PROPRIEDADES DE TRANSPORTE DA PERCOLAÇÃO DE FASE LÍQUIDA EM RAMOS DE POLÍMEROS VÍTREOS ALTAMENTE PERMEÁVEIS

TRANSPORT PROPERTIES OF LIQUID PHASE PERCOLATION CLUSTER IN HIGHLY PERMEABLE GLASSY POLYMERS

ТРАНСПОРТНЫЕ СВОЙСТВА ПЕРКОЛЯЦИОННОГО КЛАСТЕРА ЖИДКОЙ ФАЗЫ В ВЫСОКОПРОНИЦАЕМЫХ СТЕКЛОБРАЗНЫХ ПОЛИМЕРАХ

SOBOLEV Vladimir D.^{1*}; YUSHKIN Alexey A.²; SABBATOVSKIY Konstantin G.³; SERGEEVA Inessa P.⁴;

^{1,3,4} Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences. Russia.

² Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences. Russia.

* Correspondence author
e-mail: vladimir.sobolev@mail.ru

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RESUMO

A porosidade, permeabilidade e condutividade das membranas de poli[1-(trimetilsilil)-1-propino] (PTMSP) em misturas de etanol-água foram determinadas através da análise das características de impedância. Foi calculada a fração crítica de volume da porosidade na qual os canais de condutividade são formados. Quando o teor de álcool na solução aumenta foi de 0,29; quando diminui foi de 0,17. As dependências obtidas indicam que a transferência de matéria na membrana ocorre com os elementos da fase líquida, formando um ramo de percolação à medida que a quantidade de líquido absorvido aumenta. O efeito da histerese foi observado nos valores medidos de porosidade, permeabilidade, condutividade e capacidade. A estrutura porosa de uma membrana seca de PTMSP consiste em elementos de volume livre que não estão conectados entre si. Com aproximadamente 30% de concentração de álcool, através dos canais, começam a se formar, conectando os dois lados da membrana. Nesse caso, a permeabilidade e a condutividade elétrica aumentam como uma função exponencial, em contraste com a porosidade que aumenta linearmente. A fórmula de Lichtenecker e Rother ajudou a calcular as frações de volume das fases condutora e não condutora do sistema. Os valores obtidos da quantidade de líquido na membrana em vários arranjos espaciais dos canais permitiram estabelecer a estrutura dos canais cheios de líquido. A melhor concordância com os valores experimentais foi obtida para a estrutura caótica. Isso é consistente com as idéias existentes sobre a estrutura das membranas estudadas e confirma a suposição de que o ramo de percolação é formado a partir de elementos de volume livre preenchidos com a fase líquida. Os baixos valores observados do potencial zeta e, consequentemente, os baixos valores do componente eletrostático da pressão de cunha indicam que o aumento no tamanho ou no número de canais de transporte está associado a forças não eletrostáticas.

Palavras-chave: membrana, porosidade, impedância, permeabilidade, ramo de percolação.

ABSTRACT

Porosity, permeability, and conductivity of PTMSP membranes in ethanol-water mixtures were determined by analyzing the impedance characteristics. The critical volume fraction of porosity at which through conductivity channels are formed was calculated. When the alcohol content in the solution increases, it was 0.29; when it decreases, it was 0.17. The obtained dependencies indicate that the transfer of matter in the membrane occurs the liquid phase elements, forming a percolation cluster as the amount of sorbed liquid increases. The hysteresis effect was observed in the measured values of porosity, permeability, conductivity, and capacity. The porous structure of a dry PTMSP membrane consists of free volume elements that are unconnected to each other. At ~30% alcohol concentration, through channels, begin to form, connecting both sides of the membrane. In this case, both permeability and electrical conductivity increase as a power function, in contrast to the porosity that increases linearly. Lichtenecker and Rother's formula helped to calculate the volume fractions of the conducting and non-conducting phases in the system. The obtained values of the amount of liquid in the membrane at various spatial arrangements of the channels made it possible to establish the structure of the liquid-filled channels. The best agreement with the experimental values was obtained for the

chaotic structure. This is consistent with the existing ideas about the structure of the studied membranes and confirms the assumption that the percolation cluster is formed from free volume elements filled with the liquid phase. The observed low values of the zeta potential and, consequently, the low values of the electrostatic component of the wedging pressure indicate that the increase in the size or the number of transport channels is associated with non-electrostatic forces.

