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Control of Ionic Interactions in Silver Salt−Polymer Complexes with Ionic Liquids: Implications for Facilitated Olefin Transport

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The ionic liquids 1-butyl-3-methyl imidazolium $BMIM^+NO_3^-$ and $BMIM^+BF_4^-$ have been successfully utilized to increase the activity in reversible π-complexation with olefins of silver cations in silver polymer electrolytes consisting of $AgNO_3$ dissolved in poly(2-ethyl-2-oxazoline) (POZ). In the absence of the ionic liquids, $AgNO_3$ is not readily dissolved in POZ and is instead because of its high lattice energy present mostly as chemically less active ion pairs or higher order aggregates. The activation of Ag^+ in silver polymer electrolytes in the presence of these ionic liquids is principally due to the reduction of the interactions between Ag^+ and NO_3^- produced by the interaction between $BMIM^+$ and NO_3^-, and this effect does not occur in the presence of common salts such as $NaNO_3$. We investigated these systems with FT-IR, FT-Raman, and XPS and calculated the theoretical electronic structures of the relevant species. The increased activity in these membranes of Ag^+ in reversible π-complexation with olefins was further confirmed by evaluating the sorption and desorption behavior of propylene and the performances of the membranes in the separation of olefin/paraffin mixtures.

Introduction

Ionic liquids have recently attracted much interest because of their unique physical and chemical properties.[1] Their highly charged nature means they can be utilized, for instance, as biphasic reaction media and as eco-friendly solvents instead of volatile organics in chemical processes. Their unique physicochemical properties have been tested in new applications such as dye-sensitized solar cells [DSSCs] and membranes for the separation of CO_2 and chiral mixtures.[1e−1h]

In this paper we report the successful use of ionic liquids to control the interactions between silver cations and nitrate anions, with the result that the silver cations become chemically more active in forming silver−olefin complexes, in which an olefin molecule donates π electrons to the empty s orbital of a silver ion to form a coordinative bond.[2,3] It is well-known that most silver salts with a low lattice energy such as $AgBF_4$ are readily dissolved in common polar polymers such as poly(2-ethyl-2-oxazoline) (POZ), poly(ethylene oxide), and poly(*N*-vinyl pyrrolidone), generating free anions as a result of the coordinative interaction between the silver ions and the oxygen atoms. However, $AgNO_3$ does not readily dissolve in these polar polymers to produce free ions and is instead present mostly as ion pairs or higher order aggregates, which are chemically less active in the formation of silver−olefin complexes. The unfavorable dissolution behavior of $AgNO_3$ may be principally due to its high lattice energy.

Silver ions are generated by the dissolution of silver salts in the polar polymer solvent and react with olefin molecules to form reversible silver−olefin complexes. Such reversible silver−olefin complexation properties can be used in membrane separation and in pressure or thermal swing adsorption processes for olefin purification.

Among the many silver salts capable of forming reversible silver−olefin complexes, $AgBF_4$ has been commonly used because of its highly favorable formation of such complexes.[3d,4]

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However, $AgBF_4$ is easily reduced to metallic silver,[5] resulting in the deterioration of its complex formation ability.[5] On the other hand, $AgNO_3$ is not readily reduced, but is rather inactive in complex formation.[3e,4] Thus, we have investigated the use of ionic liquids to control the interactions between Ag^+ and NO_3^- in order to improve this salt's complex formation activity and take advantage of its resistance to reduction to metallic silver.

In this study, the ionic liquids 1-butyl-3-methyl imidazolium $BMIM^+NO_3^-$ and $BMIM^+BF_4^-$ were introduced into silver polymer electrolytes consisting of silver salts dissolved in POZ. The positive charge of the $BMIM^+$ ions is expected to interact with the NO_3^- anions and reduce the interactions between Ag^+ and NO_3^-, making the silver ions more active in reversible olefin complexation. The resulting activated silver ions were then used in facilitated transport membranes for the separation of olefin/paraffin mixtures.

Experimental Section

Materials. Silver nitrate ($AgNO_3$, 99%) and poly(2-ethyl-2-oxazoline) (POZ, $M_w = 5.0 \times 10^5$ g/mol) were purchased from Aldrich Chemical Co. The ionic liquids 1-butyl-3-methylimidazolium nitrate ($BMIM^+NO_3^-$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$) were purchased from C-TRI Co. All the chemicals were used as-received.

