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POLYMERIC MEMBRANES CONTAINING SILVER SALTS FOR PROPYLENE/PROPANE SEPARATION

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Abstract - The separation of olefin/paraffin mixtures is one of the most important processes of the chemical industry. This separation is typically carried out by distillation, which is an energy and capital intensive process. One promising alternative is the use of facilitated transport membranes, which contain specific carrier agents in the polymer matrix that interact reversibly with the double bond in the olefin molecule, promoting the simultaneous increase of its permeability and selectivity. In this study, polyurethane (PU) membranes were prepared using two different silver salts (triflate and hexafluorantimonate). The membranes were structurally characterized and their performance for the separation of propylene/propane mixtures was evaluated. The results of the characterization analyses indicated that the triflate salt was the most efficient carrier agent. The membranes containing this salt showed the best performance, reaching an ideal selectivity of 10 and propylene permeability of 188 Barrer.

Keywords: Gas separation; Propylene facilitated transport; Silver ions; Polyurethane.

INTRODUCTION

In the petrochemical industry, propylene is an important industrial feedstock, being used as a raw material for products such as polypropylene, acrylonitrile, propylene oxide among others. The separation of propylene/propane mixtures is highly energy and capital intensive and is typically carried out by distillation (Humphrey and Seibert, 1992; Eldridge, 1993). As propylene and propane have similar molecular sizes and relative volatilities, distillation columns with more than 200 plates and high reflux ratios are needed to achieve efficient separation.

The use of membrane separation as an alternative approach for propylene/propane separation has been investigated and reported in recent years (Ferraz *et al.*, 2007; Burns and Koros, 2003; Kang *et al.*, 2004; Liu *et al.*, 2004). Due to the similar physical and chemical properties and molecular size of propane and propylene, conventional polymeric membranes are not competitive for the separation of these mixtures based only on the sorption/diffusion mechanism. One alternative that has been sought is a simultaneous increase of permeability and selectivity by incorporating specific agents in the polymer matrix that interact reversibly with propylene but not with propane. In this way, propylene permeation would occur by a facilitated transport mechanism.

Transition metal cations are used as carriers for propylene transport due to their capacity to react specifically and reversibly with unsaturated hydrocarbons. The interaction between the double bond of the olefin and the transition metal cations follows the model of π-complexation and is based on molecular orbital theory. The complexation reaction involves forming a sigma-type donation bond from the filled π-orbitals of the olefin to the empty s-orbital of the metal, followed by a π back-donation bond from the filled d-orbitals of the metal to the empty π^*-orbital of the olefin. The stability of the olefin-metal complex depends on electronic and

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*To whom correspondence should be addressed steric factors, such as the metal valence and the presence of electron-withdrawing groups on the olefin carbons (Cotton *et al.*, 1995). The bond strength between the cations and the olefin must be weak enough to allow release and transportation of the olefin towards the permeate side.

The facilitated transport membranes for propylene/propane separation are mainly achieved with silver and copper ions as carrier agents. This is because the complexes that silver and copper ions form with olefins have lower stability in comparison with the complexes formed with other transition metals (Kim *et al.*, 2000; Ho *et al.*, 1998; Baker, 2002).

The carrier can be mobile or fixed. In the first case, the membrane is effectively a liquid in which the carrier is dissolved. The carrier-propylene complex is formed at the feed/membrane interface and then diffuses across the membrane to the permeate side, where the olefin is released from the membrane phase. The free carrier diffuses back to the feed/membrane interface, repeating the process. These membranes, however, present limitations because the loss of the carrier may occur either by evaporation of the solvent or by washing out of the support membrane under an applied feed pressure (Kim *et al.*, 2005).

In the fixed-site carrier membranes, the carrier is chemically or physically bound to the polymer matrix, which restricts its mobility. According to Cussler *et al.* (1989), the transport mechanism is based on jumps or "hops" of the olefin from one fixed carrier to the other. If the interaction strength between the cation and the anion or the electron donor groups of the polymer is very high, the metallic cation will not be readily available to interact with the olefin. In addition, the polymer is required to have low barriers to bond rotation to provide sufficient segmental motion of the chains, which is better achieved by using an elastomeric polymer (Yoon *et al.*, 2000; Kim *et al.*, 2004; Duarte *et al.*, 2005).

