Olefin-polymethylsiloxane membrane composition for oxygenates removal from wastewater by pervaporation

E A Grushevenko, A A Knyazeva, I A Podtynnikov, O A Sharova and I L Borisov

A.V. Topchiev Institute of Petrochemical Synthesis RAS, 119991, Russia, Moscow, Leninsky pr., 29.

Abstract. To separate oxygenates from aqueous effluents by pervaporation first obtained and studied composite membrane material based on 1-hexene and polymethylsiloxane (C6). Synthesis of the composite membrane material was performed by hydrosilylation reaction between polymethylhydrosiloxane, 1-hexene and 1,7 octadiene. The synthesized composite membrane material characterized by FTIR spectroscopy and studied its sorption properties in relation to the alcohols: ethanol, n-propanol and n-butanol. It was found that affinity of the composite membrane materials to alcohols is increasing with an increase in their molecular weight. First studied pervaporation properties of the composition C6 and compares its separation characteristics of the commercial high-penetrability membrane polymer polydimethylsiloxane (PDMS) and compositions based polymethylsiloxane and 1-octene (polyoctylmethylsiloxane) for the task allocation of n-butanol, n-propanol and ethanol from dilute aqueous solutions by vacuum pervaporation. It is shown that a C6-based membrane is most effective in the separation of oxygenate-water mixtures by vacuum pervaporation. When compared to the PDMS flow of butanol, the membrane based on composition C6 exhibits a high separation factor of butanol-water 78.

1. Introduction
In the scientific and technical literature, pervaporation refers to the process of evaporation through a membrane, the essence of which is that the liquid mixture (raw material) is brought into contact with one side of the non-porous membrane selective for the target components, and also through the membrane permeate is a product enriched with the target component of the mixture being separated, is removed as a vapor from the back side of the membrane. Hydrophobic pervaporation in recent years has proved to be a competitive process for the purification of wastewater drains polluted by various organic components, including oxygenates [1, 2, 3]. Oxygenates (alcohols and ethers) pollute water runoffs of various chemical, petrochemical and refinery industries. For example, in wastewater plants for synthetic liquid fuels by the Fischer-Tropsch process contains a significant (12 g per 1 m³ CO + H₂) water-soluble oxygen-containing compounds [4], in case of isomerization processes, the oxygenate content reaches up to 20 g/l [5].

Since oxygenates are substances with high added value, their allocation is not only associated with a reduction in the environmental load of production, but also with the possibility of returning valuable products to the economy. In this regard, it becomes important to make the process of separation not only productive but also highly selective. The selectivity of the pervaporation separation is determined by the selectivity of the membrane material. The most common materials in the industry for the membrane separation of organic vapors are silicone rubbers. Primarily polydimethylsiloxane (PDMS) [6], as well as polyoctylmethylsiloxane (POMS) [7], which are a composition of two polymer chains:
polysiloxane and olefin. Membranes based on PDMS have a higher permeability due to the high mobility of the polymer chain. At the same time, for POMS membranes (19.7) there are large separation factors for n-butanol-water mixture compared to PDMS (18.8) [8]. The introduction of a long hydrocarbon fragment into the polysiloxane chain leads to hydrophobization of the membrane material and an increase in sorption selectivity [9]. However, it was shown in [10] that as the length of the hydrocarbon fragment increases, the permeability of the membrane decreases, i.e. there is a decrease not only in the flow of water but also in the flow of the organic component. Thus, an important task for the initial separation of oxygenates from water is the creation of membrane materials based on olefin and polymethylsiloxane compositions with enhanced pervaporation separation efficiency.

In this connection, the goals of this work are to obtain a composite membrane material based on the polymethylsiloxane and olefin and to study its pervaporation characteristics in the process of removal oxygenates from aqueous media using the example of binary water-alcohol mixtures.