Keywords: *membrane, porosity, impedance, permeability, percolation cluster.*

АННОТАЦИЯ

Путем анализа импедансных характеристик были определены пористость, проницаемость и проводимость ПТМСР мембран в смесях этанола и воды различной концентрации. Рассчитана критическая объемная доля пористости, при которой происходит образование сквозных каналов проводимости. Для случая, когда содержание спирта в растворе увеличивается, она равна 0,29, а когда уменьшается 0,17. Полученные зависимости свидетельствуют о том, что перенос вещества в мембране осуществляется через элементы жидкой фазы, образующие перколяционный кластер, который формируется по мере увеличения количества сорбированной жидкости, и, в последствие, сохраняется при уменьшении сорбции. Наблюдался эффект гистерезиса в измеренных значениях пористости, проницаемости, проводимости и ёмкости. Пористая структура сухой мембраны из ПТМСР состоит элементов свободного объема практически не связанных друг с другом. При концентрации спирта около 30% начинают образовываться сквозные каналы, соединяющие обе стороны мембраны. При этом и проницаемость и электрическая проводимость возрастают по степенному закону в отличие от пористости, которая увеличивается линейно. Используя формулу Лихтенеккера, были рассчитаны объёмные доли проводящей и непроводящей фазы в системе. Полученные значения количества жидкости в мембране при различных значениях параметра пространственного расположения каналов позволили установить структуру каналов заполненных жидкостью. Наилучшее совпадение с экспериментальными значениями было получено для хаотической структуры каналов. Это согласуется с представлениями о структуре исследованных мембран и подтверждает предположение о том, что перколяционный кластер формируется из элементов свободного объёма, заполненных жидкой фазой. Наблюдаемые низкие значения дзета-потенциала и, следовательно, низкие значения электростатической составляющей расклинивающего давления, свидетельствуют о том, что увеличение размеров или количества транспортных каналов связаны с силами не электростатического характера.

Keywords: *мембрана, пористость, импеданс, проницаемость, перколяционный кластер.*

1. INTRODUCTION

The separation and the purification of liquids have the largest share in the market of membrane processes (Baker, 2012; Nunes and Peinemann, 2006). In filtration or electrodialysis, the membrane wettability is the essential prerequisite of good transport performance. On the other hand, gas-liquid membrane contactors operate efficiently only if the membrane pores are filled with the gas phase, although one or two sides of the membrane stay in contact with the liquid (Drioli *et al.*, 2006).

Depending on the conditions, the same membranes can be used both in membrane contactors and in filtration processes. For example, polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF) membranes are suitable for both carbon dioxide removals in membrane contactors and for liquid filtration (Curcio and Drioli, 2005; Kang and Cao, 2014; Zaidiza *et al.*, 2016; Mansourizadeh and Ismail,

2009), just as polypropylene, polyethylene, polysulfone, polyetherimide, etc. membranes (Zhang *et al.*, 2006; Faiz *et al.*, 2013; Atchariyawut *et al.*, 2007). In the processes associated with high transmembrane pressure, the upper layer of the membrane is usually made of non-porous (elastomers) or micro-heterogeneous (glassy polymers) materials (Volkov *et al.*, 2008; Marchetti *et al.*, 2014).

In such dense layers, the transfer of matter occurs through the free volume. In flexible chain polymers such as rubbers, free volume elements are dynamically formed due to the statistical fluctuation of polymer segments. If the size of the free volume elements is sufficient, the molecules of the filtered liquid fill them, and the matter flows through the membrane. In glassy polymers, free volume elements are formed during polymer deposition. In the presence of bulky pendant groups and a rigid polymer chain, the dense packing of macromolecules becomes difficult. The most studied polymers of this class

are PIM-1, poly[4-methyl-2-pentyne], and poly[1-(trimethylsilyl)-1-propyne] (Srinivasan *et al.*, 1994; Harms *et al.*, 2012; Budd *et al.*, 2005; Fritsch *et al.*, 2012; Shantarovich *et al.*, 2000; Volkov *et al.*, 2009; Morisato and Pinnau, 1996; Khotimsky *et al.*, 2003). These polymers exhibit large free volume fractions, up to 30%, and more. As a result, free volume elements form coherent pore-like structures that facilitate the transfer of matter in the membrane, thus increasing gas and liquid permeability (Srinivasan *et al.*, 1994; Starannikova *et al.*, 2008; Volkov *et al.*, 2013; Yushkin *et al.*, 2015).

It was previously shown that the transfer of solvents through microporous membranes is nonlinearly related to the content of these solvents in the membrane under equilibrium conditions, i.e., to the solvent sorption (Volkov *et al.*, 2013; Yushkin *et al.*, 2015). It was noted that the sorption of liquid from aqueous ethanol solutions to PTMSP increased in the areas where the concentration of ethanol reached 10–20%, while the flow through the membrane was observed only at alcohol concentrations of greater than 50%. Hydrodynamic flow through the membrane occurs when there are fluid-filled channels connecting the opposite sides of the membrane. In this case, the fluid-filled pores act as conductors that form the system of transport channels. In polymers of internal microporosity, such transport channel systems are the free volume elements.

