

# Polyheptylmethylsiloxane—A Novel Material for Removal of Oxygenates from Water by Pervaporation

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**Abstract**—A new membrane for the removal of oxygenates from wastewater by pervaporation has been prepared on the basis of polymethylsiloxane bearing 1-heptene as a substituent on the side chain. The synthesized membrane material has been characterized using Fourier-transform IR spectroscopy, and its sorption properties with respect to C<sub>2</sub>–C<sub>4</sub> alcohols have been examined. It has been found that polyheptylmethylsiloxane (PHepMS) has a greater affinity for the C<sub>3</sub> and C<sub>4</sub> alcohols to be separated than its closest analogue known from the literature (polyoctylmethylsiloxane (POMS)), which makes the PHepMS membrane promising for the pervaporative separation of aqueous solutions of these alcohols. The pervaporation properties of PHepMS have been studied for the first time, and its separation characteristics have been compared with those of the commercial highly permeable membrane polymer polydimethylsiloxane (PDMS) and POMS in relation to the problem of recovery of *n*-butanol, *n*-propanol, and ethanol from dilute aqueous solutions by vacuum pervaporation. It has been shown that PDMS has the highest separation efficiency for *n*-propanol–water mixture and PHepMS is the most promising membrane material for the pervaporative separation of water–butanol mixtures. Having a butanol flux comparable to that through PDMS, the PHepMS membrane demonstrates a record-breaking value of butanol/water separation factor of 97.

**Keywords:** polyheptylmethylsiloxane, polyoctylmethylsiloxane, pervaporation, recovery of oxygenates from water, separation of water–alcohol mixtures

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## INTRODUCTION

In recent decades, great attention has been paid to the treatment of wastewater from oil refineries and petrochemical enterprises. In various processes, such as the Fischer–Tropsch synthesis, dehydrogenation, isomerization, and alcohol production, oxygenates (lower alcohols and ethers) are undesirable reaction products, which are subsequently concentrated in wastewater effluents [1]. The main method of treating such effluents is biological treatment [2]. Despite the high degree of removal of oxygenates (up to 5 µg/L) [3], the biological method of purification has the following drawbacks: it requires a considerable dilution of wastewater with clean water to reduce the concentration of pollutants and controlling the level of biological oxygen demand (BOD) and the concentration of biogenic elements (in the form of compounds), trace elements, and growth factors to maintain the metabolism of microorganisms, aside from the high cost of both microorganisms capable of processing oxygenates and the purification process itself [4–7].

For example, a significant amount of oxygenates is formed in the aqueous phase (12 g per 1 m<sup>3</sup> of CO + H<sub>2</sub>) in Fischer–Tropsch processes [8]. However, they

are not isolated as a separate value-added product from Fischer–Tropsch derived water, but the total wastewater stream is treated in the flotation and flocculation unit to remove suspended particles before being sent to a bioreactor in which organic components are processed to a level that allows discharge of wastewater into water bodies [9].

According to published data [10], the concentration of alcohols in the aqueous phase of the products obtained in the process for the manufacturing of alcohols from synthesis gas reaches 50%, of which more than 60% are C<sub>2</sub>–C<sub>4</sub> alcohols. Thus, these alcohols must be concentrated to have a commercial product.

A promising alternative to biological purification in the process of removal of oxygen-containing organic compounds from water is pervaporation [11]. The main advantages of pervaporation include a reagentless platform, the possibility of recovering oxygenates at relatively low temperatures, and no need of regeneration of the auxiliary phase (adsorbent, extractant, sweep gas, etc.) [12, 13].

Despite a significant number of works on the separation of oxygen-containing organic compounds from aqueous media by pervaporation, the range of membrane materials used for this purpose is rather narrow.

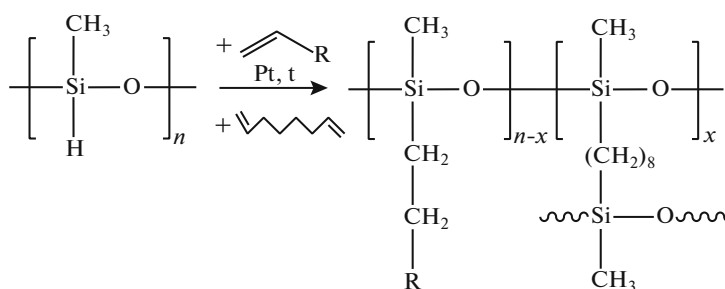


Fig. 1. Reaction scheme for the synthesis of side chain-substituted polymethylsiloxanes.

