Membranes Comprising Silver Salts Physically Dispersed in Poly(dimethyl siloxane) for the Separation of Olefin/Paraffin

Jong Hak Kim†, Byoung Ryul Min, Jongok Won*, and Yong Soo Kang*‡

Department of Chemical Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea
* Department of Applied Chemistry, Sejong University, Seoul 143-747, Korea
** Division of Chemical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea

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Abstract: Inert composite membranes, in which silver salts are physically dispersed in rubbery poly(dimethyl siloxane) (PDMS), were prepared and tested for the separation of propylene/propane mixtures. Physical dispersion of silver salts in the PDMS matrix without specific interaction leads to very low separation performances initially. However, as the permeation time increases, both the selectivity and the permeance increase continuously to finally reach equilibrium values. These unusual permeation properties are likely to be due to the conversion of the initially inactive silver ionic aggregates into the more active free ions through the coordination of propylene to the silver ions under a propylene environment. Physical dispersion of the salts and the dissolution behavior by propylene were investigated using FT-IR and FT-Raman spectroscopy and wide-angle X-ray scattering (WAXS). The separation performance of the membrane for propylene/propane mixtures is to our knowledge the highest ever reported for the solid state; the mixed gas selectivity was ~ 200.

Keywords: facilitated transport, membrane, silver, propylene PDMS

Introduction

Olefins, such as ethylene and propylene, are among the most important products in the petrochemical industry; they are mainly used in the production of polymers, acids, alcohols, esters, and ethers. Generally, olefins are obtained by separating olefin/paraffin mixtures, which is performed mostly through cryogenic distillation. Because this distillation process is energy-intensive, alternative separation techniques are necessary, e.g., adsorption, absorption, and membrane techniques [1-4]. Among these approaches, facilitated transport membranes containing silver ions as olefin carriers are a possible alternative to distillation, exhibiting high selectivity as well as permeance through the membranes. Initial investigations have been performed using liquid membranes, such as immobilized liquid membranes, solvent-swollen membranes, and ion exchanged membranes [5-9]. However, evaporation of the liquid media in the membranes is a critical problem for practical applications.

Recently, facilitated transport membranes utilizing silver polymer electrolytes, in which low lattice silver salts, such as AgBF₄, AgClO₄, AgSbF₆, and AgCF₃SO₃, are dissolved in polar polymer matrices, such as poly(2-ethyl-2-oxazoline) (POZ) [10-14], poly(N-vinyl pyrrolidone) (PVP) [15,16], poly(ethylene oxide) (PEO) [17,18], poly(methacrylate) (PMA) [19,20], poly(vinyl methyl ketone) (PVK) [20], poly(ethylene phthalate) (PEP) [21], and nylon-12/tetramethylene oxide block copolymer (PA12-PTMO) [22], have demonstrated remarkably high separation performance for olefin/paraffin mixtures in the solid state. For example, the propylene permeance through a 1:1 POZ/AgBF₄ membrane was as high as 45 GPU [1 GPU = 10⁻⁶ cm³ (STP)/(cm² s cmHg)] at a propylene pressure of 138 kPa, while the propane permeance was as low as 0.003 GPU. Thus, the ideal separation factor of propylene over propane was more than 15000, but the mixed gas selectivity was ca. 50 because of propylene-induced plasticization of the membranes [14,20].

Fast and reversible olefin complexation with silver ions dissolved in polymer solvent is responsible for the facilitated olefin transport across the membranes. Thus,
the dissolution behavior of the silver salt into the polymer matrix has a significant bearing on determining the facilitated transport property. For instance, it has been found that free silver ions are more likely to be formed when the cation/anion interaction is weak; they are the most active olefin carriers among the various ionic constituents, including ion pairs and higher-order ionic aggregates [13]. To promote dissolution of silver salts, polar polymers containing amide, ester, ketone, or ether groups are commonly employed [10-22]. Thus, the preferred polymers are those that can form electron-sharing bonds with silver ions by means of electron-donating atoms such as O, N or S, known as heteroatoms.

It has been reported recently that all ionic constituents of the silver salt are completely dissolved into free ions under an olefin environment, suggesting that the olefin molecule is a good ligand for the silver salts, forming complexes of the silver cations with the olefin [13]. Based on this experimental finding, novel membranes have been developed recently by utilizing olefin molecules directly as ligands to dissociate silver salt, rather than using polymer matrices containing functional groups [23]. Especially, the replacement of polar polymer matrices, such as POZ, PVP, and PEO, is desirable because these polymers are also reducing agents for silver salts, leading to their decreased separation performance over time [24-28]. In this study, poly (dimethyl siloxane) (PDMS), a material highly permeable to the gases, was used as the polymer matrix. It may not dissolve silver salts, but instead disperse them physically, because it does not contain any functional groups. The facilitated olefin transport through the resulting membranes was evaluated with the aim of investigating the feasibility of developing membrane materials for olefin/paraffin separation.