The situation when the fluid flows through the membrane arises only when sorption reaches critical values, is similar to the percolation theory, which is applied to analyze a wide range of systems (Stanley *et al.*, 1999; Essam, 1980; Parlar and Yortsos, 1988; Berezina and Karpenko, 2000). What also points to this is the finding (Yushkin *et al.*, 2008) that the electrical resistance of membranes decreased for liquids whose permeability increased. In membrane technology, the percolation theory has been widely used in mixtures of electrically conductive and non-conductive materials. The observation of the conductivity threshold in carbon nanotube composites showed that the addition of a certain amount of conductive carbon nanotubes, dispersed in a non-conducting polymer, abruptly increases the conductivity of the system (Bauhofer and Kovacs, 2009; Fangming *et al.*, 2005; Grekhov and Eremin, 2015).

To determine the impedance of a membrane, researchers usually examine the characteristics of an electric circuit in the alternating current mode with and without a

membrane installed (Canas *et al.*, 2001; Coster *et al.*, 1992; Gaedt *et al.*, 2002; Park *et al.*, 2005, 2006; Bannwarth *et al.*, 2015; Sistat *et al.*, 2008; Sedkaoui *et al.*, 2016; Hosseini *et al.*, 2017; Meier *et al.*, 2011). Since solvents have a rather low intrinsic conductivity, electrolytes containing monovalent Na^+ , K^+ , and Cl^- ions are used to improve the measurement sensitivity (Han *et al.*, 2016; Oliot *et al.*, 2016). In the general case, the impedance of the system should be calculated by solving a set of simultaneous equations that describe an equivalent electrical circuit consisting of many elements. However, in most cases, the task is greatly simplified. At low frequencies, the impedance of the system is equal to the summed impedances of the liquid and the membrane (Park *et al.*, 2006).

Previously, the impedance measurements under various conditions were used to assess the thickness of the selective layer in reverse-osmosis and nanofiltration membranes (Canas *et al.*, 2001; Malmgren-Hansen *et al.*, 1989; Asaka, 1990), the porosity of individual membrane layers (Coster *et al.*, 1992; Gaedt *et al.*, 2002), the wetting of membranes (Bannwarth *et al.*, 2015), and also to control the surface contamination (Gaedt *et al.*, 2002; Park *et al.*, 2005; Marbelia *et al.*, 2016). Such data can be obtained by measuring the spectra of electrochemical impedance in a wide frequency range (Canas *et al.*, 2001; Coster *et al.*, 1992; Gaedt *et al.*, 2002; Park *et al.*, 2005, 2006; Bannwarth *et al.*, 2015; Sistat *et al.*, 2008; Malmgren-Hansen *et al.*, 1989; Asaka, 1990).

The aim of this work is to study the patterns of filtration characteristics and conductive behavior of PTMSP associated with the change in the porous structure of the polymer when it swells depending on the properties of the solution in contact with the membrane.

2. MATERIALS AND METHODS

A glassy polymer of internal microporosity poly[1-(trimethylsilyl)-1-propyne] (PTMSP) (Gelest Inc., USA) was used in the experiments. Continuous membranes (films) were made of PTMSP by pouring the polymer solutions (0.5 wt %) in chloroform on to cellophane and drying at room temperature. To remove the tangential stresses after drying, the film samples were kept in butyl alcohol, then placed in ethanol and washed successively in ethanol-water solution, shaving a gradually decreasing concentration of

ethyl alcohol, according to the procedure used in (Volkov *et al.*, 2013). It was previously shown that when filtering ethanol-water solutions through PTMSP, the ratio of components does not change (Volkov *et al.*, 2013). In that research, the experiment with solutions containing NaCl gave a similar result. Therefore, in the calculations, it is assumed that the properties of the liquid in the membrane are the same as in the bulk solution where the membrane was placed.

To study the impedance characteristics of the membrane, it was placed in a cell (Figure 1), having a Teflon body (1), between two platinum electrodes (2, 4). The cell was previously described in detail by Berezkin *et al.*, 2012. The volume on both sides of the membrane (3) was filled with the studied fluid. The membrane was preliminarily kept in the solution for 24 hours, and after that, it was placed in the chamber pre-filled with the solution above the electrode (2). The active membrane area in the cell was 1 cm². It was shown in (Yushkin *et al.*, 2018) that after the membrane is placed in the solution, it takes less than three hours to reach the stationary values of the membrane electrical conductivity. The membrane was placed in the solution 24 hours before measuring the impedance characteristics, and this ensured that the measured values were stationary.

