices with a pore diameter of the order of units and tens of nanometers. Porous glassy membranes (PGs) have a number of advantages compared with other porous membrane materials: homogeneous chemical composition, low impurities, thermal, chemical and microbiological stability, transparency in the visible part of the spectrum, adjustable structural characteristics. In this work, iron-containing PGs were produced by introducing an iron (III) oxide into the batch during a melting of sodium borosilicate glass. PGs produced in this way are essentially membrane materials of new generation, important for various practical applications. Analysis of the literature data shows that in recent years the number of studies of morphology and physical characteristics (magnetization, dielectric constant, electrical conductivity, spectral characteristics, etc.) of iron-containing porous glasses has increased, while their characteristics in electrolyte solutions remain unexplored. In this regard the study and comparison of the transport characteristics (filtration coefficient, counterion transport numbers, surface conductivity, streaming potential) of iron-containing micro- and macroporous (MIP and MAP) glasses (Fe-4) in 10^{-1}-10^{-4} M solutions of an indifferent electrolyte NaCl [1,2] and of KNO_3 specific to the silica surface with the parameters of MIP and MAP glasses previously obtained from basic sodium borosilicate (8V) glass were carried out. Taking into account the fact that triply charged counterions have the maximum capacity for specific adsorption, a comparative analysis of transport characteristics of basic 8V membranes in NaCl, KNO_3 and $FeCl_3$ [2] solutions was also carried out.

Experiments

The sodium borosilicate glasses without or with iron oxide (8V or modified Fe-4 glasses) were chosen as objects of study. To obtain MIP glasses (as defined by S.P. Zhdanov [3]), two-phase 8V and Fe-4 glasses in the form of polished discs with diameter of 30 mm and thickness of about 1 mm were leached in 3M solutions of hydrochloric or nitric acid. To obtain MAP glasses (as defined by S.P. Zhdanov [3]), the MIP samples were treated with 0.5M KOH solution at 20 ^{0}C for 4 hours (porous glasses 8V), or for 1, 2.5 and 4 hours (porous glasses Fe-4). Macroporous iron-containing glasses are marked as “1”, “2” and “3” in order of increasing alkaline treatment time.

X-ray phase analysis method was used to identify the magnetite phase in MIP and MAP iron-containing glasses. The iron content (averaged over 5–9 EDX spectra for each PG sample) in micro- and macroporous iron-containing membranes is shown in Table 1.

Table 1: The relative iron content in the samples of porous glass

Iron content	Membranes			
	Fe-4 MIP	Fe-4 MAP-1	Fe-4 MAP-2	Fe-4 MAP-3
weight %	2.59	6.31	6.83	10.49
atomic %	1.14	2.36	2.38	3.76

Results and Discussion

Filtration coefficients G used to calculate the through pore radius (r) were measured for MAP 8V and Fe-4 glasses in 0.1 M NaCl [1,2], KNO_3 and $FeCl_3$ [2], solutions before and after the measurements of electrosurface transport characteristics. It was found that with increasing alkaline treatment time of Fe-4 MIP membranes from 1 to 4 hours, the filtration coefficient increases in accordance with the removal of secondary silica from the pore space. During long-term contact (about 4 weeks) of iron-containing MAP glasses with KNO_3 solutions, the filtration coefficient increased 1.5–2 times, which corresponds to an increase in average pore radius from 6.3-15 nm up to 7.0-17.7 nm. Note that the tendency of an increase in G and r values for Fe-4 MAP glasses during the contact of membranes with 1:1 electrolytes in the neutral pH region was more pronounced than for 8V MAP glasses (their r values changed from 13 up to 13.9 nm in NaCl solutions and from 15 up to 15.6 nm in KNO_3 solutions). This phenomenon can be explained by the greater dissolution of the silica skeleton of Fe-4 glasses than that of 8V. It was also obtained that the values of G and r for 8V MAP in the $FeCl_3$ solutions in the acidic pH region remained practically unchanged (15.1 and 15.6 nm for parallel samples).