2. Experimental part

2.1. Synthesis and membrane formation

Composite membrane materials obtained by recently proposed [12], according to which a new one-step in situ method for the synthesis and vulcanization of polymethylsiloxane and olefin compositions. The reaction scheme is shown in Figure 1. For this, 3.0 wt %. solution of polymethylhydrosiloxane (PMHS) with a average molecular weight of 1700-3200 g / mol (Sigma Aldrich) in hexane was mixed with 1-alkene and 30 μl of the Carsted catalyst (1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum complex in a solution of xylene, Sigma Aldrich). The reaction mixture was then stirred at 60 °C for 2 hours under reflux. Thereafter, 1,7-octadiene (Sigma Aldrich) (cross-linking agent) was added to the solution, the amount of PMHS was adjusted to a stoichiometric ratio and the reaction mixture was allowed to stir for 1 hour at a temperature of 60 °C. The membrane is prepared by casting on a stainless steel mesh (mesh size 40 mm) fixed on a Teflon surface, followed by drying to a constant weight at 60 °C for 24 hours. The thickness of the films varied in the range 40-50 μm. In this work as olefins are used 1-hexene and 1-octene (as a comparison sample) (Sigma Aldrich), the symbols for the resulting composite membranes are listed in Table 1.

| Table 1. Composite membrane legend. |
|-------------------------------------|
| Initial membrane composition        |
| C6  | PMHS + 1-hexene + 1,7-octadiene + Pt cat |
| C8  | PMHS + 1-octene + 1,7-octadiene + Pt cat |

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

![Figure 1. A reaction scheme for the preparation of composite membrane materials based on polymethylsiloxane and olefin.](image-url)
2.2. FT-IR spectroscopy
The completeness of the hydrosilylation reaction was confirmed by IR Fourier spectroscopy. The IR spectra were recorded in the mode of reflection from the surface of the films on an HYPERION-2000 IR microscope conjugated with an IFS 66 v / s Bruker IR Fourier spectrometer (Ge crystal, scan-50, resolution 2 cm\(^{-1}\), 500-4000 cm\(^{-1}\)).

2.3. Sorption
To determine the sorption of solvents (n-butanol, n-propanol, ethanol), a gravimetric method was used in continuous membranes: the polymer samples were held for 48 hours in a solvent medium to reach a constant mass, then weighed on an analytical scale of Sartorius Analytic, surface..

2.4. Vacuum pervaporation
Pervaporation experiments were performed on the installation shown in Figure 2. Initial separable mixture of a thermostated vessel (1 l) (1) was fed to the liquid circuit by means gear pump Ismatec (2) which provides the circulation of separated mixture through the heat exchanger (3) and the membrane module (4), and then return it back to the vessel (1). The volume flow of the separated mixture was 150 ml/min. Effective membrane area was 13.85 cm\(^2\). Permeate vapors were condensed in glass traps placed in Dewar vessels with liquid nitrogen (-196°C) (5). The presence of two parallel traps provided continuous operation of the installation throughout the entire experiment. Maintenance of the temperature of the separated mixture with an accuracy of ± 0.1° C was carried out using a liquid thermostat LOIP LT-100 (6). To create the driving force of the process of mass transfer in the sub-membrane space, a pressure of ~ 0.05 mbar with a vacuum pump Ebara PDV-250 (7). The trap (8) prevented the permeate vapor from entering the vacuum pump.

![Figure 2](image-url)

**Figure 2.** The scheme of installation of vacuum pervaporation: 1 - a container with a mixing device, 2 - a gear pump, 3 - a heat exchanger, 4 - a membrane module, 5 - traps for collection of permeate, placed in Dewar vessels with liquid nitrogen, 6 - a thermostat, 7 - a vacuum pump, 8 - safety trap, I - initial separation mixture, II - retentate, III - permeate, IV - heat carrier.

The pervaporation was carried out at a temperature of the separated mixture of 30.0 °C. The binary aqueous solutions of alcohols containing n-butanol, n-propanol and ethanol 1.0, 1.0 and 3.0 wt. %, respectively.

The concentration of the initial mixture and permeate was determined by gas chromatography using a Crystallux-4000M chromatograph (OOO NPF Meta-Chrom) equipped with a thermal
conductivity detector. The conditions for carrying out the chromatographic studies were as follows: the evaporator temperature was 230°C, the column temperature was 180°C, and the detector temperature was 230°C. The analyzes were carried out using a packed column chromatography, with a length of 1 meter, with a wall thickness of 0.5 mm and an outer diameter of 4 mm filled with Porapak Q sorbent.

The vacuum pervaporation process was characterized by the following parameters: penetrant flow, separation factor.