**Experimental**

Poly(dimethyl siloxane) (PDMS, RTV, 3-1744) was purchased from Dow Corning. Silver tetrafluoroborate (AgBF₄, 98 %), silver perchlorate (AgClO₄, 99.9 %), silver trifluoromethanesulfonate (AgCF₃SO₃, 99 + %), silver hexafluoroantimonate (AgSbF₆, 98 %), and silver nitrate (AgNO₃, 99 + %) were purchased from Aldrich Chemical Co. All chemicals were used without further purification. PDMS solutions were prepared by dissolving 20 wt% PDMS in 1-hexene (99 + %, Aldrich). Silver salts were added to these polymer solutions depending on the weight fraction of salts. After complete dissolution, the solutions were coated onto polyester membrane substrates (Whatman, 0.1 µm) using an RK Control Coater (Model 101, Control Coater RK Print-

![Figure 1. SEM image of composite membrane consisting of PDMS/Ag salt top layer and polyester substrate.](image)

Coat Instruments LTD, UK). The resulting membranes were dried under N₂ and further dried in a vacuum oven for two days at room temperature. The permeation experiments were performed using the constant pressure/variable volume method. The mixed gas (50:50 vol % of propylene/propane mixture) separation performance of each membrane was evaluated using a gas chromatograph (Hewlett Packard G1530 A, MA) equipped with a TCD detector. The stage cut (θ), the ratio of permeate to feed flow rates, was always less than 2 %. The units of gas permeance were GPU, where 1 GPU = 1×10⁻⁶ cm³(STP)/(cm² s cmHg). The thickness of the top selective layer was ca. 2 µm, determined by scanning electron microscopy (SEM; Figure 1). Raman spectra were collected for the membranes at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman. This experimental apparatus included a neodymium-doped yttrium aluminum garnet (NdYAG) laser operating at 1064 nm. IR measurements were performed on a 6030 Mattson Galaxy Series FT-IR spectrometer; 64~30 scans were signal-averaged at a resolution of 2 cm⁻¹. Raman and IR spectroscopic characterization was performed using a pressure cell equipped with quartz and CaF₂ windows, respectively. Wide-angle X-ray diffraction was utilized with Cu Kα radiation to determine the value of the d-spacing in the silver polymer electrolytes at a scanning speed of 10°/min.

**Results and Discussion**

**Physical Dispersion of Silver Salt in PDMS Matrix**

Because of the poor electron donating ability of PDMS, the silver salts were expected to be dispersed physically in the PDMS matrix without any specific interactions
between them [29]. Figure 2 shows the FT-IR spectra of pure PDMS and a PDMS/AgSbF$_6$ membrane at a silver weight fraction of 0.57. Because the anion vibration mode of AgSbF$_6$ is not overlapped with the Si-O-Si stretching bands of PDMS in the range 1200–300 cm$^{-1}$, AgSbF$_6$ was chosen among the various PDMS/silver salt composite membranes for characterization of its FT-IR spectra. The stretching vibration bands of Si-O-Si for PDMS/AgSbF$_6$ at 1105 and 1024 cm$^{-1}$ are nearly coincident with those for pure PDMS. This result demonstrates that PDMS does not interact specifically with silver ions and, thus, silver salts are merely dispersed in the polymeric matrix physically.

It has been observed previously that the ionic constitution strongly depends on the nature of the polymeric ligand. For example, ion pairs are more likely to be formed in the presence of polymeric ligands in the order ester > ketone > amide [20]. The FT-Raman spectra of PDMS/Ag salt composites were measured to investigate the dissolution behavior of the silver salt. Figure 3 presents the Raman spectra of the ν$_1$ symmetric stretching mode of the ClO$_4$$^-$ anion. Irrespective of the silver concentration, the position of the strong peak at 920 cm$^{-1}$ in the membranes, which is attribute to ionic aggregates of the ClO$_4$$^-$ anion, remains invariant. The spectrum of pure AgClO$_4$ was also included in the plots to confirm this ionic state in the PDMS/AgClO$_4$ membranes. This result demonstrates that PDMS cannot dissolve the silver salt because of the lack of specific interactions between them. However, PDMS might disperse the salt uniformly, without large defects, because of its highly flexible chains. The FT-Raman spectra for PDMS membranes containing other silver salts, i.e., PDMS/AgNO$_3$ and PDMS/AgCF$_3$SO$_3$, were also measured (Figure 4). Similar results, i.e., that all silver salts were present as ion aggregates in the PDMS matrix, were observed. The well-known peaks for SO$_3$$^-$ at 1048 cm$^{-1}$ and NO$_3$$^-$ at 1046 cm$^{-1}$ are assigned to higher-order ionic aggregates of the salts [30-32].

