

Composite Membranes with a Polyvinyltrimethylsilane Skin Layer for Separation of Water–Alcohol Mixtures

V. V. Teplyakov^{a, b, *}, M. G. Shalygin^{a, b}, A. A. Kozlova^{a, b}, and A. I. Netrusov^{a, b}
^a*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*
^b*Faculty of Biology, Moscow State University, Moscow, 119992 Russia*

*e-mail: tepl@ips.ac.ru

Received March 21, 2018

Abstract—The paper presents the characteristics of a laboratory-made water-selective composite membrane with a selective layer of hydrophobic polyvinyltrimethylsilane (PVTMS) for use in the processes of vapor-phase membrane recovery of alcohols from dilute aqueous alcohol mixtures of biogenic origin. The support is a polyacrylonitrile ultrafiltration membrane, and the PVTMS skin layer of the resulting composite membrane has a thickness of 3 to 4 microns. The vapor transport and separation characteristics of the membrane for water–ethanol and water–butanol mixtures in the temperature range of 60–80°C have been studied. It has been shown that the membrane selectivity varies in the range of 23–39 for the water/ethanol pair or 100–140 for the water/butanol pair. A specific feature of the hydrophobic water-selective membrane as applied to the vapor-phase process is the stability of its characteristics due to the absence of swelling, in contrast to hydrophilic water-selective membranes whose characteristics substantially depend on the activity of water vapor. The process of vapor-phase membrane recovery of ethanol and butanol from dilute aqueous alcohol mixtures of biogenic origin with their initial concentrations of 10 and 1 wt %, respectively, has been mathematically modeled on the basis of the experimental data. The calculation results show that the composite membrane obtained makes it possible to concentrate ethanol and butanol to 95 and 98 wt % with degrees of recovery of more than 0.8 and more than 0.9, respectively.

Keywords: membrane separation of vapors, water–alcohol mixtures, recovery of alcohols, composite membranes

DOI: 10.1134/S0965544118110075

INTRODUCTION

The task of separating water–alcohol mixtures arises in the case of using biomass fermentation processes to produce alcohols as renewable energy sources. In general, the world is experiencing an exponential growth in the production and use of various types of biofuels: biomethane, biohydrogen, biodiesel, and bioalcohols (bioethanol and biobutanol) [1–6].

The problem of separation of liquid energy carriers is particularly acute for biocompounds, since the result of fermentation is dilute aqueous alcohol solutions. Thus, ethanol and butanol concentrations above 10 and 1.5 wt %, respectively, inhibit the process; therefore, continuous removal of the organic product during the fermentation process is required in order to increase the productivity and the depth of processing [7]. For the separation of bioalcohols, the use of pervaporation through polydimethylsiloxane (PDMS) membranes having a predominant permeability to bioalcohols has traditionally been considered. For example, commercially available PERVAP™ 1060, MTR-100, GKSS PDMS, and MPF-50 membranes

have been most studied as organoselective materials for the recovery of biocompounds [8, 9].

In [10], we proposed a vapor-phase membrane separation method for the recovery of butanol from fermentation broths, which combines the treatment of the bioreactor contents by gas stripping with the subsequent membrane separation of the vapors recovered. A comparison was made of the pervaporation and the hybrid vapor-phase membrane separation of water–alcohol mixtures. It was shown that the vapor-phase method allows continuous extraction of butanol in the form of vapor from the fermentation broth at low temperatures, and the step of vapor-phase membrane separation ensures its efficient concentration and separation from other components. Furthermore, it was shown that glassy polymers with a high free volume (poly-4-methyl-2-pentyne (PMP), poly-1-trimethylsilyl-1-propyne (PTMSP), and their copolymers) have predominant permeability to butanol (to a lesser extent, to ethanol) in comparison with water vapor, a property that can be used to concentrate butanol as a *permeate*, for example, from 1 to 37 wt %. On the other hand, it was noted [11] that the use of hydrophilic

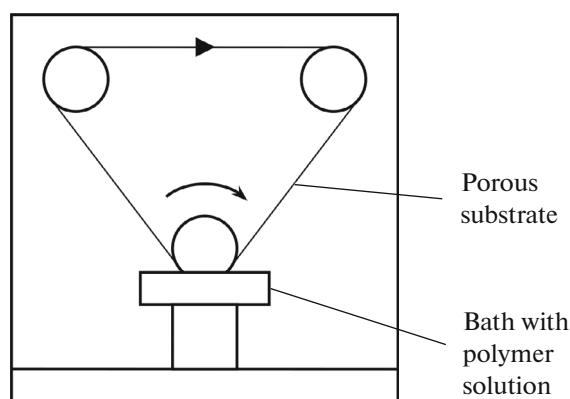


Fig. 1. Schematic of the unit for fabricating composite membranes by self-layering.