Penetrant flux \( J_i \) \( \text{r/m}^2\text{h} \) was calculated by the formula (1):

\[
J_i = \frac{m}{S \cdot t}
\]

where \( m \) – penetrant mass (g), penetrated through the membrane area \( S \) (m\(^2\)), for a certain period of time \( t \) (h).

Separation factor \( \alpha \) was calculated by the formula (2):

\[
\alpha = \frac{y_o \cdot x_w}{y_w \cdot x_o}
\]

where \( x_o \) and \( x_w \) – mass fractions of the organic component and water in the mixture to be separated, \( y_o \) и \( y_w \) – mass fractions of the organic component and water in the permeate.

It is worth noting that the above listed parameters strongly depend on the experimental conditions: temperature, composition of the separated mixture, pressure in the sub-membrane space and membrane type \([13]\). Therefore, it is preferable to compare transport properties of membranes using process parameters such as: permeability (P/l) and selectivity, which was determined from the ratio of the permeability of the i-th component to the water permeability.

Permeability coefficient \( P \) (mol m/(m\(^2\) h kPa)) for i-th component was calculated by the formula (3):

\[
P = \frac{J_i l}{(p_i^i - p_i^p)}
\]

where \( J_i \) – mol flux of component i (mol/(m\(^2\) h)), \( p_i^i \) and \( p_i^p \) – vapor pressure of i-th component in initial mixture and in permeate (kPa), respectively. To determine the vapor pressure of the permeate and the initial mixture in the case of binary mixtures of n-propanol-water and ethanol-water, activity coefficients were calculated using Aspen Plus 8.6 software package by model NRTL (Non-Random Two-Liquid) \([14]\). In the case of a binary n-butanol-water mixture, an approximate 4-parameter Margulis equation was used to calculate the activity coefficients \([6]\).

3. Results and discussion

3.1. FT-IR spectrometry of composite membrane

IR spectra of the original PMHS (1) and composite membrane materials C6 (2) and C8 (3), respectively, are presented in Figure 3. C6 and C8 samples completely lack Si-H bonds (band 2168 cm\(^{-1}\)) and double bonds from olefins, as indicated by the absence in the spectra of bands above 3000 cm\(^{-1}\) from = CH\(_2\), 1640-60 cm\(^{-1}\) from C = C and 910 cm\(^{-1}\) from the deformation vibrations at the CH = CH\(_2\) site, as well as saturated groups - CH\(_2\), bands from Si-O (1000-1100 cm\(^{-1}\)) and Si-C (900-800 cm\(^{-1}\)) bonds ). Thus, IR spectra confirm complete hydrosilylation in composite samples.
Figure 3. IR-spectrum PMHS (1), C8 (2) and C6 (3).

3.2. Study of sorption polymer-penetrant
Since membrane-based membranes are characterized by the thermodynamic selectivity of transport, a large role is played by the polymer-penetrant interaction, which can be estimated from the sorption of pure solvents (ethanol, n-propanol, n-butanol) in C6 and C8 polymer films (table 2). The amount of alcohol sorption increases with the increase in its molecular weight. The sorption of butanol and ethanol in the C8 material is higher than in C6. However, proportional sorption for C8 and C6 is observed for propanol, which requires a more detailed study of the polymer-solvent system. Unfortunately, the accuracy of this method does not allow us to estimate the sorption of water in the polymer, since its value is orders of magnitude lower than for alcohols. For this reason, the selectivity of sorption of alcohols with respect to water in the materials studied has not been evaluated.

| Solvent       | C6  | C8  |
|---------------|-----|-----|
| ethanol       | 0.03| 0.08|
| n-propanol    | 0.21| 0.20|
| n-butanol     | 0.50| 0.59|

3.3. Investigation of the Separation Properties of Membrane Compositions in the Process of Pervaporation
Pervaporation properties of membranes in the separation of binary mixtures 1.0 wt. % n-butanol-water, 1.0 wt. % n-propanol-water and 3.0 wt. % ethanol-water are shown in Table 3. It is shown that the penetrant flow and the alcohol/water separation factor increase with increasing molecular weight of alcohol from ethanol to n-butanol. This fact is apparently due to the fact that the solubility of alcohols in the membrane increases from ethanol to butanol (table 2), which in turn leads to an
increase in organic component of flow of water flow in this case remains constant regardless of the nature of the second component. The water flow for the investigated membranes was: C6 - 8.3 g / (m² · h), C8 - 6.6 g / (m² · h). With increasing length of the hydrocarbon side chain radicals from C6 to C8 observed decrease water flow, which confirms the expected increase in the hydrophobicity of the material.