WAXS spectra also support the notion that the silver salts are dispersed physically in the PDMS, as seen in the Figure 5(a). The spectrum of pure PDMS exhibits an amorphous peak centered at 2θ = ca. 11.8°, whereas that of pure AgCF$_3$SO$_3$ shows several crystalline peaks at ca. 8.0, 16.2, 24.7, and 41.5°. The d-spacing estimated from the Bragg relation in pure PDMS was 7.49 Å, suggesting high intesegmental distances and possibly high gas permeability. Upon incorporation of AgCF$_3$SO$_3$ into PDMS, the respective peaks of both PDMS and the Ag salt are observed, demonstrating a lack of specific interactions between the components and suggesting that the silver salts are present as ionic aggregates.
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Dissolution of Silver Salts by Propylene Coordination
The constituents of silver ions may possibly change in the propylene environment, as observed by in situ FT-Raman spectroscopy [13]. Thus, the time evolution WAXS spectra for the PDMS/AgCF$_3$SO$_3$ membrane at a silver weight fraction of 0.73 were obtained at a propylene pressure of 138 kPa [Figure 5(b)]. The PDMS/AgCF$_3$SO$_3$ membrane prior to propylene contact possessed only silver ionic aggregates among the various ionic constituents, as shown by the several sharp crystalline peaks. As the contact time between propylene and the membrane increased, the intensity of the crystalline peaks in AgCF$_3$SO$_3$ gradually decreased, implying that the ionic aggregates were dissolved. This notable observation clearly indicates that propylene is a good ligand for silver salts physically dispersed in the PDMS membranes, accelerating the solvation of ions under the propylene environment is possible because the coordination sites of the silver ions can be occupied by the π-electrons of propylene and, consequently, the interaction of the silver cation with its counteranion becomes weak. Therefore, propylene acts as a solvent for silver salts that are physically dispersed in the PDMS membranes, accelerating the solvation of ions.

Effect of Salt Dissolution on Facilitated Propylene Transport
Figure 6 shows the selectivity change of propylene/propane through the PDMS/AgBF$_4$ membranes with different concentrations of silver salt as a function of permeation time. At the initial time of permeation experiment, the membranes exhibit a low separation performance, i.e. the selectivity of propylene/propane is around
Table 1. Normalized Gas Permeance of Propylene and Propane and the Mixed Gas Selectivity of Propylene/Propane Through PDMS and PDMS/Ag Salt Membranes at a Silver Weight Fraction of 0.57

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Propylene Permeance (GPU)</th>
<th>Propane Permeance (GPU)</th>
<th>Mixed Gas Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>24.6</td>
<td>22.40</td>
<td>1.1</td>
</tr>
<tr>
<td>PDMS/AgBF$_4$</td>
<td>12.9</td>
<td>0.08</td>
<td>158.1</td>
</tr>
<tr>
<td>PDMS/AgClO$_4$</td>
<td>12.0</td>
<td>0.29</td>
<td>42.0</td>
</tr>
<tr>
<td>PDMS/AgCF$_3$</td>
<td>7.7</td>
<td>7.7</td>
<td>9.4</td>
</tr>
<tr>
<td>PDMS/AgSbF$_6$</td>
<td>9.2</td>
<td>1.13</td>
<td>8.1</td>
</tr>
<tr>
<td>PDMS/AgNO$_3$</td>
<td>6.8</td>
<td>6.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 8. Selectivity of propylene/propane through PDMS/AgBF$_4$ complex membranes as a function of the weight fraction of silver salt.

Figure 9. Selectivity of propylene/propane through PDMS/silver salt membranes at a silver weight fraction of 0.57 as a function of time.

1.0. However, as the permeation time increases, the selectivities increase gradually to finally reach equilibrium values. It is very intriguing to see the remarkably high separation performance of the PDMS/AgBF$_4$ membranes. Initially, the silver salts are dispersed physically in PDMS as higher-order ionic aggregates, which are inactive olefin carriers, and, thus, the selectivity of propylene/propane is very low. However, with increasing permeation time, the ionic aggregates dissolved gradually by means of propylene coordination to silver ions; these free silver ions are active olefin carriers, resulting in enhancement of the facilitated propylene transport. The time required to reach the equilibrium state seems to be quite insensitive to the concentration of the silver salt.