The objectives of this study are to investigate the effects of adding silver salts to PU membranes and to evaluate their performance for the separation of propylene/propane mixtures. PU was chosen as the polymer matrix not only due to its high segmental mobility, but also because it contains functional groups that can coordinate with silver ions. Two different kinds of silver salts - silver triflate ($AgCF_3SO_3$) and silver hexafluorantimonate ($AgSbF_6$) - were selected as carrier agents. The membranes were produced with 20% (w/w) of the silver salt and further characterized by FT-IR spectroscopy and X-ray diffraction.

Conductivity experiments under argon were carried out to evaluate the strength of the interactions between the ions and the PU chains, whilst conductivity experiments under propylene were used for the characterization of the interactions between the ions, the PU chains and the propylene molecules. The interaction between the propylene molecules and the silver ions was characterized by TD analysis. Permeation tests with pure gas (propane and propylene) were performed at room temperature to evaluate the permeability and selectivity of the facilitated transport membranes.

EXPERIMENTAL

Materials

Polyurethane was purchased from BASF and used as received. Silver triflate, silver hexafluorantimonate and tetrahydrofuran (THF) solvent (synthesis grade) were purchased from Aldrich Chemical Co. and used without purification. The propylene and propane gases (>99.5% purity) were acquired from Linde and used as received.

Membrane Preparation

To prepare dense films, the polymer was previously dried in an oven at 60ºC for 24 hours and then dissolved in THF solvent. The silver salt was then added to the polymer solution, which was further stirred for approximately 5 h and then immediately cast over a flat Teflon$^{@}$ plate. This entire procedure was carried out within a dark chamber constantly purged with nitrogen, at room temperature, in order to prevent the silver ion photo-reduction. The solvent was allowed to evaporate for 48 hours and then dried in a vacuum oven for at least 8 hours before the permeation and characterization tests. The films presented a thickness of 200 μm and silver salt concentrations (v/v) of 14% ($AgCF_3SO_3$) and 8% ($AgSbF_6$).

Membrane Characterization

The dense silver salt-PU films were characterized by X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR) and Thermal Desorption (TD). These analyses were carried out in order to investigate the nature of the membrane structure and the propylene facilitated transport behavior.

X-Ray Diffraction Analysis

The crystalline structure of the PU membranes was determined by XRD using a Rigaku Miniflex diffractometer with monochromatic Cu Kα radiation with a wavelength of 1.54 Å.

Fourier Transform Infra Red Spectroscopic Analysis

A FTIR spectrophotometer (PerkinElmer Spectrum 100) with attenuated total reflection device was used to investigate the chemical structure of the polymeric films with and without silver ions. The spectra were recorded by taking 16 scans at a resolution of 4 cm^{-1}.

Thermal Desorption Analysis

Thermal desorption (TD) analysis was performed in a chemisorption equipment including a quartz glass tube to load the sample and a gas flow meter (Matheson 8274). The gases desorbed were monitored by a quadrupole mass spectrometer (QMS 200 - Prisma). In the TD experiments, 0.6 g of membrane was put into the quartz reactor and placed in an oven with controlled temperature. The sample was saturated with the gas, propane or propylene, at 25°C for thirty minutes. After gas exposure, the sample was purged with helium gas flow until equilibrium and the propane or propylene desorption experiments were run by increasing the temperature from 25°C to 60°C at a heating rate of 10°C/min under an atmosphere of helium. The isothermal level of 60°C was maintained until complete desorption of the gas, the evolution of the signal of the specific mass fragment being monitored by mass spectrometer.

Ionic Conductivity Measurements

Conductivity data were obtained using AC impedance measurements carried out with a Solatron 1255 frequency response analyzer and 1187 electrochemical interface. A polarizing potential of 20 mV was fixed and data were collected over the frequency range of 1 Hz – 400,000 Hz. The PU films were sandwiched between two stainless steel plates in a two-electrode cell which was located within an argon filled stainless steel chamber. The chamber was placed in a thermostatic bath in order to control the temperature of the cells. The conductivity values were estimated according to Bruce (1989).

Gas Permeation Test

The experimental set-up used for the gas permeation tests is illustrated in Figure 1. The experiments were performed with pure gases (propane and propylene) at room temperature.