Figure 1. Cell for studying the impedance characteristics of membranes: 1 – cell body, 2 – lower electrode, 3 – membrane, 4 – upper electrode, 5 – sliding cylinder

A Teflon cylinder (5) with an electrode (4) slid into the chamber with the membrane from above. The distance between the electrodes was set remotely with an accuracy of 1 μm. The voltage in the cell and the phase difference between current and voltage were measured with

an accuracy of ~1% in the frequency range from 1 Hz to 2.6 MHz. The impedance characteristics were recorded automatically using the RLC-2010 impedance analyzer.

To measure the PTMSP surface flow potential, a polymethylmethacrylate slit device consisting of two symmetric parts was used (Figure 2).

Figure 2. Slit device for measuring the ζ -potential of the membrane surface: 1 – cell body, 2 – membrane, 3 – channel, 4 – silver-chloride electrodes, 5 – multimeter, 6 – voltage source

Two identical PTMSP films (2) were stuck onto the cell body (1). During measurements, the channel width (3) in the device was $b = 2.5$ mm, the channel length was $l = 20$ mm, and the channel height h was altered using gaskets. The height was 70 μm while the membrane was dry, and decreased to 8 μm as the membrane swelled, depending on the percentage content of ethanol. The exact height of the slit was calculated by the flow rate of the solution passing through the channel:

$$h = \frac{\sqrt{12Q\mu l}}{\sqrt{b\Delta p\Delta t}} \quad (\text{Eq. 1})$$

when Q is the volume of fluid passing through the slit at pressure Δp for time Δt , and μ is the solution viscosity.

Silver-chloride electrodes (4) and a multimeter (5), consisting of the U5-12 amplifier (Russia) and the GDM-8246 voltmeter (GW Instek, Taiwan), was used to record the flow potential values. The input impedance of the amplifier in the potential measurement mode was 100 TΩ. The electrical conductivity of the slit was determined by the dependence of the current

on the voltage supplied from the DC power source (6). The method for measuring the ζ -potential is described in (Nebavskaya *et al.*, 2016, 2017).

The mixtures of water and ethanol in various mass concentrations C_0 were used as the liquid phase. To increase the electrical conductivity, 0.5 g/L NaCl was added to the solutions. The conductivity of the mixtures decreases as the ethanol concentration increases, which is associated with the transition from a strong electrolyte (NaCl in water) to a solution with ion associates (NaCl in alcohol). The formation of associates reduces the number of ions, which are the main charge carriers in the system (Harned and Owen, 1950) (Figure 3).

Figure 3. Conductivity κ_0 of ethanol-water solutions with 0.5 g/L NaCl

Before being placed in the cell, the films were kept in the NaCl-water solution for 24 hours. After that, they were placed in the device, filled with the studied mixture, for measuring electrical conductivity. Next, the program for automatic registration of impedance characteristics was launched. Successively increasing the frequency from 1 Hz to 2.66 MHz, the program recorded capacitance (C), conductivity (σ), resistance (R), imaginary (ImZ), and real (ReZ) parts of the complex impedance, and phase shift (ϕ).

After the recording cycle, the sample was placed in the NaCl solution in a mixture of 10% ethanol and 90% water for 24 hours. After that, the entire measurement procedure was repeated. For each sample, the impedance characteristics were measured in ethanol-water solutions, the ethanol concentration changing in the following

order: 0-10-20-30-40-50-60-70-80-90-96-90-80-70-60-50-40-30-20-10-0%.

The electrical conductivity of the membrane κ_m was determined by Equation 2:

$$\kappa_m = \frac{l}{R_m S} \quad (\text{Eq. 2})$$

where R_m is the electrical resistance of the membrane. The through porosity a_r , i.e., the ratio of the electrical conductivity of the membrane to the electrical conductivity of the same layer of volume electrolyte, is equal to $a_r = \kappa_m / \kappa_0$

where κ_0 is the electrolyte conductivity.

The filtration experiments were carried out in dead-end cells previously described in (Volkov *et al.*, 2009), at transmembrane pressure 30 bar and room temperature. The active membrane area in the cells was $33.3 \cdot 10^{-3} \text{ m}^2$. To minimize the concentration polarization effect, the cells were equipped with suspended magnetic anchors and magnetic stirrers that mixed the liquid near the membrane surface. The volume of the primary solution was 800 ml. The membrane permeability was found by the gravimetric method. To do this, a receiving vessel was installed at the cell outlet. The vessel was designed in such a way as to minimize the evaporation of the liquid. The permeability coefficient P was used to characterize the membranes. It was calculated according to Equation 3:

$$P = \frac{m \cdot l}{S \cdot \Delta t \cdot \Delta p} \quad (\text{Eq. 3})$$

where m is the mass of permeate (kg) that passed through a membrane having the area S (m^2) over the period of time Δt (h) under the action of applied transmembrane pressure (Δp). The normalization of the membrane thickness (l) makes this parameter independent of the membrane thickness in the case of symmetrical membranes.

