

# ELECTRODIFFUSION AND STRUCTURE CHARACTERISTICS OF PERFLUORINATED MEMBRANES MODIFIED WITH HALLOYSITE

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## Introduction

Components of organic and inorganic nature are successfully used as modifiers of ion-exchange membranes to convey them new functional properties and expand their applications. Nanotubes of halloysite are among the promising modifiers [1, 2]. Metal nanoparticles can be deposited on their surface, which will give the membrane additional catalytic properties. However, the risk of formation of large cavities and pores is probable. It can lead to an increase of membrane diffusion permeability for electrolyte solutions and gases, as well as a decrease of membrane selectivity.

The aim of this work is to investigate the effect of halloysite nanotubes on the diffusion permeability, selectivity, and current-voltage curves of perfluorinated membranes in NaCl solutions.

## Experiments and Results

The objects of the study were MF-4SK membranes, obtained by casting from a polymer solution in isopropanol and dimethylformamide (DMFA). The samples contained 4% of halloysite nanotubes with platinum and palladium nanoparticles. Concentration dependencies of the integral coefficient of diffusion permeability of the initial and modified membranes for NaCl solutions are presented in Fig.1. As can be seen from Fig.1 the membranes should be cast from the polymer solution in DMFA to obtain samples with reduced diffusion permeability. The intercalation of the modifier increases the diffusion characteristics of the membrane by almost 2 times in the investigated range of NaCl solution concentrations, except for the sample modified by the halloysite nanotubes (HNT) with platinum, which has the same diffusion characteristics as the unmodified membrane.

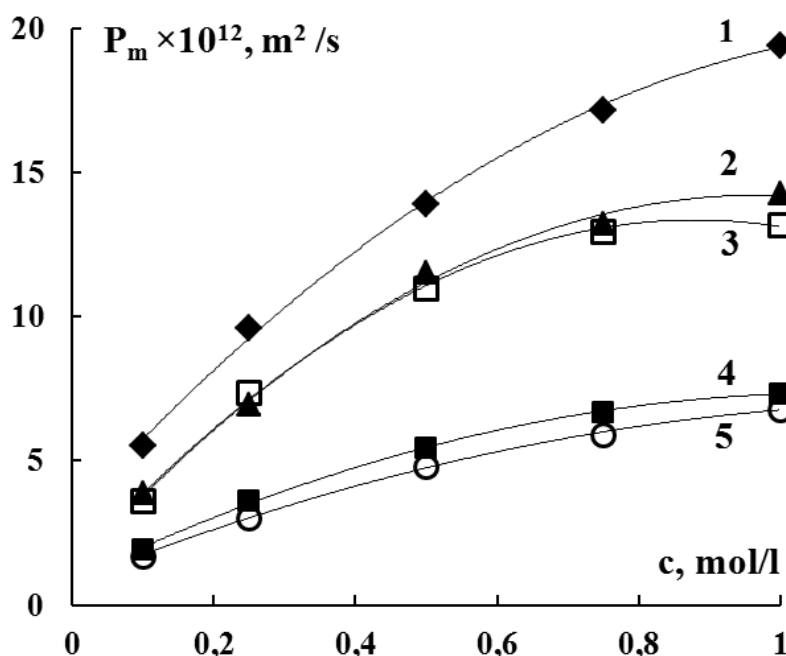


Figure 1. Concentration dependencies of the integral coefficient of diffusion permeability for perfluorinated membranes cast from polymer solution in isopropanol (1) and DMFA (2-5): 2 – MF-4SK/HNT, 3 – MF-4SK/HNT (Pd), 4 – MF-4SK, 5 – MF-4SK/HNT (Pt)

The differential coefficient of diffusion permeability was calculated from the experimentally obtained concentration dependences of the diffusion flux to estimate the modified membrane selectivity, using also data on the electrical conductivity of the samples in NaCl solutions of the same concentration.

The independent estimation of selectivity of modified perfluorinated membranes was fulfilled on the basis of analysis of water distribution by effective radii of pores and binding energies of wares obtained by the standard contact porosimetry (Fig. 2). The fraction of micro- and mesopores in the total pore volume of the membrane is the criterion for its selectivity. For the initial membrane it is 0.80 and for the modified sample it equals to 0.78. This fact indicates that the introduction of HNT modified with platinum nanoparticles has practically no effect on the selectivity of perfluorinated membrane. Evaluation of the structural characteristics of membranes from porosimetric curves showed that the maximum porosity decreases from 0.3 cm<sup>3</sup>/g to 0.27 cm<sup>3</sup>/g after modification, and the specific internal area decreases from 244 m<sup>2</sup>/g to 216 m<sup>2</sup>/g.