The main representatives of such materials are hydrophobic silicalites [14], silicone rubbers (PDMS, POMS) [15–18], and high-permeability glassy polymers (PTMSP, polynorbornenes, polybenzodioxanes) [19, 20].

The most common materials in the industry for the membrane separation of organic vapors are polydimethylsiloxane (PDMS) [15] and polyoctylmethylsiloxane (POMS) [16]. Membranes based on PDMS have a higher permeability due to the high mobility of the polymer chain. At the same time, POMS membranes have a higher *n*-butanol/water separation factor (19.7) as compared to PDMS (18.8) [21]. An increase in the length of the hydrocarbon chain leads to hydrophobization of the membrane material, which results in an increase in the selectivity of sorption of organic substances with respect to water [22]. However, it was shown [23] that membrane permeability decreases with an increase in the length of the hydrocarbon substituent on the side chain; i.e., there is a decrease not only in the water flux, but also in the flux of the organic component. Thus, an important task for the pervaporative recovery of oxygenates from water is the creation of membrane materials based on polymethylsiloxanes with enhanced selectivity and efficiency of pervaporation separation.

Thus, the objectives of this study were to synthesize a new membrane material based on polymethylheptylsiloxane and examine its pervaporation characteristics in the process of recovery of oxygenates from aqueous media using water–alcohol binary mixtures as an example.

Table 1. Designation of membrane samples with different side substituents

Membrane notation	Initial composition of reaction mixture
PHepMS	PMHS + 1-heptene + 1,7-octadiene + Pt cat
POMS	PMHS + 1-octene + 1,7-octadiene + Pt cat