water-selective membranes can provide even greater separation efficiency, since the liquid–vapor phase diagrams of the water–butanol and water–ethanol systems show positive deviations from Raoult’s law [12–14]. Thus, in the case of hydrophilic cellophane membranes, a butanol concentrate of up to 95 wt % can be obtained as the *retentate* at a recovery of up to 90% [15]. The problem here is the stability of the membrane parameters. In addition, hydrophobic water-selective membranes, for example, those based on polyvinyltrimethylsilane (PVTMS) can be used in the process [16]. Thus, three groups of polymeric membranes (membrane materials) suitable for vapor-phase membrane separation of water–alcohol mixtures can be distinguished: (1) organophilic polymers comprising elastomers based on polymethylalkylsiloxanes and their compositions, as well as high-permeability organophilic glassy polymers of some disubstituted polyacetylenes [11, 15, 17], which are characterized by the dominance of permeability to alcohols in some cases; (2) hydrophilic water-selective polymer membranes, for example, of the PERVAP™ series from SULZER [18], which are used in the processes of pervaporation of alcohols; and (3) hydrophobic water-selective polymer membranes, for example, based on PVTMS. Earlier, in the study of the transport of individual components, it was shown that commercial highly permeable gas-separating asymmetric PVTMS membranes have water-selective properties [11], but their ideal water/ethanol and water/butanol selectivity

values are low, probably due to the presence of micro-defects in a thin (about 0.2 μm) selective layer and to swelling in saturated ethanol and butanol vapors. In this work, we prepared and studied composite membranes with a selective PVTMS layer of 3 to 4 μm in thickness, which exhibit good separation characteristics for concentrating bioalcohols (ethanol and butanol) from dilute aqueous alcohol mixtures.

EXPERIMENTAL

Preparation of Composite Membrane with Selective PVTMS Layer

Flat-sheet hydrophobic composite membranes (CMs) based on PVTMS (contact angle of water is 110° [19]) were obtained under laboratory conditions by contact immersion of a porous substrate in a polymer solution in toluene as shown in Fig. 1, which sketches a diagram of a laboratory unit for the fabrication of flat sheet CMs. The PVTMS source was asymmetric membranes manufactured by the Kuskovo Chemical Plant (Moscow, Russia) according to TU 6-05-111-267-81 [20], which were dissolved in high-purity toluene to obtain a solution with a PVTMS concentration of 3 wt %.

The porous substrate was fixed to the shafts, and the PVTMS solution was poured into the contact bath at the bottom of the unit. The solution was applied by contact immersion of the support in the bath with the solution via rotating the drive shaft at a predetermined speed controlled by a stepper motor. The substrate was a GMT-L-1 ultrafiltration membrane with a total thickness of 150–170 μm consisting of a layer of non-woven (polyester) serving as the basis responsible for mechanical strength and a polyacrylonitrile (PAN) ultrafiltration layer of a 30–40 μm thickness as the support. The characteristics of the substrate, presented by the manufacturer GMT Membrantechnik GmbH (Germany), are shown in Table 1.

The choice of the substrate is due to the small pore size, high surface porosity, high permeability, and stability in both the solvents used and water–alcohol mixtures.

A defect-free selective PVTMS layer of a 3–4 μm thickness was provided by selecting the contact time (speed of drawing the porous substrate through the contact bath). After drying the membrane in air at room temperature for 24 h (to constant weight), samples were cut from it and their permeability to nitrogen and oxygen was measured. For experiments with water–alcohol mixtures, membrane samples with oxygen/nitrogen selectivity parameters close to those of homogeneous PVTMS films were selected, which parameters suggest that the applied selective layer is defect-free. The membrane samples were also investigated by scanning electron microscopy (SEM) for uniformity of the polymer coating of the support.

Table 1. Characteristics of the porous substrate GMT-L-1

Parameter	GMT-L-1
Water permeability, L/m ² h bar	397
Molecular cutoff, kDa	633 ± 123
Roughness, nm	1440 ± 359
Contact angle of water, deg	44
Average pore size, nm	9 ± 4

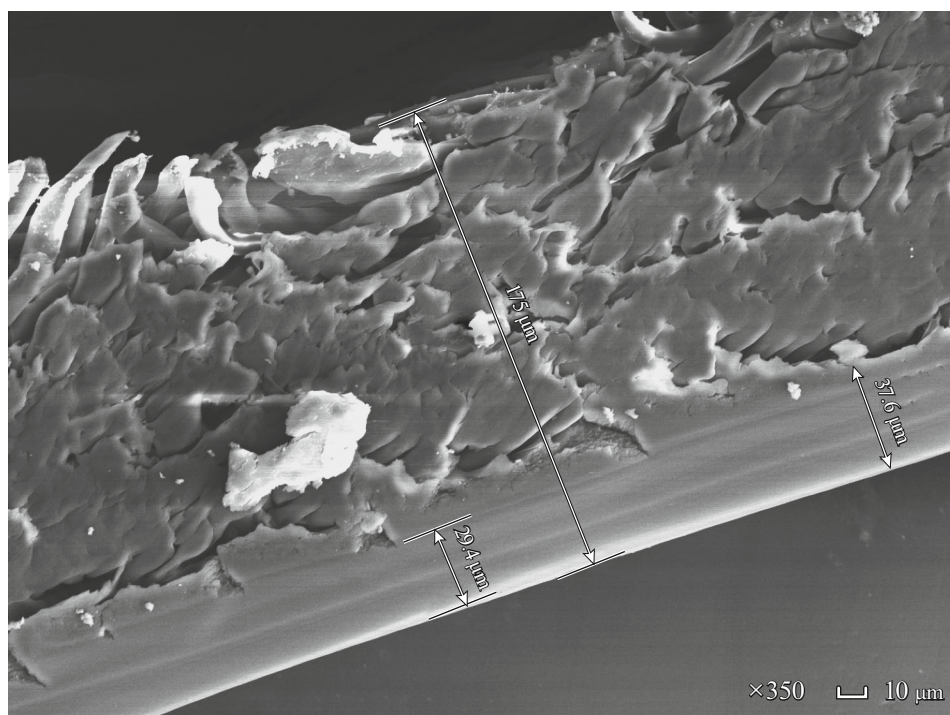


Fig. 2. Photomicrograph of a cross section of the porous substrate GMT-L-1.

