Synergy of selective gas transport in bilayered membranes

D S Bakhtin, I L Borisov, V G Polevaya, P M Budd and A V Volkov

1A.V.Topchiev Institute of Petrochemical Synthesis, RAS, 119071, Moscow, Russia
2Department of Chemistry, University of Manchester, M13 9PL, Manchester, UK

E-mail: db2@ips.ac.ru

Abstract. Dense bilayer PTMSP/PIM-1 membranes and PTMSP/PIM-1 blends were prepared and studied in order to obtain insight into the recently observed synergistic effect of increased CO₂/N₂ selectivity for thin-film composite (TFC) membranes consist of PIM-1 (selective layer) and PTMSP (gutter layer). It was shown that the mixing of these two polymers does not lead to a synergistic effect in gas permeance, since dense films made by blending of PIM-1 and PTMSP showed classical trade-off permeation/selectivity behavior. Analysis of gas-transport property data using a bicomponent resistance-in-series model allowed us to conclude that the increased N₂ transport resistance of the layer formed on the border of the two polymers is presumably responsible for the increased ideal selectivity.

1. Introduction

Currently, carbon dioxide capture and storage (CCS) is considered an important technology for reducing CO₂ emissions to the atmosphere, in order to mitigate climate change. Membrane technologies for flue gas capture can offer clear advantages over alternative amine-based methods, as they are simple, compact and environmentally friendly processes. Due to the high flue gas flow rate, large membrane surface areas are required. Therefore, highly permeable polymer membrane materials are currently the most promising option for CO₂ capture in the most common coal-fired power plants [1]. In addition to chemical and mechanical stability under operating conditions, membranes must have extra high gas transport properties [2,3]. A promising type of membrane is represented by our recently developed TFC membranes based on a PIM-1 selective layer on top of an ultra-permeable support consisting of a cross-linked PTMSP/PEI gutter layer coated on a MFKK-1 microfiltration support (Vladipor, Russia) [3]. Optimization of various parameters enabled us to obtain a series of membranes with CO₂ permeance of 13-22 m(STP)³/m²·h·bar and CO₂/N₂ selectivity of 36-56. It is worth noting that dense PIM-1 films of about 30 μm showed CO₂/N₂ selectivity in the range of 15-22, depending on the preparation protocol. Thus, for the first time, a synergy effect was demonstrated in gas selectivity for thin bilayered gas separation membranes. SEM and TEM analysis revealed that the overall selective layer thickness of optimized TFC membranes was in the range of 2.0-2.5 μm, whereas the thickness of the PIM-1 layer on top of a cross-linked PTMSP gutter layer was about 0.4-0.5 μm. This study was focused on evaluation of the transport properties of thick bilayer dense membranes with different ratios of PTMSP and PIM-1 layers.
2. Experimental

Highly permeable glassy polymers PTMSP \((M_w = 900 \ 000 \ \text{g/mol})\) [5] (Figure 1) and polybenzodioxane PIM-1\((M_w = 270 \ 000 \ \text{g/mol}; \ \frac{M_w}{M_n} = 2.8)\) [4] (Figure 2) were used as membrane materials. The method of slow evaporation of the solvent was used for thick bilayer dense membrane preparation. The required amount of 1.5 wt.% PIM-1 solution in chloroform was cast onto a cellophane substrate and covered with a Petri dish for several hours (from 2 to 4 hours depending on the amount of solution) until almost complete solvent evaporation. Then a 0.5 wt.% PTMSP solution in hexane was carefully cast onto the surface of a partially dried PIM-1 layer and then covered with a Petri dish (from 1 to 5 days depending on the amount of solution) until the solvent completely evaporated. The amount of PTMSP and PIM-1 solution was calculated in advance to ensure the desired thickness of each layer. The total thickness of each sample was 20 μm. The membrane was removed from the hydrophilic cellophane substrate with a small amount of water and dried at room temperature. The bilayer membrane thickness was measured by a MITUTOYO ABSOLUTE Digimatic Quick Mike 293-666 micrometer to confirm the desired total thickness of 20 μm.