## EXPERIMENTAL

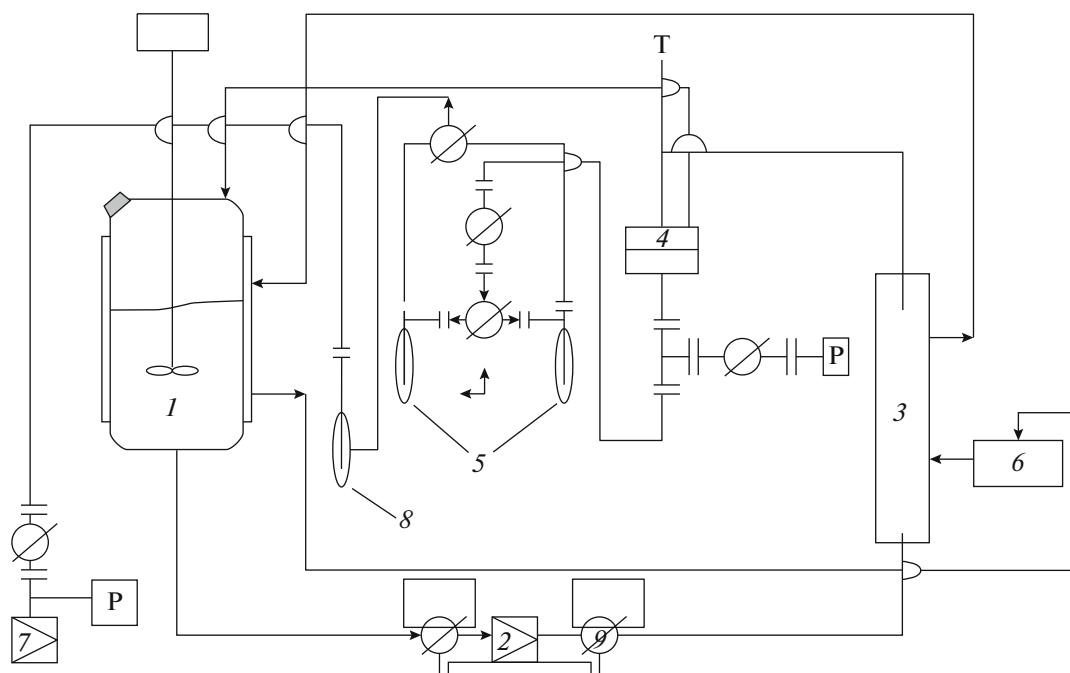
### Membrane Synthesis and Preparation

The casting solution and dense membranes were prepared according to the recently proposed procedure [24] using a novel single-step in situ method for synthesizing and curing of side chain-substituted polymethylsiloxane. The reaction scheme is shown in Fig. 1. To run the reaction, a 3.0 wt % solution of polydimethylhydrosiloxane (PMHS) with a number-average molecular mass of 1700–3200 g/mol (Sigma Aldrich) in hexane was mixed with 1-alkene (a modifier) and 30  $\mu$ L of Karstedt's catalyst (platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Sigma Aldrich). The reaction mixture was then stirred at 60°C for 2 h under reflux. Thereafter, 1,7-octadiene (Sigma Aldrich) (crosslinking agent) was added to the solution, the amount of PMHS was brought to the stoichiometric ratio, and the reaction mixture was stirred for 1 h at a temperature of 60°C. The membrane was prepared by casting onto a stainless steel mesh (mesh size 40  $\mu$ m) fixed on a Teflon surface, followed by drying to constant weight at a temperature of 60°C for 24 h. The thickness of the films varied in the range of 40–50  $\mu$ m. In this work, 1-heptene and 1-octene (reference sample) (Sigma Aldrich) were used as modifying agents—notation for the resulting membranes is given in Table 1.

As a reference, a PDMS membrane was studied. The membrane was prepared by casting, similar to the membranes based on substituted polymethylsiloxane. The crosslinker used for vinyl-capped PDMS (Sigma Aldrich) was PMHS. The crosslinking was carried out in the presence of the Karstedt catalyst (PDMS : PMHS : catalyst ratio was 10 : 1 : 0.01).

### Fourier-Transform IR Spectroscopy

The completeness of the hydrosilylation reaction was confirmed using Fourier-transform IR spectroscopy. The IR spectra were recorded in the mode of reflection from the surface of films on an HYPERION-2000 IR microscope interfaced to a Bruker IFS 66 v/s FTIR spectrometer (Ge crystal, 50 scans, resolution 2  $\text{cm}^{-1}$ , 500–4000  $\text{cm}^{-1}$ ).



**Fig. 2.** Schematic diagram of the vacuum pervaporation unit: (1) tank with a stirrer, (2) gear pump, (3) heat exchanger, (4) membrane module, (5) permeate collection traps placed in Dewar vessels with liquid nitrogen, (6) thermostat, (7) vacuum pump, (8) guard trap, (9) feed mixture sampling valve. P and T denote electronic pressure and temperature sensors, respectively.

#### *Differential Scanning Calorimetry (DSC)*

Calorimetric studies were performed on a Mettler Toledo DSC823 differential scanning calorimeter in an argon atmosphere over the temperature range of  $-140$  to  $100^{\circ}\text{C}$  at a temperature change rate of  $10^{\circ}\text{C}/\text{min}$ .

#### *Sorption*

The sorption of solvents (*n*-butanol, *n*-propanol, ethanol) in dense membranes was determined gravimetrically: pre-weighed polymer samples were held for 48 h in a solvent medium to achieve constant weight and then weighed on a Sartorius Analytic A 120 S analytical balance after the removal of excess solvent from the surface [25].

#### *Vacuum Pervaporation*

Pervaporation experiments were performed on the setup shown in Fig. 2. The mixture to be separated was poured into 1-liter container 1 and pumped in a circulation mode using Ismatec CH-8162 gear pump 2. The volumetric flow rate of the feed mixture was  $150\text{ mL}/\text{min}$ . The mixture heated in heat exchanger 3 was conveyed into membrane module 4. The effective membrane area was  $13.85\text{ cm}^2$ . The permeate vapor was condensed in glass traps placed in Dewar vessels 5 with liquid nitrogen ( $-196^{\circ}\text{C}$ ). The presence of two alternately working traps ensured the continuous operation of the unit throughout the experiment.

Guard trap 8 prevented the permeate vapor from entering the vacuum pump. The temperature of the feed mixture was maintained with an accuracy of  $\pm 0.1^{\circ}\text{C}$  using LOIP LT-100 liquid thermostat 6. To create the driving force of the mass transfer process, a pressure of  $\sim 0.05\text{ mbar}$  was maintained downstream of the membrane with Ebara PDV-250 vacuum pump 7.