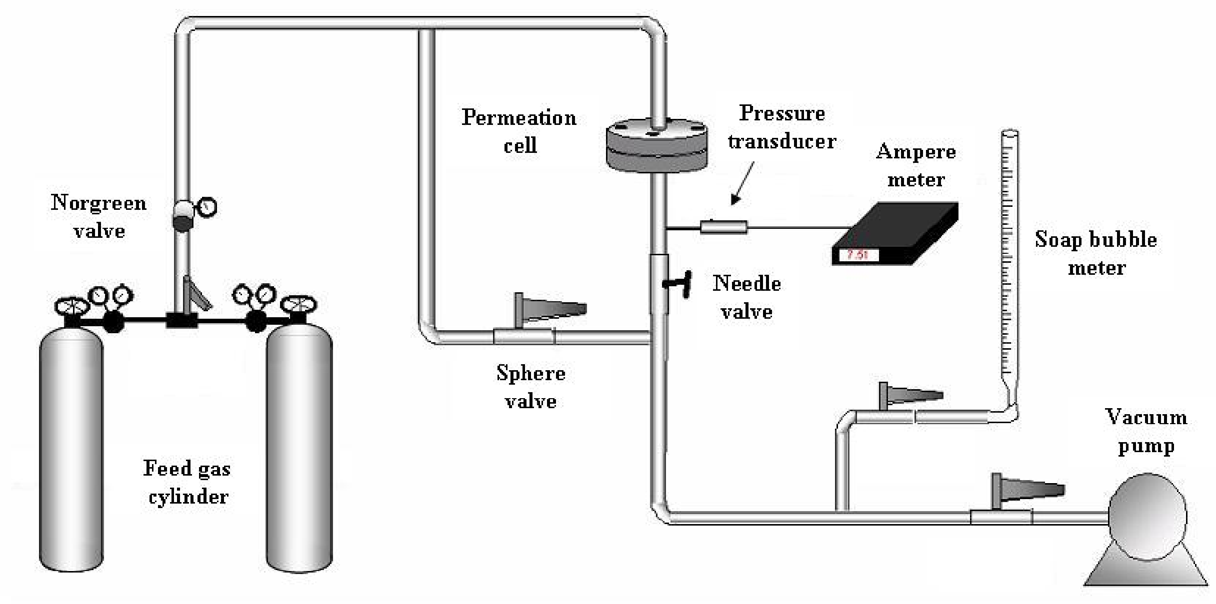

Figure 1: Schematic diagram of the equipment for the gas permeation tests.

The permeation cell was hermetically closed with Teflon@ o-rings and screws. In order to clean the permeation system, the permeate and feed lines were evacuated with a vacuum pump, then the feed gas was introduced at 2 bar in the membrane cell. Atmospheric pressure was maintained on the permeate side to establish a pressure difference of about 1 bar. This procedure was carried out for each gas (propane and propylene) separately. The gas permeance measurement was carried out by the acquisition of the signal of current density. A calibration curve allowed the conversion of the current density signal to pressure values. The pure gas permeance was estimated from the equation below:

$$\frac{P}{l} = \frac{dp}{dt}\left(\frac{Vs}{A \cdot \Delta p}\right)\left(\frac{T(STP)}{T(RT)p(STP)}\right) \quad (1)$$

where (P/l) is the membrane permeance expressed in Barrer (1 Barrer = $1\mathrm{x}10^{-10}$ cm^3(STP) cm/(cm^2 s cmHg); dp/dt is the pressure rate in the permeate (cmHg/s); Δp is the pressure difference across the membrane (cmHg); A is the effective membrane area (cm^2); p(STP) e T(STP) are the standard (STP) pressure and temperature, respectively; Vs is the volume of the permeation system (cm^3); T(RT) is the room temperature.

The membrane ideal selectivity, (α C_3H_6/C_3H_8), has been calculated in terms of ratio between the gas permeability coefficients of the pure gases according to the following equation:

$$\alpha_{C_3H_6/C_3H_8} = \frac{P_{C_3H_6}}{P_{C_3H_8}} \quad (2)$$

RESULTS AND DISCUSSION

X-Ray Diffraction

XRD results of PU and of the 20% (w/w) of PU/$AgCF_3SO_3$ and PU/$AgSbF_6$ membranes are presented in Figure 2. The PU spectrum (A) shows a rather broad band centered near a diffraction angle (2θ) of 20°, which is due to the hard segment of PU (Cho and So, 2006). This profile indicates that the polymer is completely amorphous. The spectra of PU containing 20% (w/w) of silver salt (B and C) are very similar to the XRD spectrum of the PU membrane without silver salt. This behavior suggests that both $AgCF_3SO_3$ and $AgSbF_6$ are well dispersed in the PU matrix at this concentration. The good dispersion of the silver salts may be attributed to the specific interaction originated from the coordination between electron donor groups in PU chains and silver ions, as reported in previous studies (Wen *et al*., 2001; Kim *et al*., 2002).