Characterization. IR spectra were obtained with a 6030 Mattson Galaxy Series FT-IR spectrometer; 64-200 scans were signal-averaged with a resolution of 4 cm^{-1}. Raman spectra were collected for the POZ/$AgNO_3$/$BMIM^+BF_4^-$ films at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman with a resolution of 1 cm^{-1}. This spectrometer is equipped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 1064 nm. The spectroscopic data were obtained using a pressure cell with CaF_2 windows.

X-ray photoelectron spectroscopy (XPS) data were acquired using a Perkin-Elmer Physical Electronics PHI 5400 X-ray photoelectron spectrometer. This system was equipped with a Mg X-ray source operated at 300 W (15 kV, 20 mA). The carbon (C 1s) line at 285.0 eV was used as the reference in our determinations of the binding energies of the silver ions.

Sorption and Desorption of Propylene. A quartz crystal microbalance (QCM) was used to measure weight changes with time upon propylene exposure. For the preparation of each film, a 3 wt % polymer solution containing $AgNO_3$ and the ionic liquid were cast onto a quartz crystal with a spin-coater at 1000 rpm. Each coated film was dried overnight in a vacuum oven before the propylene sorption test was carried out at 1 atm.

Separation Performance. The POZ/$AgNO_3$/ionic liquid electrolytes were prepared by dissolving $AgNO_3$ and each ionic liquid in a water solution containing 20 wt % of POZ. The [C=O]:[Ag] molar ratio was fixed at 1:1 and the amount of the ionic liquid was varied. For the fabrication of the separation membranes, the mixed solution was coated onto polysulfone microporous membrane supports (Seahan Industries Inc., Seoul, Korea) using an RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The molar ratio of $BMIM^+NO_3^-$ to $AgNO_3$ was fixed at 0.1 for the separation membranes; this molar ratio provided the best separation performance. After evaporation of the solvent in a convection oven at room temperature under nitrogen, the POZ/$AgNO_3$/$BMIM^+NO_3^-$ complex was dried completely in a vacuum oven for 2 days at room temperature. The thickness of the top polymer electrolyte layer was found to be approximately 1 μm with SEM. Gas flow rates or gas permeances were measured with a mass flow controller (MFC). The unit of gas permeance is GPU, where 1 GPU $= 1 \times 10^{-6}$ cm^3 (STP)/(cm^2 s cmHg). The mixed gas (50:50 vol % propylene/propane mixture) separation properties of the POZ/$AgNO_3$/$BMIM^+NO_3^-$ complex were evaluated using a gas chromatograph (Hewlett-Packard G1530A, MA) equipped with a TCD detector and a unibead 2S 60/80 packed column.

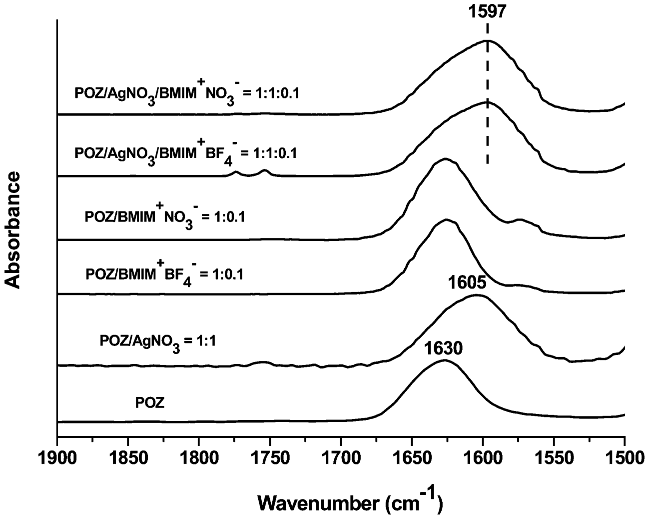

Figure 1. FT-IR spectra of neat POZ, 1:1 POZ/$AgNO_3$, 1:0.1 POZ/$BMIM^+BF_4^-$, 1:0.1 POZ/$BMIM^+NO_3^-$, 1:1:0.1 POZ/$AgNO_3$/$BMIM^+BF_4^-$, and 1:1:0.1 POZ/$AgNO_3$/$BMIM^+NO_3^-$.