The pervaporation was carried out at a feed-mixture temperature of  $30.0^{\circ}\text{C}$ . The mixtures to be separated were binary solutions of *n*-butanol, *n*-propanol, and ethanol in water with organic contents of 1.0, 1.0, and 3.0 wt %, respectively. All the solutions were prepared gravimetrically from the reagent-grade organic solvents (Khimmed Sintez).

The feed mixture and permeate concentrations were determined by gas chromatography using a Kristalluks-4000M chromatograph (NPF Meta-Khrom) equipped with a thermal conductivity detector. The chromatographic analysis conditions were as follows: an evaporator temperature of  $230^{\circ}\text{C}$ , a column temperature of  $180^{\circ}\text{C}$ , and a detector temperature of  $230^{\circ}\text{C}$ . The analyses were carried out using a Porapak Q packed chromatographic column of 1 m in length, 0.5 mm in wall thickness, and 4 mm in outer diameter.

The vacuum pervaporation process was characterized by the following parameters: permeate flux, separation factor, and pervaporation separation index.

The total permeate flux ( $J$ ,  $\text{kg}/(\text{m}^2\text{ h})$ ) was calculated by Eq. (1):

$$J = \frac{m}{St}, \quad (1)$$

where  $m$  is the total mass of the permeate (kg) penetrated through the membrane with an area  $S$  (m<sup>2</sup>) over a known time interval  $t$  (h).

The separation factor ( $\alpha$ ) was determined as defined by Eq. (2):

$$\alpha = \frac{y_o x_w}{y_w x_o}, \quad (2)$$

where  $x_o$  and  $x_w$  are the mass fractions of the organic component and water in the feed mixture, and  $y_o$  and  $y_w$  are the mass fractions of the organic component and water in the permeate, respectively.

It should be noted that the above listed parameters strongly depend on the experimental conditions: temperature, feed mixture composition, pressure downstream of the membrane, and membrane type [26]. Therefore, it is preferable to compare the transport properties of membranes using process parameters, such as permeability ( $P/l$ ) and selectivity, wherein the latter is determined from the ratio of the permeability of the  $i$ th component to the water permeability.

The permeability coefficient ( $P$ , mol m/(m<sup>2</sup> h kPa)) for component  $i$  was calculated according to equation (3):

$$P = \frac{J_i l}{(P_i^f - P_i^p)}, \quad (3)$$

where  $J_i$  is the molar flux of the  $i$ th component (mol/(m<sup>2</sup> h)) and  $p_i^f$  and  $p_i^p$  are the vapor pressures (kPa) of component  $i$  in the feed mixture and permeate, respectively. To determine the vapor pressure of the permeate and the feed mixture in the case of  $n$ -propanol–water and ethanol–water binary mixtures, activity coefficients were calculated using the software package Aspen Plus 8.6 according to the NRTL (Non-Random Two-Liquid) model [27]. As was shown in [28], in the case of  $n$ -butanol–water binary mixture, it is preferable to use the approximated four-parameter Margules equation to calculate the activity coefficients (Eqs. (4), (5)).

$$\log y_b = (1 - x_b)^2 [A + 2(B - A - D)x_b + Dx_b^2], \quad (4)$$

$$\log y_w = x_b [B + 2(A - B - D)(1 - x_b) + 3D(1 - x_b)^2]. \quad (5)$$

where  $A$ ,  $B$ , and  $D$  are the parameters of the Margules equation and  $x_b$  is the mass fraction of butanol.

## RESULTS AND DISCUSSION

### FTIR Spectroscopy of Membrane Materials PHepMS and POMS

Figure 3 shows the IR spectra of (1) parent PMHS and the 1-heptene- and 1-octene-modified materials (2) PHepMS and (3) POMS, respectively. The spectra

display neither Si–H bonds (2168-cm<sup>-1</sup> band) nor olefinic double bonds in the PHepMS and POMS samples, as indicated by the absence of bands above 3000 cm<sup>-1</sup> due to =CH<sub>2</sub>, 1640–1660 cm<sup>-1</sup> due to C=C, and 910 cm<sup>-1</sup> due to bending vibrations in the CH=CH<sub>2</sub> moiety, whereas the appearance of saturated –CH<sub>2</sub>– groups (bands at 2840–2960 cm<sup>-1</sup>,  $\nu_{\text{CH}}$ ; 1380–1460 cm<sup>-1</sup>,  $\delta_{\text{CCH}}$ ; 1250 cm<sup>-1</sup>,  $\delta_{\text{CCH}}$  in the Si(CH<sub>3</sub>)<sub>2</sub> moiety) and bands due to Si–O (1000–1100 cm<sup>-1</sup>) and Si–C (900–800 cm<sup>-1</sup>) bonds is clearly seen. Thus, the IR spectra confirm the complete hydrosilylation in both the PHepMS ( $T_g = -100^\circ\text{C}$ ) and POMS ( $T_g = -93^\circ\text{C}$ ) samples.