The results of measurements of the specific electrical conductivity of the membranes were used to calculate the specific surface conductivity K_S, the cause of which is the excess ion density in the electrical double layer (EDL) in the pore space of the membranes and efficiency ratio α (equal to the ratio of the specific electrical conductivities of pore and free solutions). An analysis of the results shows that the specific surface conductivity in 1:1 electrolyte solutions for both PG compositions has the usual order — 10^{-10} Ω. The K_S values of MIP glasses in NaCl and KNO_3 (fig. 1) solutions are close to each other and tend to slightly increase with increasing electrolyte concentration, which is characteristic of PG, in the pore space of which secondary silica is contained. A decrease in the degree of its swelling with increasing concentration leads to an increase in the average mobility of counterions, which, along with an increase in the absolute value of the surface charge, increases the surface conductivity. Note that a decrease in the amount of secondary silica due to additional alkaline treatment of MIP glasses, leading to an increase in the size of the pore channels, leads to an increase in the average pore mobility of Na^+, K^+ ions and an increase in K_S values. This phenomenon is associated with a large surface charge of the MAP glass compared with MIP glass. The results of the study showed that the α obtained for microporous 8V and Fe-4 glasses are close in a neutral pH region and more than one both in NaCl solutions and in KNO_3 solutions, whereas both for MIP and MAP 8V membranes in the $FeCl_3$ solution there are concentration regions in which the electrical conductivity of the free solution exceeds the electrical conductivity of the pore solution ($\alpha < 1$). That leads to the negative K_S values in these concentration regions as a result of a sharp slowdown in the mobility of specifically adsorbed Fe^{3+}ions in a pore liquid.

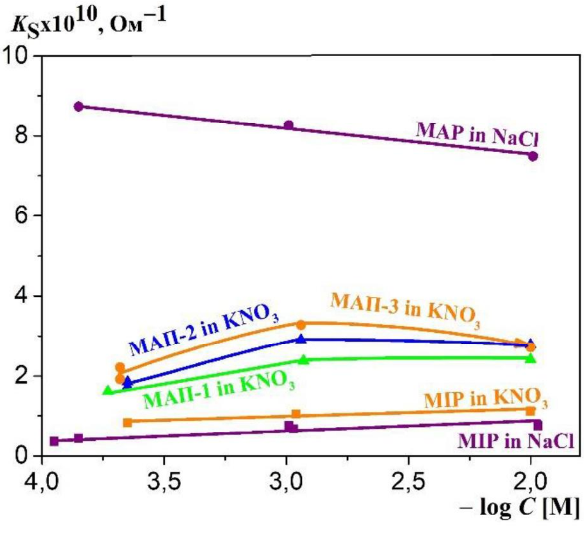

Figure 1. Dependencies of specific surface conductivity of iron-containing Fe-4 porous glasses on the concentration of NaCl[1] and KNO_3 solutions.

It was found that the values of the transport numbers of sodium and potassium counterions (n_+) practically do not depend on the composition of the MIP PGs. As the concentration of the electrolyte increases, the values of n_+ decrease in accordance with the decrease in the contribution of ions of DEL to membrane transport processes. The counterion transport numbers of MAP Fe-4 were larger than those of MAP 8V membranes due to the larger surface charge $|\sigma_0|$ of Fe-4 porous glass. With an increase in the treatment time of the Fe 4-6 MIP membranes with an alkali solution, that is, with an increase in the pore size, the values of transport numbers K^+ decrease. Note that n_+ values of Na^+ ions are larger than those for specifically adsorbed K^+ ions at C≤0.01 M. At $C = 10^{-4}$ M all membranes have high selectivity ($n_+ = 0.87– 1.00$).

From the measured values of the streaming potentials for all the porous membranes under study, the values of the zeta-potentials (ζ) were calculated taking into account the electrical conductivity of the pore solution and the overlapping of DEL. Comparison of the values of ζ-potentials found in NaCl and KNO_3 solutions shows that the values of |ζ| for MAP membranes with the same size of pore channels (8V MAP and Fe-4 MAP-3) decrease during the transition from NaCl to KNO_3 due to the pronounced specificity of potassium ions, resulting in a greater degree of Stern layer filling, and, therefore, to a decrease in the absolute values of the electrokinetic potential. For MAP membranes, the ratios |ζ| for basic PG 8V and a Fe-4 membrane, the same: at concentrations of $C > 10^{-3}$ M, the values of |ζ| in NaCl solutions are higher than in KNO_3 solutions, and at $C < 10^{-3}$ M, the values of |ζ| in both electrolytes converge. The observed patterns are associated both with different specificity of counterions and with the influence of secondary silica contained in the pore space of the MIP glass on all transport characteristics of PG. Electrokinetic potential is negative in the whole study area of NaCl and KNO_3 concentrations and only at very low concentrations of $FeCl_3$. As the $FeCl_3$ concentration increases, the system passes through the isoelectric point and the ζ values become positive.

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