Abstract: The paper describes the creation process for an active layer of pervaporation membrane containing ionic liquid achieved by its appropriate blending with PDMS and hardening by way of polycondensation. The test was performed with the use of hydrophobic ionic liquids with butanol selectivity – 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and 1-hexyl-3-methylimidazilium hexafluorophosphate. The influence of mass content of components and the type of supporting layer on the membrane process parameters was analyzed. Then the prepared membranes were tested in pervaporation process of biobutanol concentration from the model quaternary solution of acetone-butanol-ethanol-water. The process was carried out continuously in a steady state conditions. The permeate side pressure was 30 mbar, feed temperature was 50°C and the feed flow rate was 40 dm³/h. Compositions of permeate and retentate were analyzed using gas chromatography.

Preparation of membranes obtained by polycondensation hardening of the solution consisting of ionic liquid and PDMS enabled us to provide the most appropriate membranes for pervaporation process. The observed permeate fluxes were at relatively low levels due to additional resistance caused by the thickness of PDMS layer.

Keywords: membrane, ionic liquid, pervaporation, biobutanol

Biobutanol is a modern fuel and alternative source of energy. As its properties are similar to petrol, it can be used as petrol additive for internal combustion engines. Relatively low heat of vaporization is one of its advantages as it facilitates engine start up at low temperatures. It is less susceptible to separation from petrol in the presence of water than ethanol. Moreover, it contains less oxygen per mass unit and thus can be added to petrol at higher volumes. Typical blends of ethanol with petrol contain 5–20% of ethanol, while blends with butanol contain 8–32% of butanol.
Biobutanol is obtained mainly by way of biomass fermentation which results in the acetone-butanol-ethanol aqueous solution (ABE fermentation) with the 3:6:1 mass ratio. Typical raw materials include sugar cane, corn or wheat but other cellulose containing materials, such as wood waste could also be used, which would greatly decrease the cost of biobutanol production. As a result of ABE fermentation butanol of the concentration of up to 3 wt. % is obtained. Isolation of the product from fermentation broth constitutes a serious technological issue as traditional distillation is not profitable.

Studies indicate that the modern membrane technology of pervaporation (PV) can be utilized for isolation of butanol from the broth. Pervaporation is a separation technique which involves phase change of the first type combined with mass transfer across nonporous composite membrane, which allows for separation and concentration of the product within a single process. In the case of ABE post-fermentation product, the organic fraction: butanol, acetone and ethanol are transported across the hydrophobic membrane. Literature provides examples of studies about \textit{n}-butanol separation and recovery from aqueous solutions by PV with the use of both, commercially available and independently manufactured silicone membranes [1–4]. Contemporary scientific research indicates possibility of incorporation of ionic liquids, which are selective for butanol, into pervaporation membranes.

Ionic liquids (ILs) for that application are liquids in room temperature and consist of ions only. They usually consist of a large, asymmetrical cation and a wide range of anions which influence melting point of the compound, depending on their structure and composition.

Ionic liquids are called designer solvents which means that their properties can be adjusted to match the requirements of a given process [5]. The key factors in separation of mixtures are low volatility and high incidence in liquid state (often above 200 °C) [6] which enables their easy regeneration and recirculation to the process. Low solubility in aqueous solutions of the ionic liquid used as extraction solvent is crucial for separation of biobutanol.

There are some methods for use ILs as an active separation layer in membranes. The first approach is the linking of polymerisable groups to the IL molecules and the direct crosslinking of the ILs by covalent bonding. In this case, membrane exhibits different permeation behaviour than without ILs [7]. The second approach represents ion exchange membranes where anions or cations of ILs might be immimmobilised in membrane material. In another approach ILs can be solidified by use of gelling agents [8, 9]. Gelators allow to obtain high IL contents, but show low chemical and mechanical stability limit their suitability for pervaporation. In related approach, ILs are often solidified by dissolving these liquids in a polymer. In the literature, some polymers using to this method preparation has been reported, eg polyvinyl alcohol (PVA), polyvinyl chloride (PCV), poly(dimethyl siloxane) (PDMS), poly(ether block amide) (PEBA) [10, 11]. In this paper the last method creation of pervaporation membrane was used. The membranes were achieved by appropriate blending ionic liquid with PDMS and hardening it by polycondensation.
Materials

Pervaporation membranes were formed with the use of commercially available, two component liquid silicone rubber (POLSIL Solar) hardened at room temperature to a transparent rubber with Solar catalyst, made by Chemical Plant “Polish Silicones” Ltd). 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF6] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf2N] (see Figure 1 for chemical structure) obtained from IoLiTec (Ionic Liquid Technologies, Germany) were used as ionic liquids with low water solubility and affinity for butanol [12, 13]. Acetone, ethanol and \( n \)-butanol (POCh) were used for pervaporation tests.