PTMSP/PIM-1 blend membranes were obtained by casting polymer solutions on cellophane and drying at ambient temperature for at least 7 days until complete solvent evaporation. Solutions of PIM-1 and PTMSP, both in chloroform (0.5 wt.%), were mixed to obtain the desired PIM-1/PTMSP ratio; then the casting solution was stirred for at least 1 hour before casting onto a cellophane substrate. The thicknesses of all membranes prepared were in the range of 25–30 μm.

![Figure 1. Chemical structure of PTMSP.](image1)

![Figure 2. Chemical structure of PIM-1.](image2)

The gas permeance of dense membranes for individual gases (in the following order: \(N_2, O_2, CO_2\)) was measured by the barometric method at room temperature \((23.0 \pm 2.0^\circ \text{C})\) in the range of transmembrane pressures from 0.5 to 2.0 bar. The schematic diagram of the set-up is presented in Figure 3. The PIM-1 layer was faced to the feed side and the PTMSP layer to the permeate side (Figure 4).
Figure 3. Schematic diagram of gas permeation set-up.
1, 2, 5, 7, 9, 12 – valves, 3 – pressure regulator, 4 – membrane cell, 6 – pressure indicator, 8 – vacuum pump, 10 – three-way valve, 11 – buffer volume, 13 – control panel combined with a pressure indicator.

3. Results and Discussion
Figure 5 presents the N\textsubscript{2}, O\textsubscript{2} and CO\textsubscript{2} permeance and ideal selectivity for three pairs of gases for dense bilayer films of 20 μm thickness, with different PIM-1/PTMSP thickness ratios. It should be pointed out that there are noticeable deviations in the results obtained, even in the case of different membrane samples with the same PIM-1/PTMSP thickness ratio. To interpret the data obtained, a resistance-in-series model (RM) was employed (Figure 4). The model allows us to evaluate the contribution of each layer to the total permeability of the composite membrane [6]. According to this model, the inverse permeability of the $n$-layer composite is equal to the sum of the inverse permeability of each layer.

Figure 4. Representation of a bilayer composite membrane: resistance-in-series model. $R_{PIM}$ и $R_{PTMSP}$ are resistance of the PIM and PTMSP layers, respectively.
The overall gas transfer equation through the bilayer membrane in the resistance model has the form:

\[
\frac{1}{Q_{\Sigma}} = \frac{1}{Q_{\text{PIM}}} + \frac{1}{Q_{\text{PTMSP}}}
\]  

(1)

Where \(Q_{\Sigma}\), \(Q_{\text{PIM}}\) and \(Q_{\text{PTMSP}}\) are the gas permeability through the bilayer composite membrane, PIM-1 and PTMSP layers, respectively. Equation (1) can also be written as:

\[
\frac{1}{Q_{\Sigma}} = \frac{l_{\text{PIM}}}{P_{\text{PIM}}} + \frac{l_{\text{PTMSP}}}{P_{\text{PTMSP}}}
\]  

(2)

Where \(l_{\text{PIM}}, l_{\text{PTMSP}}, P_{\text{PIM}}\) and \(P_{\text{PTMSP}}\) are the thickness and permeability coefficients of polymeric materials, respectively.

![Graph a](image1)

![Graph b](image2)
Figure 5. RM and experimentally obtained data of gas-transport characteristics of composite bilayer PIM-1/PTMSP membranes vs PTMSP layer thickness: (a) comparison of CO₂, N₂ permeance and α(CO₂/N₂) ideal selectivity with RM prediction, (b) comparison of O₂, N₂ permeance and α(O₂/N₂) ideal selectivity with RM prediction, (c) comparison of CO₂, O₂ permeance and α(CO₂/O₂) ideal selectivity with RM prediction.