To determine the open porosity of the membrane a_o , i.e., the ratio of the pore volume occupied by the liquid to the membrane volume, 100 μm thick PTMSP films were cast. The mass of dry membranes was measured first, and then

they stayed in the studied solution for one week. The films were soaked in a sealed container in order to exclude the impact of solvent evaporation on the obtained sorption values. Next, the membrane was removed from the studied solution, the excess liquid was removed from its surface with filter paper, and the sample was weighed. The open porosity α_o was calculated by the gravimetric method by the formula:

$$\alpha_o = \frac{m_1 - m_0}{\rho_s V_m} \quad (\text{Eq. 4})$$

where m_1 is the mass after soaking in the solution, m_0 is the initial mass of the sample, ρ_s is the density of the solution, and V_m is the volume of the membrane.

3. RESULTS AND DISCUSSION

The threshold nature of the water-alcohol mixture flow through PTMSP and other highly permeable glassy polymers has already been shown (Yushkin *et al.*, 2015). This phenomenon is associated with the formation of a percolation cluster through which the liquid is transferred at high concentrations of alcohol.

Figures 4 and 5 demonstrate the dependence of the change in porosity and permeability of the solution on the concentration of ethanol in the solution. The nature of the concentration dependences apparently varies. While the change in porosity occurs at small alcohol concentrations, the permeability is not observed until the alcohol concentration reaches 50%, and only then the permeability manifests itself clearly. From this, it follows that first, the solution fills the existing free volume elements, which are unconnected to each other; and only after the porosity increases to $0.45 \text{ cm}^3/\text{cm}^3$, permeable channels appear and filtration begins. If the alcohol concentration in the solution decreased, the permeability coefficient was higher than with an increased alcohol concentration, i.e., hysteresis was observed. Hysteresis can also be observed when measuring the membrane porosity. In the case of porosity, hysteresis was less pronounced. Moreover, the presence of salt in the solution did not affect the permeability coefficient of the

studied liquids.

Figures 4. Open porosity α_o depending on the ethanol concentration in the solution: 1 – ethanol concentration increasing, 2 – ethanol concentration decreasing.

Figure 5. PTMSP permeability in ethanol-water solutions (adapted from (Yushkin *et al.*, 2018))

The wedging pressure in the membrane channels facilitates membrane swelling and formation of through infiltration channels. The main component of the wedging pressure at low electrolyte concentrations is the electrostatic one.

To assess the impact of the electrostatic component of the wedging pressure in the membrane channels on the formation of transport channels, the ζ -potential of the membrane surface was measured depending on the alcohol concentration in the ethanol-water solutions. The measurement showed that the ζ -potential was negative in an aqueous solution (Figure 6), but it

was much less than the potential of a conventional glassy polymer with a relatively small fraction of free volume (Kirby and Hasselbrink, 2004). For polystyrene in a 10^{-3} M KCl solution, the ζ -potential of the surface was -40 mV (Churaev *et al.*, 1988).

Figure 6. ζ -potential of the membrane surface at the 0.5 g/L NaCl concentration and various alcohol concentrations in the ethanol-water solutions

As the alcohol concentration increases, the ζ -potential of the PTMSP surface decreases in absolute value nearly to zero. Low potential values and, therefore, low electrostatic component values cannot increase the size or the number of transport channels. This means that an increase in the size or the number of transport channels is associated with non-electrostatic forces.

Another method for determining the porous structure of membranes is the impedance spectroscopy. The experiments were carried out with ethanol-water solutions having various alcohol concentrations and the 0.5 g/L NaCl concentration. The presence of salt made it possible to increase the conductivity of the solutions in order to cancel the contribution of the liquid layer between the membrane and the electrodes to the total resistance of the system. First, the capacitance and the resistance of the membrane and the liquid layer above it were measured at different distances between the electrodes and at several frequencies. It was found that the capacitance value or the resistance value, in the extrapolation of the dependences of the capacitance or the resistance to the zero thickness, did not differ from the same values when the electrodes were in direct contact with the membrane. Hence all further measurements were carried out with the electrodes pressed against the membrane.

a)

b)

c)

d)

Figure 7. Hodograph curves in Nyquist coordinates for a membrane soaked in solutions with various alcohol concentrations: (a) 10%, (b) 40%, (c) 80 %, (d) 96 %.