Specimens for SEM examination were prepared by cutting immediately after freezing in liquid nitrogen. A JEOL JSM 7500F high-resolution scanning electron microscope with a field emission cathode (Japan) was used to take the images. The images were obtained in the secondary electron mode, since this mode provides the highest resolution (at an incident beam energy of 5 keV, the resolution was 1.5 nm). To eliminate the effects of charging and degradation of the polymer by the action of the probing electron beam, the following methodological approaches were used: SEM studies were carried out at a low electron beam current (3×10^{-11} A), which was provided by a field emission cathode; the surface of the objects was decorated with platinum metal film of about 5 nm in a thickness deposited by magnetron sputtering. The platinum decoration served two purposes, to prevent the polymer from electron beam-induced degradation and its charging, which occurs for a dielectric exposed to electron beam radiation. The images of the sections of the substrate and the composite membrane are shown in Figs. 2 and 3. The boundary between the applied layer and the substrate is clearly visible; the cut of the substrate is also shown separately. Thus, defect-free polymeric composite membranes with a PVTMS layer thickness of 3–4 μm were obtained on porous substrates.

Measurement of Vapor Permeability through Membrane Samples

Experiments on the study of vapor permeability through the obtained composite membranes were carried out using a modified laboratory device for measuring the permeability of membranes (IGM), sketched in Fig. 4. Aqueous ethanol and butanol solutions with ethanol and butanol concentrations of about 9 and 1 wt %, respectively, were used in the experiments.

The test membrane sample was placed in a laboratory flow-through cell (having feed and discharge channels upstream and downstream of the membrane), the active area of the membrane sample in the cell was 25 cm^2 . The cell, a bubbler, a flow meter, a circulation pump, and associated connecting tubes were placed in an air thermostat (AT) to prevent condensation of vapors in the circulation loop between the bubbler and the cell. In addition, the activity of vapors was reduced by maintaining the temperature of the liquid phase (bubbler) below the AT temperature (by 10°C) using an additional circulation loop with an external heat exchanger ($\text{HE}_1\text{--}\text{HE}_2$) and regulation of the coolant (water) flow rate with a fluid pump. The cell and bubbler temperatures were monitored with temperature sensors (TS). During the preparation, a carrier gas (nitrogen) was fed from both sides of the membrane. Prior to the beginning of the experiment, the carrier gas flow downstream of the membrane was stopped by closing valve V_3 , the vacuum pump was turned on, and the carrier gas flow upstream of the

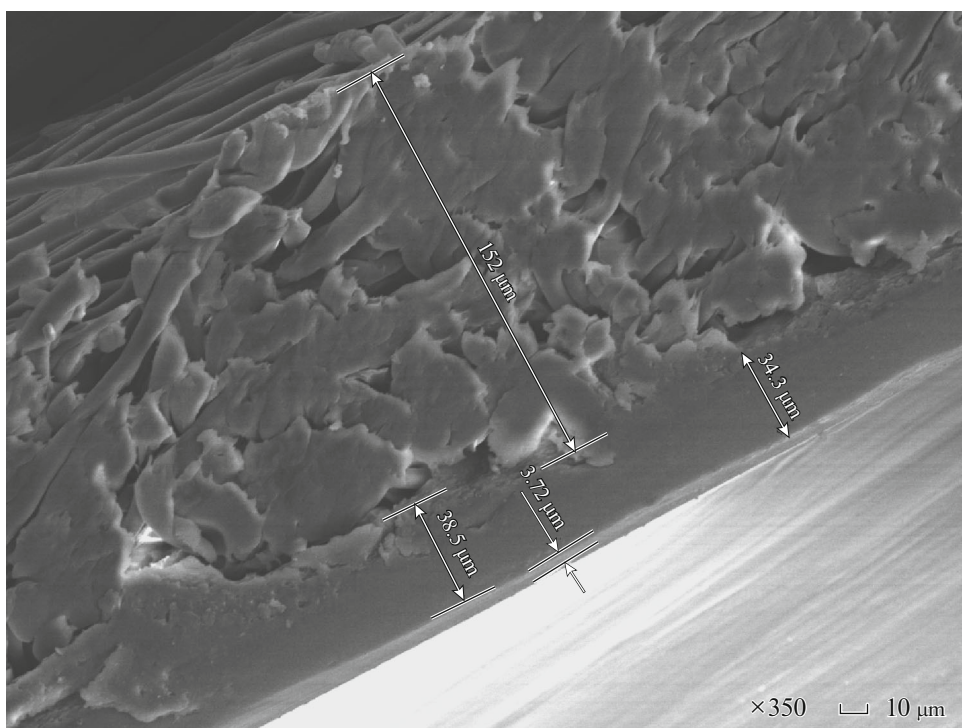


Fig. 3. Photomicrograph of a cross-section of the composite membrane PVTMS/GMT-L-1.