Flat pervaporation membranes were obtained by blending POLSIL Solar solution with a suitable ionic liquid and adding Solar catalyst. Then the solution was gently stirred and deaerated. Such solution was poured onto supporting layer of the membrane. Two types of supporting layers were used: parchment paper for food packing (39 g/m\(^2\)) covered with a layer of silicone (0.5 g/m\(^2\)) and nylon net pulled over a flat glass surface used to overcome resistance of flow of the layer. This solution poured over the supporting layer of the membrane was equally distributed all over the surface. The solution was subject to polycondensation hardening at room temperature within 48 hours. Thickness of membranes obtained was between 150 and 200 \( \mu \)m and was controlled with the amount of poured solution. The process of pervaporation was performed with the use of 160 mm discs prepared directly on parchment paper used as supporting layer as well as discs cut out from a sheet poured over nylon net.

Test methods

Obtained membranes were used for pervaporation tests of biobutanol concentration using Sulzer Chemtech laboratory apparatus. The feed consisted of aqueous solution of three organic components, acetone-butanol-ethanol with the 3 : 6 : 1 mass ratio, just as the broth after ABE fermentation. All tests were performed with fixed feed composition.
amounting to 3 wt. % of butanol to enable comparison of quality of obtained membranes. The process was carried out continuously in a steady state conditions. The permeate side pressure was 3 kPa, feed temperature was 50 °C and the feed flow rate was 40 dm³/h [14]. Chemical constitution of permeate and retentate was analyzed by gas chromatography using ThermoFinnigan apparatus and BTR-CW column. To measure the concentration, the sample was additionally diluted with 5 % aqueous methanol solution that was at the same time used as the internal standard.

Based on the experiments, permeate weight and mole fractions of individual components in the permeate \((x_{ip})\) were obtained. The data obtained was used to calculate total permeate flux and partial permeate fluxes \((J_{tot}, J_i [kg/(m²h)])\) as well as membrane diffusion coefficients for individual components \((D_i [m²/h])\). These parameters define membrane selectivity and enable comparison of pervaporation results for various membranes.

Diffusion coefficient was calculated with the use of partial permeate flux formula. The driving force behind the process of pervaporation is the difference in activity:

\[
J_j = \rho_i \frac{D_i}{\delta} \Delta a_i \left[ \frac{kg}{m²h} \right]
\]

where: \(\rho_i\) – density of component \(i\) at operating temperature [kg/m³], 
\(\delta\) – membrane thickness [m], 
\(\Delta a_i\) – difference in activity of component \(i\) in permeate and feed [-] calculated with the following formula:

\[
\Delta a_i = \gamma_{ip} x_{ip} - \gamma_{if} x_{if} [-]
\]

where: \(\gamma_{ip}, \gamma_{if}\) – activity coefficient of component \(i\) in the permeate and feed [-].

Activity coefficients of individual components \(\gamma_i\) in the liquid for the quaternary solution – acetone-butanol-ethanol-water – at atmospheric pressure (feed pressure) and reduced pressure (permeate pressure) were determined with the use of NRTL equation (Non-Random Two-Liquid) as defined in the following formula (3).

\[
\ln \gamma_i = \frac{\sum_{j=1}^{n} \tau_{ij} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{kij}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} x_k G_{kij}} \left[ \frac{\sum_{m=1}^{n} \tau_{mj} x_m G_{mij}}{\sum_{k=1}^{n} x_k G_{kij}} \right]
\]

where: \(G_{ij} = \exp(-\sigma_{ij} \tau_{ij})\); 
\(\tau_{ij} = a_{ij} + b_{ij} T + e_{ij} \ln T + f_{ij} T\); 
\(\sigma_{ij} = c_{ij} + d_{ij}(T-273,15 \text{ K})\); 
\(T\) – temperature [K].