Figure 7 shows the impedances of the membrane aged in solutions with various alcohol concentrations. Apparently, there is only one high-frequency arc on the spectrum. According to (Moya, 2016; Rubinstein *et al.*, 2009; Nikonenko and Kozmay, 2011), the high-frequency arc is determined by the geometric capacity of the membrane and its resistance. The characteristic frequency f_g , corresponding to the Nyquist section maximum, including capacitance and parallel resistance, can be determined by Equation 5 (Vorotyntsev, 2002; Barsoukov and Macdonald, 2005):

$$f_g = \frac{1}{2\pi C R_g} \quad (\text{Eq. 5})$$

where R_g is the diameter of the high-frequency arc.

The linear dependences on the right low-frequency part of the graph, which go upward with increasing the alcohol concentration in the solution, are associated with alcohol adsorption on the electrodes. The impedances of such processes can be soundly described by the Frumkin and Melik-Gaykazyan model that considers the impedance of the adsorption process in which diffusion limits the transport of matter to the electrode surface (Grafov and Ukshe, 1973; Stoyanov *et al.*, 1991; Frumkin and Melik-Gaykazyan, 1951). Figure 8 shows the model that presents our experiments very well, where R_m is the membrane resistance, C_m is the membrane capacity, C_{ad} is the adsorption capacity, R_{ct} simulates the resistance of the particles transfer from the solution to the adsorbed state, W is the diffusion limitation, and R_0 is the resistance of the solution between the membrane and the electrodes.

Figure 8. Model for calculating hodograph curves

Figure 7 reports the curves 1, which were drawn from the experimental results and which we shall refer to as Curves 1. Curves 2 were calculated using the model shown in Figure 8. The calculations were performed using an equivalent circuit analyzer DCS. The error in determining the parameters does not exceed 1.5–2%.

As illustrated in Figure 7, the resistance R_g , which is determined by extrapolating the hodograph curve to the abscissa axis, practically coincides with the doubled value of R_m , which was calculated according to the model used. As calculations pinpointed, R_0 does not exceed 0.1% of the membrane resistance and, therefore, this value can be neglected. This also proves that it is possible to obtain the impedance characteristics of the membrane when the electrodes in the device are pressed against the membrane.

Figure 9 shows the dependences of the electrical conductivity of the membrane σ_m , calculated from the measured R_m values, depending on (a) the alcohol concentration and (b) the membrane porosity.

a)

b)

Figure 9. Dependence of the electrical conductivity of the membrane on (a) the alcohol concentration and (b) the membrane porosity: Curve 1 – increasing alcohol concentration, Curve 2 – decreasing alcohol concentration.

As can be seen from Figure 9, the conductivity varies nonlinearly at increasing ethanol concentration and increasing membrane porosity. The nature of the dependence changes dramatically at a porosity of about 0.25, the ethanol concentration increasing, and about 0.15, the ethanol concentration decreasing. These values are critical because above them, and percolation clusters are formed from the conductive elements, which provide a sharp increase in electrical conductivity. Similar

dependencies were obtained in (Vysotskii *et al.*, 1995; Kirkpatrick, 1973). In some cases, the change in properties after the critical point was more abrupt, as in (Berezina and Karpenko, 2000), for ion-exchange membranes, in which additional electrostatic forces occurred due to the presence of charges.

Percolation theory approaches can be used to analyze the obtained data. As shown by theoretical and experimental studies, the electrical conductivity of composites with different ratios of conducting and non-conducting phases near the percolation threshold is described by Equation 6 (Kirkpatrick, 1973):

$$\kappa_m = \kappa_0 (f - f_k)^t \quad (\text{Eq. 6})$$

where κ_0 is the factor equal to the specific conductivity of the conductive material, f is the volume fraction of the conductive phase in the composition, f_k is the critical volume fraction of the conductor, and t is the critical conductivity index.

The critical porosity was estimated using the semi-logarithmic dependences shown in Figure 10, which made it possible to calculate the critical volume fraction of porosity a_k at which through conductivity channels are formed. When the alcohol content in the solution increases, $a_k = 0.29$, and when it decreases, $a_k = 0.17$. The critical conductivity index t is $t = 3.86 \pm 0.23$ in the first case and $t = 3.26 \pm 0.085$ in the second case. The critical conductor fraction was determined by the Monte Carlo methods (Kirkpatrick, 1973; Vysotskii *et al.*, 1995; McLachlan *et al.*, 1993; Hsu *et al.*, 1980), and it was found that this value is related to the size and the orientation of particles of both phases, and $f_k = 0.15$ for three-dimensional systems. However, in experiments with a strong asymmetry of the conducting and non-conducting forms, the values can be even larger (Kirkpatrick, 1973; Hsu and Berzins, 1985; Yushkin *et al.*, 2018). Thus, the values obtained agree with the literature data.

a)

b)

Figure 10. Change in the electrical conductivity of the membrane during swelling in the solution in the coordinates $\log \kappa_m - \log(a - a_k)$ with (a) increasing and (b) decreasing alcohol concentration in the solution.