### Study of Polymer–Penetrant Sorption

To evaluate the solvent–polymer interaction, the difference in the solubility parameters of the membrane and the solvent is often used [29]. The solubility parameters ( $\delta$ ) were calculated with taking into account group contributions according to equations (6)–(8) [30]:

$$\delta = \left( \frac{\sum_i E_{\text{coh}}^i}{\sum_i V_m^i} \right)^{1/2}, \quad (6)$$

$$E_{\text{coh}} = E_d + E_p + E_h, \quad (7)$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \quad (8)$$

where  $E_{\text{coh}}$  is the cohesive energy and  $V_m$  is the molar volume of the  $i$ th functional group of the molecule,  $E_d$  is the dispersion component of energy,  $E_p$  is the polar component of energy,  $E_h$  is the hydrogen bonding energy,  $\delta_d$  is the contribution of dispersion interaction,  $\delta_p$  is the contribution of polar interaction, and  $\delta_h$  is the contribution of the interaction of hydrogen bonds. The smaller the difference between the solubility parameters of the polymer and the solvent, the higher the affinity between them and, hence, larger values of solvent sorption in the polymer material should be expected [31]. The affinity of the  $i$ th solvent (s) to the polymer material (p) can be evaluated using the distance parameter  $\Delta_{s-p}$  (Eq. (7)): the smaller the distance parameter, the stronger the solvent–polymer interaction [32].

$$\Delta_{s-p} = \sqrt{(\delta_{d,s} - \delta_{d,p})^2 + (\delta_{p,s} - \delta_{p,p})^2 + (\delta_{h,s} - \delta_{h,p})^2} \quad (9)$$

As can be seen from Table 2, the magnitude of the distance parameters and the ratio of the polymer–alcohol to the polymer–water distance parameter for PHepMS are lower than those for POMS. This finding suggests that the sorption of C<sub>2</sub>–C<sub>4</sub> alcohols and their sorption selectivity with respect to water will be higher for the PHepMS than for the POMS membrane. The test membrane materials have the greatest affinity for  $n$ -butanol in the range of solvents under

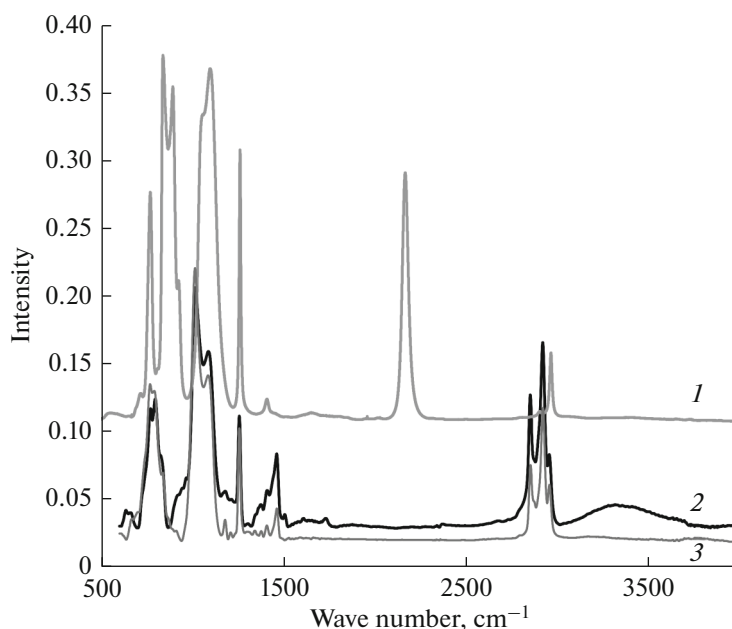


Fig. 3. IR spectra of (1) the reactant PMHS, (2) crosslinked PHepMS, and (3) POMS.

consideration. Thus, the *n*-butanol/water selectivity is expected to be much greater than the *n*-propanol/water and ethanol/water counterparts.