For some experimental points, reduced permeance and slightly enhanced selectivity may indicate the presence of additional resistance to gas transfer, which was not considered in the resistance-in-series model based on two layers. The synergistic effect in the increase of CO₂/N₂ selectivity by a factor of 2.5 for TFC membranes was explained by the appearance of a PIM-1 structured thin layer on the boundary between PIM-1 and PTMSP layers [4]. Bearing this in mind, such deviation from the calculated data based on a resistance-in-series model can also be explained by the appearance of such an additional resistance (layer) towards gas transport. It is interesting that the greater deviation between experimental and calculated data was found in the case of thinner PIM-1 layers (see Figure 6). For these samples, a larger volume of PTMSP solution was poured onto the thinner layer of PIM-1 to obtain the “sandwich”-type membranes of the same overall thickness. It can be speculated that the longer exposure time of the PIM-1 film to PTMSP solution provided greater mobility to PIM-1 chains for their further rearranging. At the same time, the mixing of these two polymers does not lead to a synergistic effect in gas permeance, since the dense films made by blending of PIM-1 and PTMSP showed a classical trade-off in permeation and selectivity, as can be seen in Figure 7. Further investigations to provide the explanation of such phenomena in the dense films with respect to materials thickness ratio are needed.
Figure 6. Difference between experimental and calculated (RM) data on gas permances for PTMSP/PIM bilayer membranes with respect to PTMSP layer thickness.

Figure 7. Trade-off dependence between CO₂/N₂ ideal selectivity and N₂ permeability coefficient for PTMSP/PIM-1 blends (25–30 μm thickness)

The dependences of ideal selectivity in Figure 8 clearly show that the reason for the deviation of the experimental data from the resistance-in-series model data is caused by the greater drop in N₂ transport rather than an increase of transport of O₂ or CO₂. Figures 8a and 8b demonstrate that for the values of ideal selectivity for CO₂/O₂ there is a limit close to the PIM-1 α(CO₂/O₂) value. At the same time, there is no such limit for α(CO₂/N₂) and α(O₂/N₂).
Figure 8. Dependencies of ideal selectivity of composite bilayered PIM-1/PTMSP membranes: (a) $\alpha$(CO$_2$/N$_2$) vs $\alpha$(CO$_2$/O$_2$) and (b) $\alpha$(CO$_2$/O$_2$) vs $\alpha$(O$_2$/N$_2$).

4. Conclusions
A series of 20 μm thick bilayer PTMSP/PIM-1 membranes was obtained and their gas transport properties were characterized by single gas permeation tests. A bicomponent resistance-in-series model was applied to describe the gas-transport properties of bilayer PTMSP/PIM-1 composite membranes. The bicomponent resistance-in-series model failed to describe the results obtained, because of possible intermediate layer formation between PIM-1 and PTMSP. The deviation of experimental data from the resistance-in-series model was greater for longer PTMSP top solution evaporation times (up to 5 days). Characterization of PTMSP/PIM-1 blends of 20-30 μm thickness showed that the effect cannot be explained only by PTMSP and PIM-1 mixing. Therefore, one could expect formation of an intermediate layer between PTMSP and PIM, which is presumably responsible for the discrepancy of experimental and theoretical data.

Acknowledgements: This work was supported by the Russian Science Foundation, project №. 18-19-00738.

References
[1] Wang Y, Zhao L, Otto A, Robinius Mand Stolten D 2017 Energy Proced. 114 650
[2] Merkel T C, Lin H, Wei X and Baker R 2010 J. Membr. Sci. 359 126
[3] Apel P, Bobreshova O, Volkov A, Volkov V, Nikonenko V, Stenina I, Filippov A, Yampolskii Y and Yaroslavtsev A 2019 Membr. and Membr. Tech. 2 45
[4] Borisov I, Bakhtin D, Luque-Alled J M, Rybakova A, Makarova V, Foster A B, Harrison W J, Volkov V, Polevaya V, et al 2019 J. Mat. Chem. A 7 6417
[5] Kossov A, Yushkin A, Khotimskiy V and Volkov A 2015 Petrol. Chem. 55 783
[6] Henis J M and Tripodi M K 1981 J. Membr. Sci. 8 233