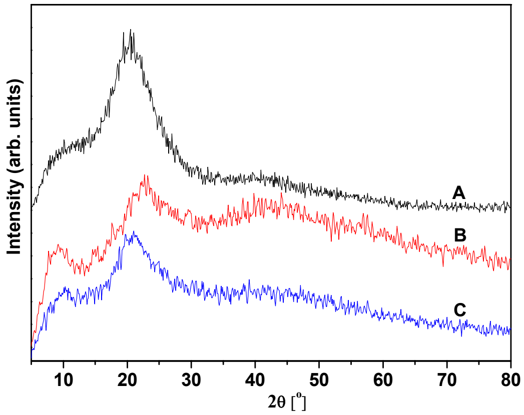

Figure 2: X-Ray diffraction spectra of a pure PU film (A), PU/$AgCF_3SO_3$ (20% w/w) (B) and PU/$AgSbF_6$ (20% w/w) (C).

Infrared Spectroscopy

FTIR spectra of the PU membranes and PU membranes containing 20% (w/w) $AgCF_3SO_3$ were analyzed to identify the changes in molecular interactions between the heteroatoms in the PU polymer and the Ag^+ ions. In the PU host matrix, the main regions of interest are: i) the N-H region, where the –NH absorption peak is observed at 3328 cm^{-1} due to the hydrogen bonded –NH in the urethane linkage; ii) the carbonyl region which is defined by two carbonyl stretching vibrations, the non hydrogen-bonded C=O (1726 cm^{-1}), and the hydrogen-bonded C=O (1700 cm^{-1}); iii) and the ester C(O)–O stretching (1166 cm^{-1}), as reported by Ferry *et al*. (1996). The carbonyl peaks around 1700 cm^{-1} are unresolved due to the superposition of peaks from urethanes and ester-polyols (Dan *et al*., 2006). The solvation of the salt in polyurethanes involves coordination of the cation to the electron donor groups of the polymer network, promoting changes in the stretching vibrations. Figure 3 shows the FTIR spectra of PU and PU containing silver triflate. Three regions were specifically investigated: the symmetric stretching mode of the triflate anion (1025 and

634 cm^{-1}), the hydrogen-bonded NH band (3328 cm^{-1}), and the ester C(O)–O stretch (1166 cm^{-1}), as shown in Figures 4, 5 and 6, respectively (Suthanthiraraj *et al*., 2009).

The triflate anion shows a vibrational spectrum with a frequency at ~1025 and 634 cm^{-1}, which is very sensitive to its state of coordination, and the changes in SO_3 stretching are associated with ion–ion interactions. The ion pairs (Ag^+ - $CF_3SO_3^-$) exhibit vibrational frequencies at ~ 1038 and ~ 833 cm^{-1}, which is not observed in the PU/ $AgCF_3SO_3$ spectrum illustrated in Figure 4. It is possible therefore to confirm that the silver salt is well dissociated by the polymer and that the triflate anions are free (Dan *et al*., 2006). This corroborates the observations previously made for the XRD results.

In Figure 5, the band position of hydrogen bonded -NH shows slight shift from 3328 cm^{-1} for PU to 3323 cm^{-1} for PU/ $AgCF_3SO_3$. This feature, a band shift to lower wavenumbers, is due to the coordination of silver ion with the hydrogen bonded –NH group. The hydrogen of the NH group can be bound with oxygen of the carbonyl group or the ester group of the polymer matrix. A close examination also suggests changes in the ester oxygen, which showed a slight shift from 1166 cm^{-1} for PU to 1160 cm^{-1} for PU/ $AgCF_3SO_3$, as shown in Figure 6.

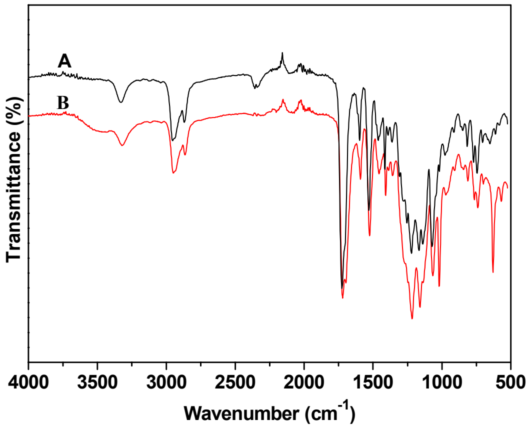

Figure 3: FTIR spectra of PU film (A) and PU/$AgCF_3SO_3$ (20% w/w) (B).