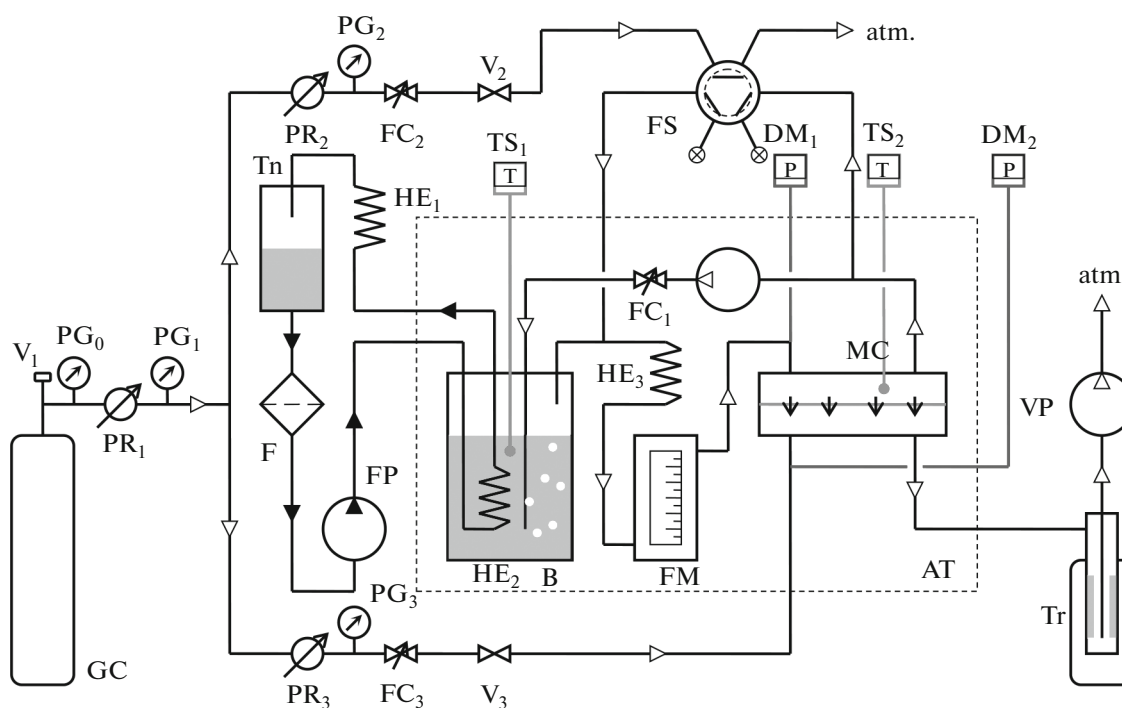


Fig. 4. Schematic diagram of the experimental facility for measuring vapor permeability: (B) bubbler, (V) valve, (VP) vacuum pump, (AT) air thermostat, (GC) gas cylinder with a carrier gas, (TS) temperature sensor, (Tn) coolant tank, (FP) fluid pump, (Tr) vapor trap, (PG) pressure gauge, (FS) flow switch, (FM) flow meter, (PR) pressure regulator, (FC) flow controller, (HE) heat exchanger, (DM) digital manometer, (CP) circulating pump, and (MC) cell with membrane.

Table 2. Characteristics of the laboratory composite membrane based on PVTMS for vapor-phase separation of water–ethanol mixture

T liquid phase, °C	T cell, °C	x_{EtOH}^L , wt %	x_{EtOH}^V , wt %	x_{EtOH}^P , wt %	$Q_{\text{H}_2\text{O}} \times 10^6$, mol/(m ² s kPa)	$Q_{\text{EtOH}} \times 10^6$, mol/(m ² s kPa)	$\alpha_{\text{EtOH}/\text{H}_2\text{O}}^{\text{PhT}}$	$\alpha_{\text{H}_2\text{O}/\text{EtOH}}^M$	$\alpha_{\text{H}_2\text{O}/\text{EtOH}}^{M*}$
50	60	9.2–9.4	47–48	2.7–3.0	170–210	4.4–5.8	8.8	28–32	35–39
60	70	8.1–9.3	44–47	2.7–2.8	160–200	4.9–5.3	8.7–8.9	29–32	33–38
70	80	9.0–9.5	46–47	3.3–4.1	160–190	6.6–7.0	8.5–8.6	21–25	23–29

membrane was redirected with a flow switch (FS) past the cell to the atmosphere. Then, the circulating pump (CP) conveying the vapor–gas mixture (carrier gas with vapors) through the bubbler and the cell was switched on and the vapors passing through the membrane accumulated in a trap (Tr) cooled with liquid nitrogen.

The circulating loop for the flow upstream of the membrane is used for the following reason: in permeability measurements, it is important to ensure the uniformity of the boundary conditions (partial pressures of the components) over the entire membrane area. In the flow upstream of the membrane, this is achieved by ensuring a low recovery of the components into the permeate stream. The recovery of the components in the experiment is controlled by varying the flow rate over the membrane. Since the test membranes are highly permeable to vapors, the required flow rate of the vapor–gas mixture above the membrane turns to be so high that there will be a quite rapid drop in the temperature of the liquid phase in the bubbler and a significant change in its composition during purging the bubbler with the pure carrier gas (without recycling the vapor–gas mixture from the cell) and the subsequent discharging of the stream from the cell to the atmosphere. The use of the circulating loop makes it possible to provide small relative recoveries of the components with retaining the composition of the liquid phase for a long time and precluding the drop in its temperature in the bubbler. During the experiment, the absolute pressure upstream of the membrane corresponded to atmospheric pressure and that downstream of the membrane was 2–2.7 kPa—the pressure was monitored using digital manometers (DM).