Results and Discussion

Coordinative Interactions. The coordinative interactions between silver ions and the polar atoms of a polymer matrix result in the dissolution of silver salts in polymer matrixes to form polymer−silver complexes or silver polymer electrolytes.[4] The extent of the dissolution is strongly correlated with the lattice energy of Ag^+ and the counteranion and the strength of the coordinative interaction between Ag^+ and the polar atoms of the polymer matrix. The changes in the coordinative interactions between Ag^+ and the C=O groups of POZ that resulted from the introduction of the ionic liquids were investigated using FT-IR spectroscopy. The FT-IR spectra for pure POZ, 1/1 POZ/$AgNO_3$, POZ/$BMIM^+BF_4^-$, POZ/$BMIM^+NO_3^-$, 1/1/0.1 POZ/$AgNO_3$/$BMIM^+BF_4^-$, and 1/1/0.1 POZ/$AgNO_3$/$BMIM^+NO_3^-$ are shown in Figure 1. The C=O stretching band of neat POZ at 1630 cm^{-1} was found to shift to a lower wavenumber at 1605 cm^{-1} upon incorporation of $AgNO_3$ into POZ, presumably due to the weakening of the C=O double bond caused by electron donation from the carbonyl oxygens to the silver ions. When the ionic liquids were added to the POZ/$AgNO_3$ complex, the position of the C=O stretching band was found to shift further, from 1605 to 1597 cm^{-1}, suggesting the strengthening of the interactions between C=O and silver ions. It was also observed that the C=O peak at 1630 cm^{-1} is not significantly affected by the addition of the ionic liquids to neat POZ, implying that the interactions between POZ and the ionic liquids are negligible. These results are attributed to the interaction between the NO_3^- anions and the silver

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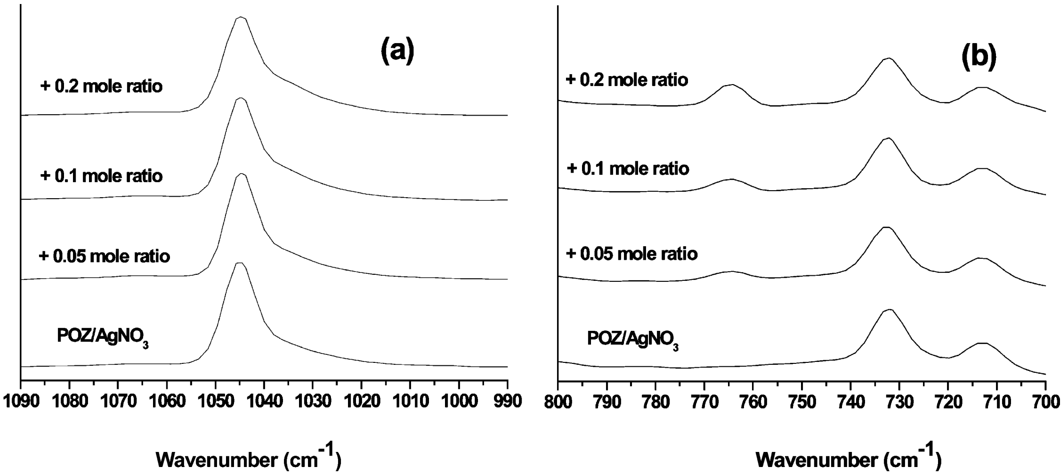

Figure 2. FT-Raman spectra of POZ/AgNO$_3$ electrolytes for various molar ratios of BMIM$^+$BF$_4^-$ to AgNO$_3$ in the (a) NO$_3^-$ stretching and (b) BF$_4^-$ stretching regions.

ions being weakened by the interaction between BMIM$^+$ and NO$_3^-$. As a result of this interaction, silver ions in the POZ/AgNO$_3$/ionic liquid complexes are more strongly coordinated with carbonyl oxygens than those in POZ/AgNO$_3$.