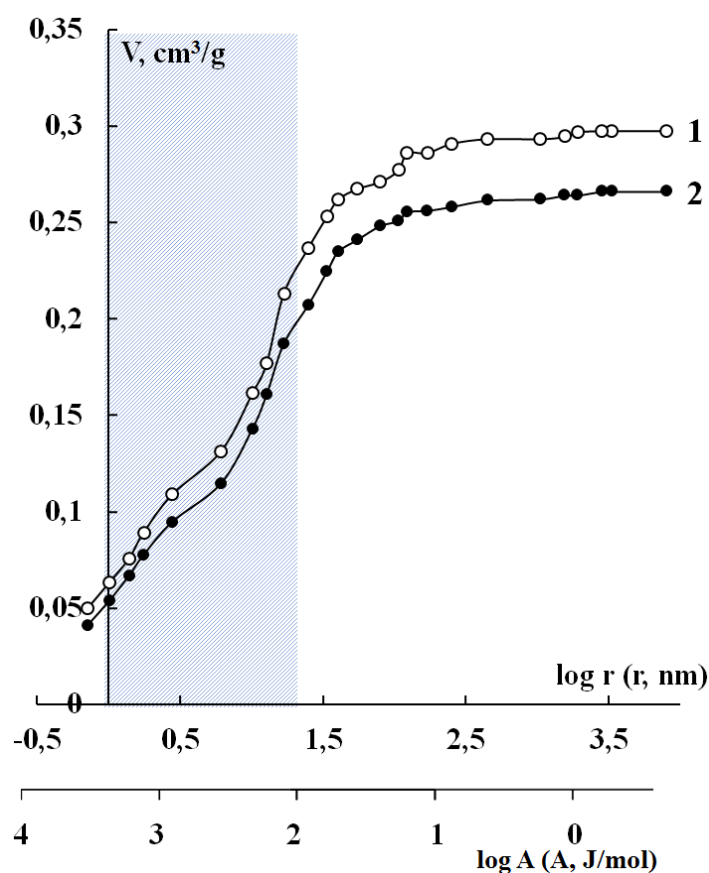


Figure 2. Integral water volume ( $V$ , cm<sup>3</sup>/g) distribution on the effective pore radii and the water binding energy for the MF-4SK (1) and MF-4SK/HNT (Pt) (2) membranes

The current-voltage curves (CVC) of the initial and modified with halloysite MF-4SK membranes were measured in 0.05 M NaCl solutions to evaluate the effect of the modifier on the electrodiffusion characteristics of perfluorinated membrane. Measurement of the CVC was carried out for different orientations of the sample in electrical field because the relief of the membrane surface affects the behavior of electromembrane system and the parameters of the CVC [3]. It was mentioned for all samples that the membrane surface which contacted with air during membrane casting is more inhomogeneous than one which contacted with the glass. The measured CVC are presented in Fig.3. As can be seen from the Fig.3, the magnitude of the limiting current, the slope of ohmic section and the overlimiting current are practically the same for the initial and modified membrane and do not depend on the heterogeneity degree of the sample surface. The inclusion of modifier and the length of limiting current plateau and the potentials of the system transitions into overlimiting state.

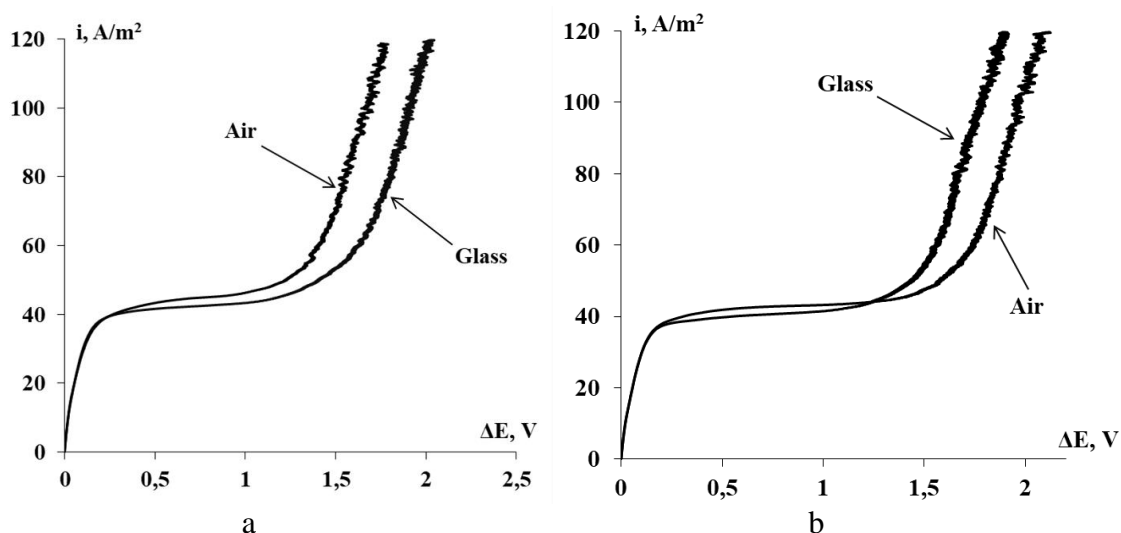


Figure 3. Current-voltage characteristics of the MF-4SK (a) and MF-4SK/HNT (b) membranes in 0.05 M NaCl solution. The cursor indicates the membrane side where the limiting state occurred

In the case of unmodified MF-4SK membrane the electromembrane system transfers into overlimiting state earlier if the more inhomogeneous membrane surface is oriented toward the counterion current. The overlimiting state comes later for MF-4SK/HNT membrane with the same orientation in the measuring cell. The reason is the combined action of two effects such as an inhomogeneity of the membrane surface and its hydrophilicity [4], which increases after introduction of halloysite nanotubes into the perfluorinated matrix.

### Conclusion

The modification of the perfluorinated membrane by the halloysite nanotubes, including the nanotubes with platinum nanoparticles, does not lead to a significant increase in the diffusion permeability, allows keeping the high membrane selectivity and practically does not change the structure characteristics and parameters of the current-voltage curve.

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### References

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