However, the critical conductivity index is much larger than the theoretically calculated one. This may be due to a change in the electrical conductivity of the liquid inside the membrane during its swelling.

If compared, the membrane permeability and the membrane conductivity demonstrate identical relationships. For clarity, Figure 11 shows the values of permeability and conductivity, normalized to the corresponding values for ethanol. The dependence of permeability is bounded from below by a value of 0.01 on the value of ethanol permeability, which is due to the inability to pinpoint such small

transmembrane flows. When measuring the conductivity, there is no such bound, and it was possible to pinpoint a change in the transport characteristics of the membrane at lower ethanol concentrations.

Figure 11. Permeability (squares) and conductivity (circles) of the PTMSP membranes in the ethanol-water solutions

As can be seen, when the ethanol concentration increases, the respective increase in conductivity begins at the ~30% ethanol concentration in the solution, and then the conductivity grows sharply with increasing the alcohol content. When the ethanol concentration decreases, the conductivity decreases slightly until the ethanol concentration reaches 40%, then decreases sharply with decreasing alcohol content, and becomes low at the 20% ethanol concentration. The membrane permeability, in the area where it was possible to measure it, behaves similarly to the conductivity. These data confirm that the conductivity and the permeability of the membrane are provided by the same transport channels formed by the percolation cluster from the liquid phase. The liquid permeability coefficient and the electrical conductivity are provided by the liquid phase inside the membrane and, therefore, the electrical resistance is a good criterion for predicting the transport properties of the membrane. As in (Yushkin *et al.*, 2018), a hysteresis of the membrane properties was observed when the ethanol concentration in the surrounding solution changed upward and downward. One of the mechanisms of the observed hysteresis is related to the fact that during the initial filling of the free volume elements, the largest free volume

elements are filled first, while the percolation cluster is formed at the ~30% ethanol concentration when the isolated elements begin to merge into a network after the smaller elements fill up. On the contrary, in desorption, the liquid first leaves the free volume elements that do not participate in the transfer of matter through the membrane, and the percolation cluster is destroyed at the ~10% ethanol concentration. In the absence of the percolation cluster, the transfer of matter is possible only by the diffusion mechanism, which provides for a significantly lower flow through the membrane.

The deformation of polymer molecules can be another mechanism supporting the hysteresis of hydraulic permeability and electrical conductivity at decreasing alcohol concentrations. Polymer swelling occurs with increasing the pressure in the free volume elements, and the deformation of the supramolecular structures of the polymer can occur, which is similar to the mechanical drawing of the polymer. The molecular orientation, which manifests itself at that, can remain intact for a long time after unloading at a temperature lower than the glass transition temperature. This created the observed hysteresis. It should also be noted that previously hysteresis phenomena were observed in various polymers with internal microporosity (Yushkin *et al.*, 2018), and in hydrophilic cellophane (Yushkin *et al.*, 2015).

Of special interest is the nature of the distribution of liquid-filled channels. A change in the volume fraction of liquid in the membrane entails a change in the dielectric constant of the membrane (ϵ), which can be determined if the capacity and the thickness of the membrane are known.

The ratio of components, including salt, did not change when passing through the membrane under the pressure drop. Based on this, it can be assumed that the concentration of components in the membrane also does not change. Then, it is possible to calculate the volume fractions of the system components (Q_m and Q_s) by Lichtenecker and Rother's mixture formula (Lichtenecker and Rother, 1931):

$$\epsilon^x = \epsilon_m^x \cdot Q_m + \epsilon_s^x \cdot Q_s \quad (\text{Eq. 7})$$

where Q_m and ϵ_m are the volume fraction and the dielectric permittivity of the polymer (membrane material), and Q_s and ϵ_s are the

volume fraction and the dielectric permittivity of the solution in the membrane.