Ionic Constituents. The intensity of the coordinative interaction between POZ and the silver salt determines the identities of the ionic constituents (i.e., free ions, ion pairs, and higher order aggregates) because it has a direct effect on the strength of the interaction of the silver ion with the counteranion. For instance, free ions are more likely to be formed when the interaction between the silver ion and its counteranion is weak. The interaction in polymer−silver complexes between the Ag$^+$ and NO$_3^-$ ions upon addition of BMIM$^+$BF$_4^-$ was investigated using FT-Raman spectroscopy. The BMIM$^+$BF$_4^-$ system was investigated because the NO$_3^-$ ions of BMIM$^+$NO$_3^-$ and AgNO$_3$ are indistinguishable. The Raman spectra of POZ/AgNO$_3$ electrolytes with and without BMIM$^+$BF$_4^-$ are shown in Figures 2a and 2b in the regions of the NO$_3^-$ and BF$_4^-$ stretching bands, respectively. Note that the NO$_3^-$ stretching bands at 1034, 1040, and 1045 cm^{-1} are assigned to free ions, ion pairs, and ion aggregates,[4] respectively. The fraction of free NO$_3^-$ in 1/1 POZ/AgNO$_3$ in the absence of BMIM$^+$BF$_4^-$ was estimated from the deconvoluted spectra to be only 13%, which is low because of the high lattice energy (∼794 kJ/mol).[6] However, the fraction of free anions was found to increase to 31% upon the addition of 0.2 molar ratio of BMIM$^+$BF$_4^-$. In addition, in the range of the BF$_4^-$ stretching bands (Figure 2b), only the peak at 765 cm^{-1} corresponding to free BF$_4^-$ is observed for all ionic liquid concentrations. Note that the peaks for ion pairs and higher order ion aggregates are at 770 and 774 cm^{-1}, respectively.[4] These Raman results suggest the following interaction scheme: (1) the ionic liquid is readily dissolved to form free ions without significant interactions with other constituents and (2) BMIM$^+$ ions interact with the NO$_3^-$ anions of the silver salt to some degree, resulting in a weakening of the interaction between Ag$^+$ and NO$_3^-$. Thus, we conclude that the concentration of free NO$_3^-$ anions increases markedly upon addition of the ionic liquids, presumably making the silver ions more active in silver−olefin complexation.

Electronic Structure and Binding Energies. The electronic energies and complexation structures were calculated using density functional theory at the B3LYP level, and the charge densities of the silver ions in these systems were obtained using natural population analysis. The structures of POZ/AgNO$_3$ with and without BMIM$^+$ are shown in Scheme 1. Since the anions of the ionic liquids are free (as was confirmed by the Raman spectra), the effects of their presence were not considered in these calculations. $CH_3CH_2CON(CH_3)CH_2CH_3$ was used to model POZ in these calculations for simplicity. Table 1 shows that the complexation energies (ΔE_C), defined as the energies required to separate the complexed molecules in the gas phase, are 53.6 and 115 kcal/mol for POZ/AgNO$_3$ electrolytes with and without BMIM$^+$, respectively. On the other hand, ΔE_C of POZ/AgBF$_4$ electrolytes is 97.6 kcal/mol. A large value of ΔE_C indicates that there is a strong ionic interaction between Ag$^+$ and NO$_3^-$. The theoretical calculations suggest that the complexation energy of the POZ/AgNO$_3$/BMIM$^+$ complex is half that of the POZ/AgNO$_3$ complex, and thus that there is a much weaker interaction between Ag$^+$ and NO$_3^-$ in this complex than in POZ/AgNO$_3$. Further, the charge density of the silver ion was found to increase from +0.796 to +0.824 with the addition of BMIM$^+$, indicating an enhancement of the chemical activity of Ag$^+$. This increase in charge density seems to be associated with an increase in the length of the bond between Ag$^+$ and NO$_3^-$, from 2.195 to 2.245 Å upon the addition of BMIM$^+$, as shown in Scheme 1, whereas the length of the bond between Ag$^+$ and the carbonyl oxygen of POZ decreases only slightly from 2.206 to 2.187 Å. For the POZ/AgBF$_4$ complex, the charge density of silver ion and the bond length between Ag$^+$ and BF$_4^-$ are +0.882 and 2.231 Å, respectively.[3b]

The binding energies of the silver ions in the POZ/AgNO$_3$ system were measured with XPS to investigate the changes in silver ion activity. The Ag 3d$_{5/2}$ regions of the XPS spectra of the polymer/silver salt complexes are very sensitive to the chemical environments around the silver ions, particularly to the strengths of the interactions of the silver ions with