Calculations of activity coefficients \(\gamma_i\) for individual components were performed with the use of a dedicated MATLAB program [15], on the basis of pairs of coefficients.
for binary solutions. Calculations of $\tau$ and $G$ intermediate constant values used in the equation (3) for the temperature of 323.15 K are shown in Tables 1 and 2.

### Table 1

<table>
<thead>
<tr>
<th>$\tau$ [-]</th>
<th>Acetone</th>
<th>Butanol</th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0</td>
<td>0.635</td>
<td>0.292</td>
<td>0.8</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.0038</td>
<td>0</td>
<td>0.398</td>
<td>0.323</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.404</td>
<td>0.264</td>
<td>0</td>
<td>0.039</td>
</tr>
<tr>
<td>Water</td>
<td>1.354</td>
<td>2.778</td>
<td>1.644</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>$G$ [-]</th>
<th>Acetone</th>
<th>Butanol</th>
<th>Ethanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1</td>
<td>0.826</td>
<td>0.916</td>
<td>0.787</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.999</td>
<td>1</td>
<td>0.888</td>
<td>0.908</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.886</td>
<td>1.082</td>
<td>1</td>
<td>1.012</td>
</tr>
<tr>
<td>Water</td>
<td>0.066</td>
<td>0.435</td>
<td>0.611</td>
<td>1</td>
</tr>
</tbody>
</table>

### Test results

Preliminary crosslinking tests of POLSIL solution with an addition of ionic liquid for catalyst amounts of 6, 8, 10 and 20 wt. % were performed. No significant influence of used amounts of catalyst on the hardening rate of the solution within the period of analysis was observed. For this reason the amount of 8 wt. % in proportion to pure solution was used, as recommended by the manufacturer.

Then examinations of POLSIL solution miscibility with ionic liquids at 25 °C were performed. Both silicone rubber and the ionic liquids are viscous solutions with different density, which results in forming of two phases after blending and setting aside for some time. In order to determine the largest possible amount of ionic liquid that can be added to active membrane layer without observing visible separation of its phases, samples of solutions in the scope of 0.1–0.6 wt. fraction of ionic liquid in the solution were prepared. Samples were set aside to enable formation of crosslinking. Then homogeneity of their structures was analyzed. Samples with high fractions of ionic liquid showed condensation and joining of droplets into larger aggregates. Apparently, 36.5 wt. % (30 % of volume) is the limit amount of 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF$_6$] that can be added to the solution. In case of 1-butyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide [Bmim][Tf$_2$N] 33 wt. % (25.8 % of volume) is the limit amount. Based on the above tests, membranes with limit
amount of ionic liquid were able to be formed and their efficiency in comparison with
pure silicon could be evaluated.

Figure 2 presents microscopic images of pure PDMS membrane made on a nylon net
support and membrane with limit amount of ionic liquid [Hmim][PF$_6$] showing low
transparency and visible condensation of ionic liquid in the membrane.

Initial tests of pervaporation separation for quaternary solution were performed on
membranes immobilized on parchment paper with 0 wt. % and 25 wt. % amounts of
ionic liquid. Distinct concentration of feed components was observed in neither case.
Additionally low permeate fluxes indicated considerable membrane flow resistance. For
this very reason parchment paper was replaced by a thin nylon net to be used as
supporting layer in order to reinforce active layer of membrane and avoid additional
resistance of flow. The thickness of membrane on the net was approximately 200 µm.

Further tests of pervaporation separation for the solution were performed on
membranes with the nylon net. Diffusion coefficients for individual components were
calculated for the tested membranes (Table 3).