At the end of the experiment, the circulation pump was turned off, the carrier gas flow was directed with a flow switch valve into the cell upstream of the membrane, the vacuum pump was turned off, and the carrier gas flow downstream of the membrane was opened. After reaching atmospheric pressure downstream of the membrane, the vapor trap was disconnected and weighed. The feed water–alcohol mixture and the vapor condensate were analyzed on a Shimadzu GC-8A gas chromatograph (evaporator and thermal conductivity detector temperatures of 160°C, a detector current of 80 mA, a Chromosorb 102 packed column of 1 m in length).

Processing of Measurement Results

The permeability of the components was calculated as follows:

$$Q_i = \frac{mx_i^P}{\mu_i At (p_i - p_i')} \quad (1)$$

The phase transition separation factor—transition of water and alcohols from the liquid to the vapor phase in the bubbler—(similar to fractionation factor in distillation) is given by:

$$\alpha_{ij}^{\text{PhT}} = \frac{x_i^V/x_j^V}{x_i^L/x_j^L} \quad (2)$$

The vapor separation factor on the membrane is

$$\alpha_{ij}^M = \frac{x_i^P/x_j^P}{x_i^V/x_j^V} \quad (3)$$

The membrane selectivity for the mixtures under the given experimental conditions was calculated as:

$$\alpha_{ij}^{M*} = \frac{Q_i}{Q_j} \quad (4)$$

The mass fractions of water, ethanol, and butanol in the vapor phase, as well as partial vapor pressures in the feed stream, were taken as calculated for vapor/liquid equilibrium using the UNIQUAC/UNIFAC activity coefficient models [21].

RESULTS AND DISCUSSION

The transport of water vapor, ethanol, and butanol from the mixtures through CM samples was investigated in the temperature range of 60–80°C. The transport and separation characteristics of the laboratory-made composite membrane based on PVTMS are presented in Tables 2 and 3.

The data presented in Table 2 show that in the investigated temperature range, the phase-transition separation factor for the ethanol/water pair is about 8.7, which leads to enrichment of the vapor phase in ethanol vapor from 9 wt % in the liquid phase to 44–48 wt % in the vapor phase, and the membrane selectivity with respect to vapors in the water/ethanol mixture reaches 39. In this case, the permeate (dis-

Table 3. Characteristics of the laboratory composite membrane based on PVTMS for vapor-phase separation of water–butanol mixture

T liquid phase, °C	T cell, °C	x_{BuOH}^L , wt %	x_{BuOH}^V , wt %	x_{BuOH}^P , wt %	$Q_{\text{H}_2\text{O}} \times 10^6$, mol/(m ² s kPa)	$Q_{\text{BuOH}} \times 10^6$, mol/(m ² s kPa)	$\alpha_{\text{BuOH}/\text{H}_2\text{O}}^{PhT}$	$\alpha_{\text{H}_2\text{O}/\text{BuOH}}^M$	$\alpha_{\text{H}_2\text{O}/\text{BuOH}}^{M*}$
50	60	1.1–1.3	26	0.28–0.29	160–180	1.3–1.6	26–27	88–120	100–140
60	70	1.3	27	0.37	160	1.5	29	99	110
70	80	1.1	26	0.36	160	1.5	31	98	110

charge stream with an ethanol content of about 3 wt % in the vapor phase) can be recycled to the fermentor.

The phase-transition separation factor for the butanol/water pair in the temperature range examined is 26–31 (Table 3), which leads to enrichment of the vapor phase in butanol from 1 wt % in the liquid phase to 20–27 wt % in the vapor phase. In this case, the membrane selectivity with respect to vapors in the water/butanol mixture reaches 140.

As can be seen from the data obtained, the permeability to water and butanol vapors varies little in the investigated temperature range; on average, a slight decrease in permeability with increasing temperature is observed for water. At the same time, the permeability to ethanol vapor is noticeable at 80°C. This leads to a decrease in the separation factor and the membrane selectivity for the water/ethanol pair with increasing temperature.

It is noteworthy that the water/ethanol and water/butanol selectivities of the laboratory composite membrane are significantly higher than the ideal selectivities obtained previously in studying the transport of the individual components through the commercial asymmetric PVTMS membrane [11], which were 11 and 6.5, respectively. Apparently, the difference is due to the fact that in the experiments with the commercial asymmetric PVTMS membrane, the ethanol and butanol vapors had a high activity (close to 1), thereby plasticizing the selective layer and enhancing the permeability of these components, with the effect being more significant for butanol vapor [22]. Under the experimental conditions of this work, the activities of ethanol and butanol vapors were about 0.05 and 0.01, respectively, which could not cause swelling of the selective PVTMS layer.