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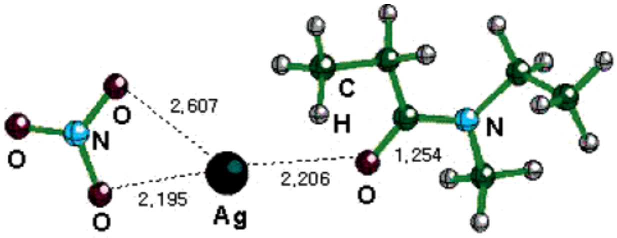
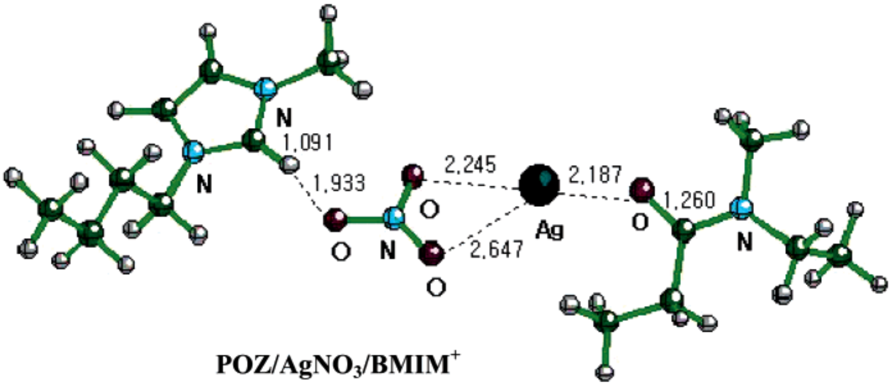
Scheme 1



POZ/AgNO$_3$



POZ/AgNO$_3$/BMIM$^+$

Table 1. Complexation Energies for Ag$^+$ and Counteranion at the B3LYP[a] Level, and Charge Densities of Ag$^+$ for POZ/AgBF$_4$ and POZ/AgNO$_3$ Complexes with and without BMIM$^+$ at 298 K

polymer/silver complexes	complexation energy[b] ΔE_C (kcal/mol)	charge density of silver ion
POZ/AgBF$_4$	97.6	+0.882
POZ/AgNO$_3$	115.0	+0.796
POZ/AgNO$_3$/BMIM$^+$	53.6	+0.824

[a] These calculations were carried out using the general basis set method and the LANL2DZ basis set for Ag. [b] The complexation energy is defined as the energy necessary to separate the complexed molecules in the gas phase.

carbonyl oxygens and with the counteranions.[7] The Ag 3d$_{5/2}$ spectrum of pure AgNO$_3$ was found to contain a single peak at 371.7 eV.[7] The addition of POZ to AgNO$_3$ resulted in a decrease in the binding energy to 369.63 eV, presumably due to the coordination of the silver ions with carbonyl oxygens (Figure 3). This value was found to decrease to 368.86 and 368.70 eV upon the addition of BMIM$^+$NO$_3^-$ and BMIM$^+$BF$_4^-$, respectively. These results indicate that the binding energies of the valence electrons in the silver atom are reduced by the weakening of the interaction between Ag$^+$ and NO$_3^-$ and that the charge density of Ag$^+$ in the silver polymer electrolytes is increased by the introduction of the ionic liquids. These XPS data are consistent with the Raman spectra and the theoretical calculations.

Propylene Sorption and Desorption. The enhancement of the activity in olefin complexation of silver ions in POZ/AgNO$_3$ upon the introduction of the ionic liquid BMIM$^+$NO$_3^-$ was investigated by characterizing the transient sorption and desorption kinetics as well as the equilibrium solubility, which were measured with a quartz crystal microbalance (QCM). The QCM data in Figure 4 show that the weight fractions of propylene ($w_{gas}/w_{complex}$) in POZ/AgNO$_3$ and POZ/AgNO$_3$/BMIM$^+$NO$_3^-$ after 225 h are 0.012 and 0.029, respectively, indicating the much higher affinity of the latter membrane. The sorption rate of the former is also much slower than the latter, as shown by their initial sorption curves. Furthermore, desorption occurred in the POZ/AgNO$_3$ system only to a small extent (less than 4% after 100 h) at an extremely slow rate, whereas in the latter system it occurred significantly (~50% after 100 h) at a much faster rate.