Table 3. Transport properties of composite membranes with pervaporation of water-alcohol mixtures.

| Component flux, g/(m²·h) | Separation factor (alcohol/water) |
|--------------------------|----------------------------------|
| ethanol                  | n-propanol                       | n-butanol | water   | ethanol | n-propanol | n-butanol |
| C6                       | 2.1                              | 2.1       | 6.7     | 8.3     | 7.8        | 25        | 78       |
| C8                       | 1.5                              | 1.5       | 4.4     | 6.6     | 9.0        | 28        | 92       |
| PDMS                     | 1.9                              | 3.7       | 8.1     | 20      | 8.5        | 17        | 38       |

Typically, the flow of the organic component in the hydrophobic pervaporation is determined by its solubility in the membrane material [15], which is in good agreement with the data in Table 2. The alcohol-polymer sorption value is higher for the C8 membrane, so it is more selective in the studied alcohols than the C6 membrane. Moreover, the membrane C6 is more permeable due to the greater diffusion component due to the more flexible polymer chain: Tg (C6) = -105°C, Tg (C8) = -93°C. Thus, depending on the separation problem, different materials will have optimal membrane properties.

The most widely used high permeability membrane material for hydrophobic pervaporation problems is polydimethylsiloxane (PDMS) [16]. For this reason, to evaluate the efficiency of the resulting membranes, a continuous membrane of PDMS was investigated (Table 3).

As can be seen from Table 3, the PDMS membrane has the highest flux values for all substances studied. However, for n-butanol, composite membrane material based on olefin and polysiloxane composition is more suitable, since with a comparable butanol stream it exhibits a nearly 3-fold higher separation factor (79-92). In the case of n-propanol, it is difficult to estimate which of the membrane materials will be most promising, since the propanol stream through the membrane of PDMS is 2 times higher than through the composite membrane, but the propanol separation factor for the composite membrane is 1.5 times greater than PDMS.

Flow, separation factor - parameters that depend on the magnitude of the driving force of the process and the thickness of the selective membrane layer. To compare the effectiveness of the materials studied, the results obtained were presented in terms of the permeability and selectivity coefficient [13] (table 4). The data in table 4 correlate well with the results, permeate fluxes and separation factors. Among the materials studied, PDMS is the most permeable for all substances studied. As the length of the hydrocarbon fragment increases, the permeability of the membrane decreases and the selectivity of separation of alcohols from water increases. Moreover, if, in the case of ethanol, the selectivity of the separation is commensurate for all the membranes studied, in the case of butanol, the introduction of an olefin into the polysiloxane chain leads to an increase in selectivity of half.

Table 4. Permeability and selectivity of the membranes under study during the first-vapour separation of binary alcohol-water mixtures.

| Component | P · 10^6, mol·m/((kPa·h·m²)) | Selectivity (alcohol/water) |
|-----------|-------------------------------|-----------------------------|
| ethanol   | n-propanol                    | n-butanol                   | water   | ethanol | n-propanol | n-butanol |
| C6        | 3.5                            | 8.8                         | 15      | 4.8     | 0.7        | 1.9        | 3.1       |
| C8        | 2.5                            | 6.1                         | 11      | 3.1     | 0.8        | 2.0        | 3.4       |
| PDMS      | 21                             | 32                          | 42      | 26      | 0.8        | 1.2        | 1.6       |

As a criterion of the effectiveness of a membrane material, by analogy with the index of pervaporation separation [17], the following quantity is proposed, which can be called the index of material efficiency (IME):

IME = P(α - 1) (5)
This value takes into account both the permeability of the material and its selectivity. In case the selectivity of the material is less than 1, the IME will take negative values. This is the criterion that the material studied is not suitable for a given separation problem. The calculated IME values are shown in Table 5.