Based on the idea that the transport of water, ethanol, and butanol vapors across the composite membrane with the PVTMS skin layer occurs via the solution–diffusion mechanism, we assume the enhanced separation selectivity in favor of water in the case of separation of water/bioalcohol mixtures to be due to the diffusion component [16], since the thermodynamic term favors the selectivity for ethanol and butanol. These properties are different from those of hydrophobic glassy polymers with a large free volume, such as PTMSP and PMP, in which increased diffusion migration of water and alcohol molecules occurs

with reduced selectivity, leading to the prevalence of transport of alcohols [15] as a result of the balance between the kinetic and thermodynamic terms of vapor transport [10, 16].

The obtained values of the transport and separation characteristics of the laboratory PVTMS-based composite membrane show that it is highly permeable to water vapor and has a significant selectivity in the separation of mixtures of water–ethanol and, especially, water–butanol vapors and can be used in the vapor-phase membrane separation process for the recovery of bioalcohols from fermentation broths.

Modeling of the Vapor Phase Membrane Separation Process for Recovery of Alcohols

Since permeability values are characteristics of the membrane, rather than the process as a whole, we performed mathematical modeling of the vapor phase membrane recovery of ethanol and butanol using the characteristics of the laboratory-made composite membrane based on PVTMS. Because the membrane is water-selective, water vapor preferably penetrates through the membrane and alcohol vapor is concentrated in the retentate; the process flow diagram is shown in Fig. 5a.

The simulation was carried out for the water–ethanol mixture with an ethanol content of 10 wt % and the water–butanol mixture with a butanol content of 1 wt %, the temperature of the liquid phase was set to be 10°C below the temperature of the membrane module. In the calculation, the membrane module was supposed to operate in the countercurrent mode and the experimental values of the membrane transport characteristics at the relevant temperatures in the range of 60–80°C were used.

The mathematical model includes the following assumptions:

- isothermicity;
- obedience of the gas–vapor mixture to the ideal gas laws;
- plug flow regime in membrane module channels;
- absence of pressure gradient along the membrane.

To calculate the mass transfer in the membrane module (Fig. 5b), the following equations were used:

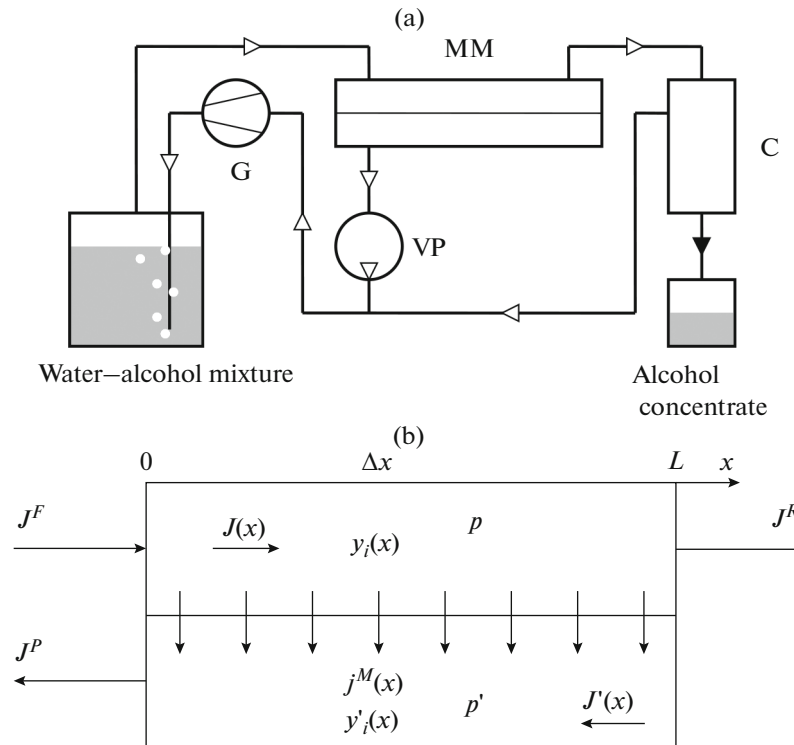


Fig. 5. (a) Process flow diagram the of vapor phase membrane recovery of ethanol from the fermentation mixture: (VP) vacuum pump, (G) gas blower, (C) vapor condenser, and (MM) membrane module used in the calculation. (b) Scheme of mass transfer in the membrane module used in the calculation.

—component flux through the membrane

$$j_i^M(x) = Q_i \Delta p_i(x) \quad (5)$$

—change in the component flux on the feed side of the membrane:

$$\Delta J_i(x) = -j_i^M(x) B \Delta x \quad (6)$$

—change in the component flux on the permeate side of the membrane:

$$\Delta J'_i(x) = j_i^M(x) B \Delta x \quad (7)$$

—driving force of the component transport through the membrane:

$$\Delta p_i(x) = p y_i(x) - p' y'_i(x) \quad (8)$$

—mole fraction of the component in the stream on the feed side of the membrane:

$$y_i(x) = \frac{J_i(x)}{\sum_i J_i(x)} \quad (9)$$

—mole fraction of the component in the stream on the permeate side of the membrane:

$$y'_i(x) = \frac{J'_i(x)}{\sum_i J'_i(x)} \quad (10)$$

—incoming fluxes:

$$J_i(0) = J^F y_i(0), \quad (11)$$

$$J'_i(L) = 0 \quad (12)$$

—outcoming fluxes:

$$J^R = \sum_i J_i(L), \quad (13)$$

$$J^P = \sum_i J'_i(0). \quad (14)$$

The system of equations was solved numerically using the finite difference method.