The normalized gas permeances of propylene and propane through PDMS/AgBF$_4$ membranes at a silver weight fraction of 0.73 are presented in Figure 7. The permeance of propylene increased gradually with increasing time during the permeation experiment to reach an equilibrium value finally after ca. 3 h. This time may be associated with the time required to dissociate the silver aggregates into free ions, similar to the behavior observed for the selectivity of propylene/propane. Meanwhile, propane passed through the PDMS/AgBF$_4$ membranes containing, different concentrations of silver salt as a function of permeation time. At the initial stages of the permeation experiment, the membranes exhibit a low separation performance, i.e. the selectivity of propylene/propane is low. The permeance of propane through the membrane almost remained unchanged with increasing permeation time, demonstrating that Fickian transport was not greatly influenced by the silver ionic constituents within this experimental range.

Threshold Concentration for Facilitated Transport

Figure 8 presents the selectivity of propylene/propane through PDMS/AgBF$_4$ membranes at the steady state as a function of the silver concentration. It is a very intriguing that facilitated propylene transport occurred in proportion to the concentration of silver salt, hardly showing the presence of a threshold silver concentration. Membranes consisting of polymer matrices containing polar functional groups commonly exhibit such a threshold concentration [20]. That is, the composition at which facilitated propylene transport occurs through the membranes changes depending on the nature of the polymeric ligand [19,20]; (1) a 0.09 silver mole fraction for esters (PMMA, PEMA, PBMA), (2) 0.14 for ketones (PVMK), and (3) 0.25 for amides (POZ, PVP). For complexes containing carbonyl groups, silver ions at low
silver concentrations are already fully coordinated by the carbonyl oxygen atoms that possess high electron donating abilities. Furthermore, the interaction between silver ions and carbonyl oxygen atoms is marginally stronger than that with olefins [14]. Therefore, olefin molecules cannot readily approach and complex with silver ions and, thus, silver ions at low silver concentrations might not be active olefin carriers. In contrast, the silver salts in PDMS/Ag salt membranes are physically dispersed in the PDMS matrix without any specific interactions because PDMS has no functional groups that can coordinate to silver ions. Thus, silver ions, even at low concentrations, can bind with propylene molecules to form π-complexes and, hence, play a role as a propylene carrier.

**Effect of Counteranion on Facilitated Propylene Transport**

The selectivities of propylene/propane through PDMS membranes containing various silver salts as a function of time are presented in Figure 9; their steady state values are summarized in Table 1. The time required to reach steady state and the corresponding value of selectivity are strongly dependent on the kind of counteranion of the salt. For the PDMS/AgBF₄ membrane, it takes a relatively long time to reach the steady state (ca. 3 h), but the membrane performance was the highest among the five systems. The facilitated propylene transport was seemingly associated with the value of the lattice energy of the salt. According to theoretical calculations based on the density functional theory, the lattice energy of silver is strongly dependent on the counteranion and the coordination number of silver. For the PDMS/AgBF₄ membrane, the lattice energy is 680 kJ/mol, which is significantly lower than that of AgClO₄ (677 kJ/mol), AgNO₃ (695 kJ/mol), and AgBF₄ (794 kJ/mol). A large value of lattice energy represents a strong interaction between silver ions and their counteranions. Thus, we expected that the PDMS/AgBF₄ membrane, with its lower lattice energies, would be more readily dissociated or dissolved to free ions by the propylene molecules, resulting in facilitated propylene transport through the membranes. Despite the similar lattice energies of AgBF₄ and AgClO₄, the difference in their transport properties is attributable to both the different coordination numbers and the dangling of the heavy anions in the membranes, as we have reported previously [34]. AgClO₄ has a higher coordination number of silver ions and heavier anions than does AgBF₄. On the basis of these different structural properties of the membranes, the approach of propylene molecules toward AgClO₄ might be unfavorable compared to that toward AgBF₄, even though the lattice energies of the two salts are similar. On the other hand, PDMS/AgNO₃, which has a lattice energy higher than that of the other salts by around 100 kJ/mol, hardly exhibits any separation performance, demonstrating that π-complexation between propylene and AgNO₃ is not sufficiently strong to dissociate AgNO₃.

**Conclusions**

We have developed novel membrane materials that consist of silver salts physically dispersed in inert polymer matrices without any specific interactions between them. The separation performance indicates clearly that the novel membranes are successful as facilitated transport membranes for the separation of olefins/paraffins. The high separation properties arise from the in situ dissociation of silver ionic aggregates into free ions that act as active olefin carriers through π-complexation with the olefin molecules. This system eliminates the need for polymer matrices containing polar functional groups and, consequently, may overcome the possible problem of the reduction of silver ions to form silver nanoparticles.

**References**