### Table 5. IME for siloxane membrane.

|        | C6 | C8 | PDMS |
|--------|----|----|------|
| IME (alcohol/water) | | | |
| ethanol | -0.9 | -0.5 | -4.0 |
| n-propanol | 7.9 | 5.9 | 7.4 |
| n-butanol | 31 | 26 | 26 |

It was found that all the investigated membrane materials are not suitable for isolation of ethanol from aqueous media, since they have a low selectivity for this component. Indeed, it was previously shown that PDMS membranes have insufficient selectivity for the pervaporation release of ethanol from aqueous media [19, 20]. Therefore, more detailed studies are needed on the synthesis of substituted polysiloxanes with different chemical structures in order to find the relationships between the selectivity of the material and the nature of the lateral substituent and to develop a material with high separation properties for the separation of water-ethanol solutions.

Of the materials studied, C6 has the highest separation efficiency for propanol and butanol in comparison with PDMS and C8. Thus, C6 is a promising membrane material for the process of pervaporation separation of water-butanol mixtures and water-propanol mixtures.

### 4. Conclusions

The composite membrane material based on 1-hexene and polymethylsiloxane was obtained and studied for the first time in the pervaporation separation of oxygenate-water mixtures. Synthesis of membrane material was carried out by hydrosilylation reaction between polymethylhydrosiloxane, 1-hexene and 1,7-octadiene. Using the FT-IR spectroscopy method, the complete replacement reaction of Si-H bonds on Si-C bonds was confirmed, which allows to speak about achieving a high degree of substitution of the polymer. The sorption properties of the C6 membrane were compared with its closest analogue polymethyloctylsiloxane (C8). A comparison was made between the separation characteristics of a composite material and a commercial high-permeable membrane polymer, polydimethylsiloxane (PDMS), for the problem of isolating n-butanol, n-propanol and ethanol from dilute aqueous solutions by vacuum pervaporation. The membrane PDMS has the highest flux values for all the substances studied. However, for butanol and propanol, the C6-based membrane is more suitable, since it has the highest membrane efficiency index, taking into account the contribution of both permeability and selectivity.

### Acknowledgments

This work was performed at the TIPS RAS and supported by the Russian Science Foundation, project no. 17-79-20296.

### 5. References

[1] Ezeji T C, Qureshi N and Blaschek H P 2004 *TCR* 4 305
[2] Martínez R, Sanz M T and Beltrán S 2011 *J. Food. Eng.* 105 98
[3] Lukin I, Merz J and Schembecker G 2018 *Flavour. Fragr. J.* 33(3) 203
[4] Kölbl H and Ralek M 1980 *Cat. Rev.* 21(2) 225
[5] Degremont. St.Petersb.: New Journal 2007 1 143–147
[6] Borisov I L, Golubev G S, Vasilevsky V P, Volkov A V and Volkov V V 2017 *J. Membr. Sci.* 523 291
[7] Rom A and Friedl A 2016 *Sep. Purif. Technol.* 170 40
[8] Van Hecke W and De Wever H 2017 *J. Membr. Sci.* 540 321
[9] Börjesson J, Karlsson H O E and Trägårdh G 1996 *J. Membr. Sci.* 119(2) 229
[10] Stern S A, Shah V M and Hardy B J 1987 *J. Polym. Sci. B Polym. Phys.* 25(6) 1263
[11] Schultz J and Peinemann K-V 1996 J. Membr. Sci. 110 37
[12] Grushevenko E A, Borisov I L, Bakhtin D S, Legkov S A, Bondarenko G N and Volkov A V 2017 Petr. Chem. 57(4) 334
[13] Baker R W, Wijmans J G and Huang Y 2010 J. Membr. Sci. 348 346
[14] Kujawska A, Knozowska K, Kujawa J and Kujawski W 2016 Sep. Purif. Technol. 159 68
[15] Borisov I L, Malakhov A O, Khotimsky V S, Litvinova E G, Finkelshtein E S, Ushakov N V and Volkov V.V. 2014 J. Membr. Sci. 466 322
[16] Bennett M, Brisdon B J, England R and Field R W 1997 J. Membr. Sci. 137(1-2) 63.
[17] Van der Bruggen B and Luis P 2015 Progress in filtration and separation 101
[18] Hansen C.M. Boca Raton: CRC Press, 2007. 540 p
[19] O’Brien D J, Roth L H, McAloon A J 2000 J. Membr. Sci. 166(1) 105
[20] Vane L M 2013 Sep. Sci. Technol. 48(3) 429