The recovery of alcohols was calculated as:

$$\theta_{\text{Alc}} = \frac{J_{\text{Alc}}^R}{J_{\text{Alc}}^F}. \quad (15)$$

The resulting relationships of the characteristics of the vapor-phase membrane separation process for the water-ethanol mixture are shown in Figs. 6 and 7, and those for the water-butanol mixture are presented in Figs. 8 and 9.

The simulation results show that the test composite membranes with the PVTMS skin can produce an ethanol concentrate with a content of up to 95 wt % in the retentate with retaining a high level of alcohol recov-

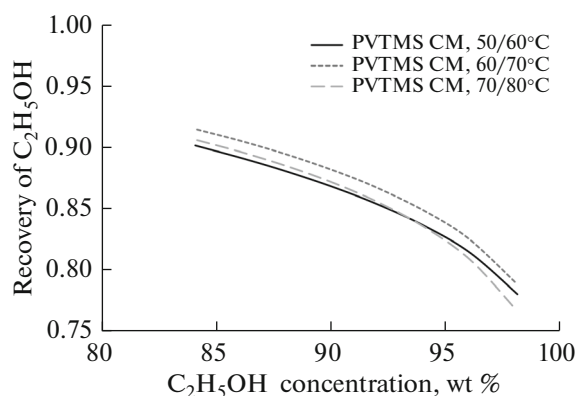


Fig. 6. Relation of ethanol recovery in the membrane module to the concentration of ethanol in the retentate at different temperatures of the liquid phase and the membrane module.

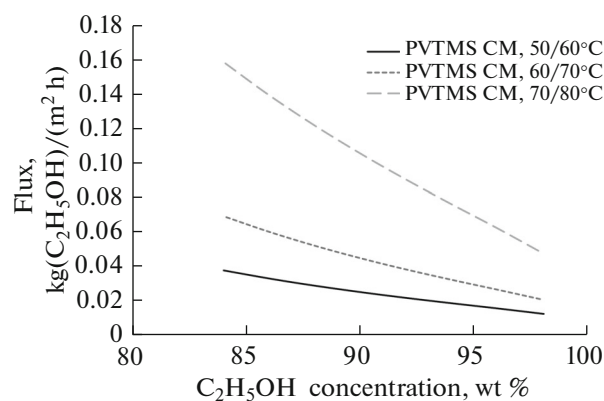


Fig. 7. Relation of the specific product (ethanol) flux in the process to the ethanol concentration in the retentate at different temperatures of the liquid phase and the membrane module.

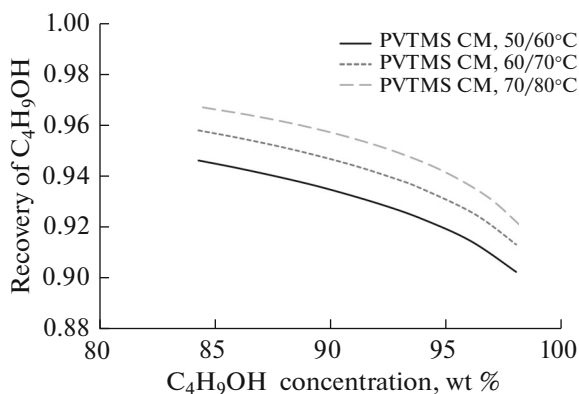


Fig. 8. Relation of butanol recovery in the membrane module to the concentration of butanol in the retentate at different temperatures of the liquid phase and the membrane module.

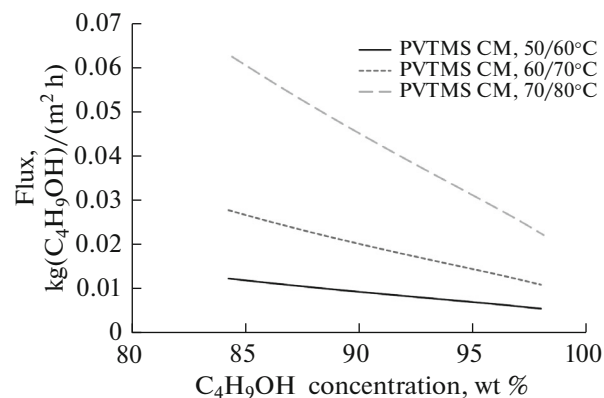


Fig. 9. Relation of the specific product (butanol) flux in the process to the butanol concentration in the retentate at different temperatures of the liquid phase and the membrane module.

ery, more than 0.8. For butanol, the concentrate may contain 98 wt % with a recovery of more than 0.9. The productivity of the process increases substantially with increasing temperature (of liquid phase), since the partial vapor pressure increases.

CONCLUSIONS

The transport and separation characteristics of a laboratory composite membrane with a selective PVTMS layer for use in the process of vapor-phase separation of ethanol and butanol from dilute water-alcohol mixtures of biogenic origin have been studied. The thickness of the selective PVTMS layer of the membrane was 3 to 4 μm . It has been found that the hydrophobic membrane exhibits significant selectivity

in favor of water vapor, up to 39 for the water/ethanol pair and up to 140 for the water/butanol pair.