The calculation results were verified by experimental data on the sorption of the pure solvents (EtOH, PrOH, BuOH) by PHepMS and POMS polymer films (Table 3). As has been predicted by the estimates of solubility parameters, the alcohol sorption increases with the length of the alcohol hydrocarbon chain. The sorption of butanol and propanol in PHepMS is higher than in POMS. However, there is the reverse trend for ethanol, which requires a more detailed study of the polymer–solvent system. Unfortunately, the accuracy of this method does not allow us to determine the sorption of water in the polymer, since its value is several orders of magnitude lower than for alcohols. For this reason, the selectivity of sorption of the alcohols with respect to water in the test materials has not been evaluated.

It is worth noting that the flux of a component through the membrane is affected not only by the value of sorption of the penetrant in the membrane material, but also by its diffusion rate and the driving force of the process. Table 4 shows the physicochemical properties of the components of the feed mixture [30].

The butanol molecule has the largest diameter among all the solvents studied, while the water molecule is the smallest. The small molecular size can facilitate the penetration of water molecules between polymer chains in the membrane structure. To evaluate the driving force in the pervaporation process, the difference in the partial pressures of the components was calculated for binary mixtures of 1 wt % *n*-butanol–water, 1 wt % *n*-propanol–water, and 3 wt % ethanol–water under conditions simulating the space upstream and downstream of the membrane in the pervaporation cell (Table 4). From the point of view of the partial pressure drop, the driving force in the pervaporation

Table 2. Solubility parameters of the polymers and solvents under investigation [32]

Component	$\delta_d$ , (J/cm <sup>3</sup> ) <sup>0.5</sup>	$\delta_p$ , (J/cm <sup>3</sup> ) <sup>0.5</sup>	$\delta_h$ , (J/cm <sup>3</sup> ) <sup>0.5</sup>	$\Delta_{\text{PHepMS}-i}$ , (MPa) <sup>0.5</sup>	$\Delta_{\text{POMS}-i}$ , (MPa) <sup>0.5</sup>	$\frac{\Delta_{\text{PHepMS}-i}}{\Delta_{\text{PHepMS}-\text{H}_2\text{O}}}$	$\frac{\Delta_{\text{POMS}-i}}{\Delta_{\text{POMS}-\text{H}_2\text{O}}}$
EtOH	15.8	8.8	19.4	15.9	16.2	0.399	0.404
PrOH	16.0	6.8	17.4	13.3	13.6	0.334	0.339
BuOH	16.0	5.7	15.8	11.4	11.7	0.286	0.292
H <sub>2</sub> O	15.5	16.0	42.3	39.8	40.1	—	—
PHepMS	16.8	2.5	4.8	—	—	—	—
POMS	16.8	2.3	4.6	—	—	—	—

**Table 3.** Sorption of solvents by PHepMS and POM films

Polymer film	Sorption, mol of solvent/mol of polymer		
	EtOH	PrOH	BuOH
PHepMS	0.076	0.223	0.622
POMS	0.082	0.184	0.595

process decreases as follows: water > ethanol > *n*-butanol > *n*-propanol.

#### *Pervaporation Properties of Membranes Based on Polysiloxanes*

Pervaporation properties of the membranes in the separation of 1.0 wt % *n*-butanol–water, 1.0 wt % *n*-propanol–water and 3.0 wt % ethanol–water binary mixtures are shown in Fig. 4. It is seen that the total permeate flux and the alcohol/water separation factor increase with increasing molecular weight of alcohol from ethanol to *n*-butanol. This trend seems to be due to the fact that the solubility of alcohols in the membrane increases from C<sub>2</sub> to C<sub>4</sub> (Table 3), which in turn leads to an increase in the flux of the organic component, with the flux of water remaining constant regardless of the nature of the second component. The flux of water through the test PHepMS and POMS membranes was found to be 0.005 and 0.004 kg/(m<sup>2</sup> h), respectively. As the length of the hydrocarbon radical of the side chain increases from C<sub>7</sub> to C<sub>8</sub>, the water flux decreases, thereby confirming the expected increase in hydrophobicity of the material.