These results suggest that the presence of the ionic liquid increases the activity in complexation with olefins of the silver ions in POZ/AgNO$_3$; i.e., it increases the solubility of propylene and results in much faster sorption and desorption

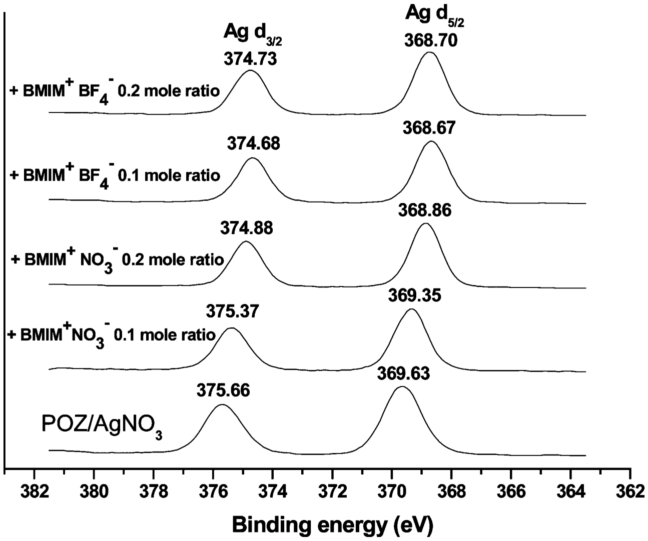


Figure 3. XPS spectra of POZ/AgNO$_3$ complexes for various mole ratios of BMIM$^+$BF$_4^-$ and BMIM$^+$NO$_3^-$, showing the binding energies of the silver ions.

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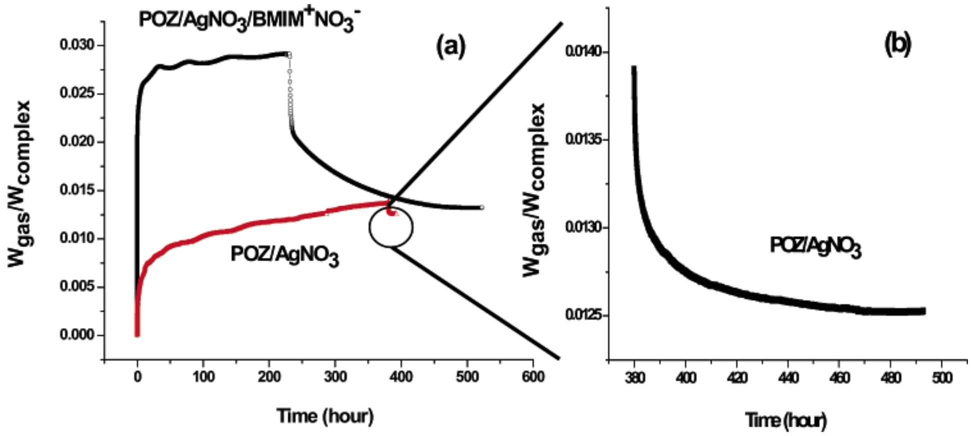

Figure 4. $w_{gas}/w_{complex}$ of propylene in (a) POZ/$AgNO_3$ and POZ/$AgNO_3$/$BMIM^+NO_3^-$ and (b) the desorption curve (enlarged) for POZ/$AgNO_3$.

Table 2. Effects of the Ionic Liquids $BMIM^+NO_3^-$ and $BMIM^+BF_4^-$ on the Mixed Gas Permeances and Propylene/Propane Selectivities of 1:1 POZ/$AgNO_3$ Membranes

membranes	total permeance (GPU)	selectivity
POZ/$AgNO_3$	0.1	0.95
POZ/$BMIM^+NO_3^-$	0.5	0.98
POZ/$AgNO_3$/$BMIM^+NO_3^-$	5.6	32
POZ/$BMIM^+BF_4^-$	0.5	0.97
POZ/$AgNO_3$/$BMIM^+BF_4^-$	5.4	32

kinetics. Desorption kinetics is known to be critically important in determining facilitated olefin transport and consequently the selectivity of membrane applications.[8] Thus, it would be interesting to test the POZ/$AgNO_3$/$BMIM^+NO_3^-$ complexes in the separation of olefins such as propylene and ethylene from their mixtures with paraffins. Note that POZ/$AgNO_3$/$NaNO_3$ does not absorb any appreciable amount of propylene ($w_{gas}/w_{complex}$ is only 0.007), indicating that the presence of $NaNO_3$ does not make $AgNO_3$ active in olefin complexation.