The advantage of using a hydrophobic water-selective membrane in the vapor-phase process is the absence of swelling in dilute aqueous alcohol media, which ensures the stability of the characteristics in practical applications.

Mathematical modeling of the vapor-phase membrane separation process for the recovery of ethanol and butanol from aqueous solutions with initial concentrations of 10 and 1 wt %, respectively, has been performed. It has been shown that the obtained composite membrane can be used for efficient recovery of alcohols and provide an ethanol or butanol concentrate with a content up to 98 wt % at high recovery. The design productivity of the process is sufficiently high

to make the practical application of composite membranes possible.

NOMENCLATURE

A	membrane area, m^2
B	width of membrane module, m
J	flow rate above the membrane, mol/s
J'	flow rate under the membrane, mol/s
j	flux, $mol/(m^2 s)$
L	length of membrane module, m
m	mass, kg
p	pressure above the membrane, kPa
p'	pressure under the membrane, kPa
Q	permeability, $mol/(m^2 s kPa)$
t	time, s
x	mass fraction
y	mole fraction
α	separation factor (separation coefficient)
α^*	membrane selectivity
μ	molar mass, kg/mol
θ	alcohol recovery
<i>Sub/Superscripts:</i>	
Alc	alcohol (ethanol, butanol)
F	feed
L	liquid phase
M	membrane
P	permeate
PhT	liquid–vapor phase transition
R	retentate
V	vapor phase

ACKNOWLEDGMENTS

The authors are grateful to N.V. Sadovskaya, the leading research associate at the Center for Collective Use, Branch of Karpov Institute of Physical Chemistry, for assistance in carrying out scanning electron microscopy of composite membranes.

The development of composite membranes with a selective PVTMS layer, the investigation of their vapor-separating properties, the designing of the unique hybrid device for measuring the vapor permeability of membranes, and the modeling of bioalcohol recovery processes were supported by the Russian Science Foundation, project no. 16-14-00098. The development of the procedure and the laboratory facility for the fabrication of various composite mem-

branes was supported by the Federal Agency of Science Institutions of Russia within the framework of the State task to the Topchiev Institute of Petrochemical Synthesis.

REFERENCES

1. I. I. Moiseev and N. A. Plate, *Chem. J.*, No. 6, 45 (2006).
2. S. Varfolomeev, *Chem. J.*, No. 8, 36 (2009).
3. P. Stepanenko, *Chem. J.*, No. 9, 30 (2008).
4. V. V. Volkov, A. G. Fadeev, V. S. Khotimskii, et al., *Russ. Khim. Zh.*, No. 6, 71 (2003).
5. N. Qureshi, et al., *Biotechnol. Prog.* **22**, 673 (2006).
6. A. Oudshoorn, A. M. Luuk, L. Wielen, and A. Straathof, *Ind. Eng. Chem. Res.* **48**, 7325 (2009).
7. N. Qureshi and H. P. Blashek, *Renew. Energy* **22**, 557 (2001).
8. L. M. Vane, *Chem. Technol. Biotechnol.* **80**, 603 (2005).
9. K. D. Jitesh, V. G. Pangarkar, and K. Niranjana, *Bioseparation* **9**, 145 (2000).
10. A. V. Yakovlev, M. G. Shalygin, S. M. Matson, et al., *J. Membr. Sci.* **434**, 99 (2013).
11. M. G. Shalygin, A. A. Kozlova, A. I. Netrusov, and V. V. Teplyakov, *Pet. Chem.* **56**, 984 (2016).
12. A. G. Morachevskii, *Thermodynamics of Liquid–Vapor Equilibria* (Khimiya, Leningrad, 1989) [in Russian].
13. E. P. Ageev and V. V. Lunin, *Laboratory Works on Physical Chemistry: Thermodynamics*, (Akademiya, Moscow, 2010), p. 224 [in Russian].
14. J. Gmehling and U. Onken, *Vapor–Liquid Equilibrium Data Collection*, vol. 1 of *Dechema Chemistry Data Series* (Dechema, Frankfurt-on-Main, 1977), part 1, p. 1.
15. V. V. Teplyakov and M. G. Shalygin, *Pervaporation, Vapour Permeation and Membrane Distillation: Principles and Applications*, Ed. by A. Basile, A. Figlioli, and M. Khayet (Elsevier, Amsterdam, 2015), p. 177.
16. A. A. Kozlova, M. G. Shalygin, and V. V. Teplyakov, *Int. J. Membr. Sci. Technol.* **3**, 56 (2016).
17. A. G. Fadeev, et al., *J. Membr. Sci.* **186**, 205 (2001).
18. www.sulzer.com//media/files/products/separationtechnology/evaporation/process_technology.ashx. Accessed March 5, 2018.
19. I. B. Elkina, A. B. Gilman, V. V. Ugrozov, and V. V. Volkov, *Ind. Eng. Chem. Res.* **52**, 8856 (2013).
20. Yu. P. Yampolskii and V. V. Volkov, *J. Membr. Sci.* **64**, 191 (1991).
21. http://vle-calc.com/phase_diagram.html. Accessed March 19, 2018.
22. A. Yushkin, A. Grekhov, S. Matson, et al., *React. Funct. Polym.* **86**, 269 (2015).

Translated by S. Zatonksy