<table>
<thead>
<tr>
<th>No.</th>
<th>w [wt.%]</th>
<th>$D_{\text{Acet}}$ [m$^2$/h]</th>
<th>$D_{\text{BuOH}}$ [m$^2$/h]</th>
<th>$D_{\text{EtOH}}$ [m$^2$/h]</th>
<th>$D_{\text{H$_2$O}}$ [m$^2$/h]</th>
<th>$J_{\text{tot}}$ [kg/(m$^2$h)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$1.37 \times 10^{-8}$</td>
<td>$1.73 \times 10^{-8}$</td>
<td>$4.15 \times 10^{-8}$</td>
<td>$5.15 \times 10^{-8}$</td>
<td>0.054</td>
</tr>
<tr>
<td>2</td>
<td>25 [Hmim][PF$_6$]</td>
<td>$1.72 \times 10^{-8}$</td>
<td>$2.32 \times 10^{-8}$</td>
<td>$4.39 \times 10^{-8}$</td>
<td>$6.39 \times 10^{-8}$</td>
<td>0.075</td>
</tr>
<tr>
<td>3</td>
<td>36.5 [Hmim][PF$_6$]</td>
<td>$1.78 \times 10^{-8}$</td>
<td>$1.91 \times 10^{-8}$</td>
<td>$3.11 \times 10^{-8}$</td>
<td>$9.11 \times 10^{-8}$</td>
<td>0.080</td>
</tr>
<tr>
<td>4</td>
<td>33 [Bmim][Tf$_2$N]</td>
<td>$2.46 \times 10^{-8}$</td>
<td>$3.08 \times 10^{-8}$</td>
<td>$1.05 \times 10^{-7}$</td>
<td>$8.82 \times 10^{-8}$</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Table 3 presents similar values of diffusion coefficients for all components. In all
cases the values are higher for membranes with ionic liquid in comparison to pure
PDMS membrane. Permeate fluxes were very low and reached the values from 0.054 to
0.1 kg/(m²h). For comparison, pervaporation concentration performed with the use of commercially available PERVAP 4060 membrane for the same feed composition resulted in the flux of about 1.2 kg/(m²h) [16]. The value suggests that thickness of active membrane layer was inadequate. Higher values of flux for membranes with ionic liquid compared with pure PDMS membrane may result from leaching of the liquid from membrane pores during the process, which was described in some papers [17, 18]. Therefore, it seems appropriate to create some additional layer to close ionic liquid within the membrane or change the method of PV membrane preparation.

Summary and conclusions

Membrane is the most important element of the PV process. It determines the separation of aqueous and organic phase. In this work membranes were obtained by polycondensation hardening of the solution consisting of ionic liquid and PDMS. Then the membranes were tested in pervaporation process. The diffusion coefficients and permeate fluxes were calculated.

The diffusion coefficients for all components through PDMS membrane are of the same order. They are higher for membranes with ionic liquid in comparison to pure PDMS membrane. The ionic liquid enhances the diffusion of all components through the membrane.

During testing of the prepared membranes with different supporting layer it was found that resistance to mass transfer is mainly connected with the thickness of its active layer. It is advisable to form thinner PDMS layers. It directly contributes to increasing the permeate flux. It was observed higher values of flux for membranes with ionic liquid compared with pure PDMS membrane.

Acknowledgements

The paper was financed from the Polish National Science Centre funds granted based on decision no. DEC-2012/07/B/ST8/03379.

References

PERWAPORACYJNA MEMBRANA Z DODATKIEM CIECZY JONOWEJ
DO ZATĘŻANIA BIOBUTANOLU

Wydział Inżynierii Procesowej i Ochrony Środowiska
Politechnika Łódzka

Abstrakt: W pracy wytworzono warstwę aktywną membrany perwaporacyjnej z dodatkiem cieczy jonowej poprzez odpowiednie zmieszanie z PDMS i polikondensacyjne utwardzenie. Do badań użyto hydrofobowych cieczy jonowych: 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide oraz 1-hexyl-3-methylimidazolium hexafluorophosphate, które wykazują selektywność w stosunku do butanolu. Przemanalizowano wpływ udziału masowego składników oraz rodzaj warstwy podporowej na parametry procesowe membrany. Na wytworzonych membranach wykonano badania perwaporacyjnego zatężania biobutanolu z modelowego czteroskładnikowego układu aceton-butanol-etanol-woda. Proces prowadzony był w sposób ciągły, w warunkach ustalonych, z ciśnieniem po stronie permeatu wynoszącym 30 mbar, w temperaturze 50 °C i z natężeniem przepływu nadawy 40 dm³/h. Skład permeatu i retentatu był analizowany za pomocą chromatografii gazowej.

Szeroka preparatyka membran otrzymanych metodą utwardzania polikondensacyjnego mieszaniny cieczy jonowej z PDMS pozwoliła wyłonić najodpowiedniejsze membrany do procesu perwaporacji. Obserwowane strumienie procesowe były relatywnie niskie i wynikały z dodatkowych oporów spowodowanych grubością warstwy PDMS.

Słowa kluczowe: membrana, ciecz jonowa, perwaporacja, biobutanol