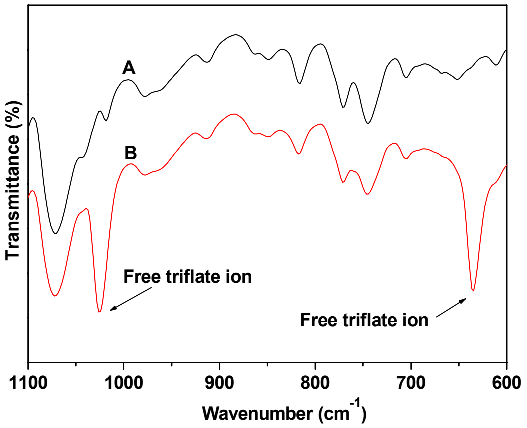

Figure 4: FTIR spectra of PU film (A) and PU/ $AgCF_3SO_3$ (20% w/w) (B) in the SO_3^{-1} symmetric stretching region.

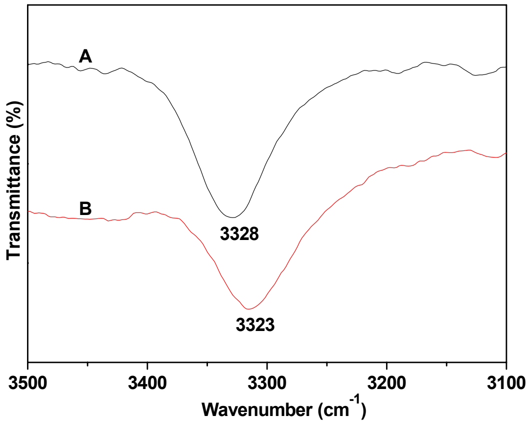

Figure 5: FTIR spectra of PU film (A) and PU/ $AgCF_3SO_3$ (20% w/w) (B) in the hydrogen-bonded NH region.

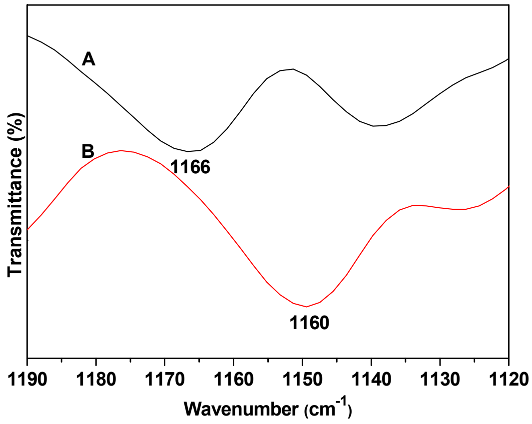

Figure 6: FTIR spectra of PU film (A) and PU/ $AgCF_3SO_3$ (20% w/w) (B) in the ester region.

Thermal Desorption

TD analyses were undertaken for PU membranes containing 20% (w/w) $AgCF_3SO_3$ and $AgSbF_6$ to investigate the silver ion influence on the sorption of propylene. The propane TD did not show any desorption profile. The effect of the interaction between silver ions and propylene in the PU membranes is presented in Figure 7. Pure PU (C profile) exhibits no propylene desorption in the time period analyzed. In the presence of silver ions (A and B profiles), propylene desorption started at 60°C, approximately. These results are clear indications of the π-complexation of silver ion with the propylene molecule and the potential ability of these PU/Ag systems to be used as facilitated transport membranes for olefin/paraffin separation.

The TD characterization allows the determination of the amount of propylene that was complexed with the silver active sites in the polymer and the comparison of different ions, counter-ions and polymers. The results show that both silver salts were efficient in the coordination with propylene, with very close estimated ratios $molC_3H_6/molAg$, of the order of 0.2. This quantitative approach seems to be quite new and indicates that TD is a promising and versatile technique.