As a rule, the flux of an organic component in hydrophobic pervaporation is determined by its solubility in the membrane material [20], which agrees well with the data in Table 3. The value of C<sub>3</sub> and C<sub>4</sub> alcohol/polymer sorption is higher for the PHepMS membrane; so it is more permeable and selective for propanol and butanol than the POMS membrane. For ethanol, there is the reverse trend: its flux and sorption are greater in the case of the POMS membrane. Thus, depending on the separation task, different materials will have optimal membrane properties.

The most widely used high-permeability membrane material for hydrophobic pervaporation pur-

poses is polydimethylsiloxane (PDMS) [33]. For this reason, to evaluate the efficiency of the membranes obtained, we investigated a dense PDMS membrane (Fig. 4).

As can be seen in Fig. 4, the PDMS membrane has the greatest flux values for all the substances studied. It also has the maximum ethanol/water separation factor. However, the PHepMS membrane is more appropriate for butanol, since it exhibits a nearly three times higher separation factor, which reaches a record-breaking value of 97, at a comparable butanol flux. In the case of propanol, it is difficult to determine which of the membrane materials will be the most promising, since the propanol flux through the PDMS membrane is three times that through the PHepMS membrane, but the propanol/water separation factor of the PHepMS membrane is two times that of PDMS.

Flux and separation factor are parameters that depend on the magnitude of the driving force of the process and the thickness of the selective membrane layer. To compare the performance of the test materials, the results obtained are presented in terms of permeability coefficient and selectivity [26] (Table 5). The data in Table 5 correlate well with the results on permeate fluxes and separation factors. Of the materials studied, PDMS is the most permeable to all the substances examined and has the highest selectivity for ethanol. Note that PHepMS has a higher selectivity for the C<sub>3</sub> and C<sub>4</sub> alcohols.

By analogy with pervaporation separation index [34], the following quantity is proposed as a criterion of the performance of the membrane material, which can be called material efficiency index (IME):

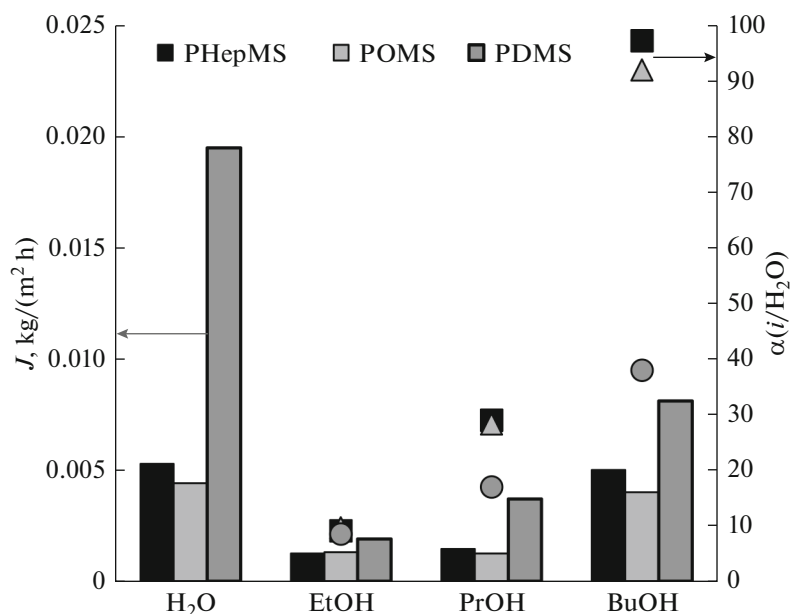
$$\text{IME} = P(\alpha - 1).$$

This quantity takes into account both the permeability of the material and its selectivity. In case the selectivity of the material is less than 1, IME will take negative values. This is the criterion that the test material is not suitable for a given separation problem. The calculated values of IMwE are given in Table 6.