The authors of (Yushkin *et al.*, 2015; Stanley *et al.*, 1999) relied on the assumption that the macroscopic properties of a liquid (by the example of viscosity and density) inside a membrane are close to the properties in a solution. By analogy, we can assume that the dielectric permittivity of the solution in the membrane is equal to the dielectric permittivity of the solution in which the membrane was soaked. The parameter x characterizes the spatial arrangement of the components. The calculations were made for the chaotic arrangement of channels ($x = 0$), for the two extreme cases of layered structures, when the liquid forms channels in the direction of the electric field (perpendicular to the membrane surface) ($x = 1$), and for the case when the liquid is arranged in layers, perpendicular to the field ($x = 1$). The average dielectric permittivity of the membrane ϵ was calculated by the standard formula for a flat capacitor:

$$\epsilon = \frac{C \cdot d}{\epsilon_0 \cdot S} \quad (\text{Eq. 8})$$

where C is the electric capacitance, d is the membrane thickness, ϵ_0 is the dielectric permittivity, and S is the area of the measuring electrodes.

Figure 12. Comparison of the membrane porosity values calculated from the measured membrane capacity at various values of the parameter x , with the values obtained by the weight method:

$x = 1$, circles; $x = 0$, squares; $x = -1$, triangles. The results of porosity measurements by the weight method are taken from Figure 4 and shown in this figure by a solid line.

The obtained amounts of liquid in the membrane, calculated in this way, were compared with the sorption values determined experimentally, and it was found that the calculations at $x \approx 0$ are in the best agreement with the experiment. This means that the channels are randomly distributed inside the membrane.

To assess the influence of transport channels located mainly along the electric field, it is necessary to evaluate through the porosity of the membrane.

Figure 13. Dependence of the through the porosity of the membrane α_L on the ethanol concentration at the (1) increasing and (2) decreasing alcohol concentrations in the solution.

Through the porosity of the membrane can be estimated by the ratio of the membrane conductivity to the conductivity of the solution layer having the same thickness and area as the membrane. Figure 13 presents such a relationship: the through porosity does not exceed 2% of the total open porosity of the membrane. Hence the through channels do not affect the calculation of the structure by Lichtenecker and Rother's formula (Lichtenecker and Rother, 1931). Therefore, the channels are mostly randomly distributed inside the membrane, and the infiltration channels make up a small part of the total number of filled-liquid

channels. This conclusion is consistent with the ideas about the structure of the studied membranes and the transfer mechanisms in them.

4. CONCLUSION

This study addressed the impedance characteristics of PTMSP membranes in NaCl solutions in ethanol-water mixtures with various alcohol content. The critical porosity was estimated, and the critical volume fraction of porosity α_k at which the through conductivity channels are formed, was calculated. When the alcohol content in the solution increases, $\alpha_k = 0.29$, and when it decreases, $\alpha_k = 0.17$. The critical conductivity index t is $t = 3.86 \pm 0.23$ in the first case and $t = 3.26 \pm 0.085$ in the second case.

The obtained dependencies indicate that the matter is transferred through the liquid phase elements. As the amount of sorbed liquid increases, these elements form a percolation cluster which remains intact at decreased sorption. The porous structure of a dry PTMSP membrane consists of free volume elements that are hardly connected to each other. At low alcohol concentrations, the transfer of liquid between them is possible only due to diffusion. However, even at low alcohol concentrations, the free volume elements are able to expand due to swell, which causes deformation of macromolecules and supramolecular structures of the polymer and a decrease in the length of diffusion gaps. The through channels, connecting both sides of the membrane, begin to form at ~30% alcohol concentration. At the same time, both the permeability and the electrical conductivity grow as a power function, in contrast to the porosity that increases linearly. The hysteresis effect was observed in the measured values of porosity, permeability, conductivity and capacity. With an increase in the alcohol content in the solution, these values are lower than with a decrease. This difference can be attributed to the relaxation of the supramolecular structures of the polymer to the initial state after its swelling. As known, the relaxation of structures in glassy polymers far from the glass transition temperature is very difficult.

Lichtenecker and Rother's formula (Lichtenecker and Rother, 1931) helped to calculate the volume fractions of the conducting and non-conducting phases in the system. The

obtained values of the amount of liquid in the membrane at various spatial arrangements of the channels made it possible to establish the structure of the liquid-filled channels. The best agreement with the experimental values was obtained for the chaotic structure. This is consistent with the existing ideas about the structure of the studied membranes and confirms the assumption that the percolation cluster is formed from free volume elements filled with the liquid phase. Through the porosity of even highly swollen membranes does not exceed 2% of the total open porosity of the membrane. Therefore, the channels are mostly randomly distributed inside the membrane, and the infiltration channels make up a small part of the total number of liquid-filled channels. The observed low values of the zeta potential and, consequently, the low values of the electrostatic component of the wedging pressure indicate that the increase in the size or the number of transport channels is associated with non-electrostatic forces.

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