Performance in Separation of Propylene/Propane Mixtures. To confirm the enhancement of the silver activity of $AgNO_3$ in the POZ/$AgNO_3$/$BMIM^+NO_3^-$ and POZ/$AgNO_3$/$BMIM^+BF_4^-$ complexes, the performances of these membranes in the separation of propylene/propane mixtures were evaluated and are summarized in Table 2. The selectivity of propylene over propane, defined as the propylene concentration ratio of the permeate to the feed, was about 0.95 for the POZ/$AgNO_3$ electrolyte without $BMIM^+NO_3^-$ with a permeance of about 0.1 GPU, where 1 GPU $= 1 \times 10^{-6}$ cm^3 (STP)/(cm^2 s cmHg). The POZ/$BMIM^+NO_3^-$ and POZ/$BMIM^+BF_4^-$ membranes exhibited practically no separation in the absence of $AgNO_3$ (their selectivity is close to unity), although olefin gases are known to be soluble in ionic liquids to some extent.[9] However, the addition of small amounts of the ionic liquids $BMIM^+NO_3^-$ or $BMIM^+BF_4^-$ significantly improves the separation performance; the selectivities of the POZ/$AgNO_3$/$BMIM^+NO_3^-$ and POZ/$AgNO_3$/$BMIM^+BF_4^-$ membranes were found to be 32 and 32, respectively, with mixed gas permeances of 5.6 and 5.4 GPU, respectively. The improved separation performance is due to the facilitated olefin transport that results from the enhanced carrier activity of Ag^+ in the complexes upon incorporation of the ionic liquids. In contrast, the POZ/$AgNO_3$/$NaNO_3$ complex exhibited no separation.

The stabilities of the long-term separation performances of the polymer/silver salt complex membranes were also tested. The POZ/$AgNO_3$/$BMIM^+NO_3^-$ membrane exhibited stable separation performance throughout continuous operation for 150 h, whereas the performance of the POZ/$AgNO_3$/$BMIM^+BF_4^-$ membrane was not stable. This is an important observation, which suggests that there is a strong dependence of the stability of the silver ion on the nature of its counteranion.

Conclusions

The introduction of the ionic liquids $BMIM^+NO_3^-$ and $BMIM^+BF_4^-$ into POZ/$AgNO_3$ complex membranes increases the activity of Ag^+ in reversible complexation with olefins, whereas the introduction of $NaNO_3$ does not result in any such increase. The enhanced olefin complexation ability of Ag^+ is presumably due to the interaction between $BMIM^+$ and NO_3^-, which weakens the interaction between Ag^+ and NO_3^-, resulting in facilitated olefin transport. The occurrence of facilitated olefin transport as a result of the enhanced carrier activity of Ag^+ was also confirmed by observations of improvements in the separation of olefin/paraffin mixtures.

The POZ/$AgNO_3$ membrane exhibited no separation of olefin/paraffin mixtures, although it has the advantage that $AgNO_3$ is easily converted into silver nanoparticles. Controlling the interaction between Ag^+ and NO_3^- by the addition of ionic liquids makes Ag^+ more active in silver−olefin complexation, resulting in facilitated olefin transport. This is mostly due to the weakening of the interaction between Ag^+ and NO_3^- that results from the presence of the ionic liquid, as was confirmed by our theoretical ab initio calculations, and with XPS and Raman spectroscopy. The addition of the ionic liquids $BMIM^+NO_3^-$ or $BMIM^+BF_4^-$ significantly improves the separation performance of the POZ/$AgNO_3$ membranes; the selectivities of the POZ/$AgNO_3$/$BMIM^+NO_3^-$ and POZ/$AgNO_3$/$BMIM^+BF_4^-$ mem-

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branes were found to be 32.0 and 31.8, with mixed gas permeances of 5.6 and 5.4 GPU, respectively.

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