It was found that all the investigated membrane materials are unsuitable for the recovery of ethanol from aqueous media, since they have a low selectivity for this component. Indeed, it has been shown earlier that PDMS membranes have insufficient selectivity

**Table 4.** Physicochemical properties of water, ethanol, *n*-propanol, and *n*-butanol [30]

Component	Molecular mass, g/mol	Kinetic diameter, nm	Molar volume, cm <sup>3</sup> /mol	Driving force, kPa
H <sub>2</sub> O	18.01	0.30	18.1	4.20
EtOH	46.07	0.43	58.4	0.55
PrOH	60.09	0.47	75.7	0.18
BuOH	74.12	0.50	91.5	0.26



**Fig. 4.** Component (BuOH, PrOH, EtOH, and H<sub>2</sub>O) partial fluxes through PDMS, PHepMS, and POMS and the alcohol/water separation factor for 1 wt % BuOH/H<sub>2</sub>O, 1 wt % PrOH/H<sub>2</sub>O, and 3 wt % EtOH/H<sub>2</sub>O binary mixtures.

for the pervaporative recovery of ethanol from aqueous media [35, 36]. Therefore, more detailed studies are needed on the synthesis of substituted polysiloxanes with different chemical structures in order to reveal the relationships between the selectivity of the material and the nature of the side substituent and to develop a material with high separation properties for the separation of water–ethanol solutions.

Of the materials studied, PDMS has the highest propanol separation efficiency. It is almost two times that for PHepMS and POMS, which, in turn, were found to exhibit a higher efficiency in separating the *n*-butanol/water mixture in comparison with PDMS. Moreover, PHepMS has the maximum IME value, which is more than four times higher than that for PDMS and 1.5 times higher than for POMS. Thus, PHepMS is a promising membrane material for the pervaporative separation of water–butanol mixtures.

## CONCLUSIONS

A membrane based on polymethylheptylsiloxane has been first obtained. The membrane material was

synthesized via the hydrosilylation reaction between polymethylhydrosiloxane, 1-heptene, and 1,7-octadiene. Measurements of FTIR spectra have confirmed the complete replacement of the Si–H by the Si–C bonds in the reaction, suggesting a high degree of substitution achieved in the polymer. The sorption properties of the PHepMS membrane have been compared with those of its closest analogue polymethyloctylsiloxane (POMS). It has been shown that the PHepMS material has high affinity for the C<sub>3</sub> and C<sub>4</sub> alcohols to be separated, thereby making this membrane promising for the pervaporative separation of mixtures of these alcohols with water.

The pervaporation properties of the PHepMS membrane have been studied for the first time. A comparison has been made between the separation characteristics of the new material and the commercial highly permeable polydimethylsiloxane (PDMS) membrane polymer and POMS as applied to the task of recovering *n*-butanol, *n*-propanol, and ethanol from dilute aqueous solutions by vacuum pervaporation. The PDMS membrane has the highest flux values for all the substances studied. It also has a maximum etha-

**Table 5.** Comparison of the transport characteristics of silicone membranes

Membrane material	$P_{\text{BuOH}} \times 10^6$ , mol m/(m <sup>2</sup> h kPa)	$P_{\text{PrOH}} \times 10^{-6}$ , mol m/(m <sup>2</sup> h kPa)	$P_{\text{EtOH}} \times 10^{-6}$ , mol m/(m <sup>2</sup> h kPa)	$P_{\text{H}_2\text{O}} \times 10^{-6}$ , mol m/(m <sup>2</sup> h kPa)	Selectivity, $\alpha(i)/H_2O$		
					BuOH	PrOH	EtOH
PHepMS	12.9	7.0	2.4	3.5	3.7	2.0	0.7
POMS	10.3	6.0	2.5	3.0	3.4	2.0	0.8
PDMS	20.5	22.9	13.1	14.2	1.4	1.6	0.9

**Table 6.** Comparison of the performance of silicone membrane materials

Membrane material	IME ( <i>i</i> /H <sub>2</sub> O)		
	BuOH	PrOH	EtOH
PHepMS	34.8	7.0	-0.72
POMS	24.7	6.0	-0.50
PDMS	8.2	13.7	-1.31

nol/water separation factor. However, the PHepMS membrane is more suitable for butanol, since it exhibits a nearly threefold higher separation factor reaching a record-breaking value of 97 at a comparable butanol flux.

It has been found that all the investigated membrane materials are unsuitable for the recovery of ethanol from aqueous media, since they have a low selectivity for this component. It has been shown that PDMS exhibits the highest propanol separation efficiency and PHepMS is the most promising membrane material for the pervaporative separation of water-butanol mixtures.

It can be concluded that there is no universal material that would be effective in the removal of oxygenates from water. For each separation problem, the membrane material must be selected individually on the basis of preliminary test experiments, depending on the composition of the mixture to be separated.

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