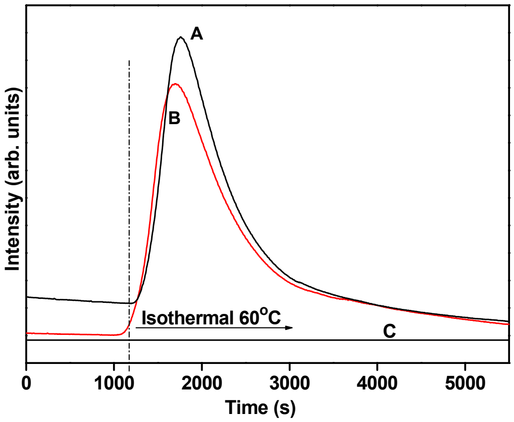

Figure 7: Temperature-programmed desorption profiles of pure PU film (C), PU/$AgCF_3SO_3$ (20% w/w) (A) and PU/$AgSbF_6$ (20% w/w) (B).

Ionic Conductivity Analysis

Figure 8 presents the concentration dependence of the ionic conductivity measured in propylene and argon atmospheres for the membranes containing $AgCF_3SO_3$. As can be observed, the ionic conductivity in propylene is higher than the values obtained for experiments carried out in argon, and increases with salt concentration (Duarte *et al.*, 2005). These results support the evidence that, in the presence of propylene, Ag^+ cations gain higher mobility than in the presence of argon. This can be attributed to the complexation between propylene molecules and Ag^+, which weakens the Ag^+-PU interactions.

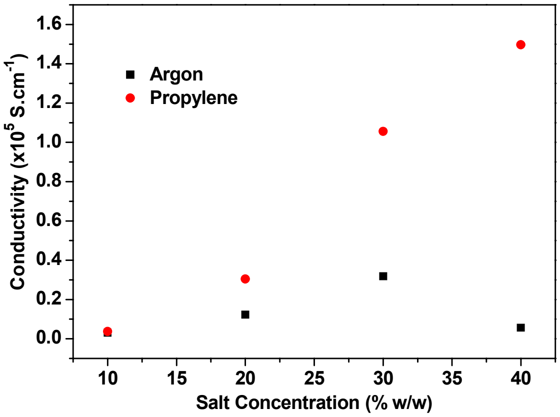

Figure 8: Ionic conductivity in propylene and argon atmospheres for the membranes containing $AgCF_3SO_3$.

Furthermore, under a propylene atmosphere, the PU membranes containing $AgCF_3SO_3$ show higher conductivity values than the ones with $AgSbF_6$, as can be seen in Figure 9. This is likely related to the larger size of the triflate anion, which is able to dissociate more easily from Ag^+ cations than SbF_6^-. Therefore, $AgCF_3SO_3$ is probably more suitable to be used as a carrier in membranes for propylene/ propane separation than $AgSbF_6$.

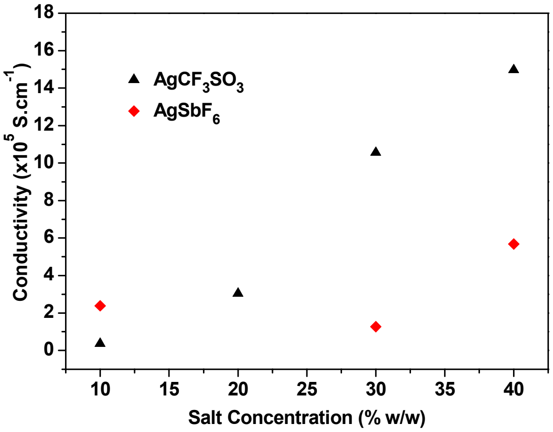

Figure 9: Ionic conductivity under a propylene atmosphere for the membranes containing $AgCF_3SO_3$ and $AgSbF_6$.

Permeation Tests

The gas permeance measurements were undertaken at a feed pressure and temperature of 2 bar and 25°C, respectively. The results of these experiments are summarized in Table 1, where it can be observed that the presence of the silver salt in PU membranes promotes an increase in the ideal selectivity. The PU/ $AgCF_3SO_3$ membrane exhibits both propylene permeability and selectivity higher than the PU/ $AgSbF_6$ membrane. This is likely to be associated with the size of the counter-ion and is in line with the results obtained in the conductivity experiments. In fact, $(CF_3SO_3)^-$ is a larger anion than $(SbF_6)^-$, and $AgCF_3SO_3$ exhibits a lower lattice energy, which leads to a weak interaction between silver ion and its counter-ion and facilitates the solvation of silver in the polymer. In this way, the silver ions in the PU/$AgCF_3SO_3$ membranes are more available for interaction with the propylene molecules than the silver ions in the PU/$AgSbF_6$ membranes.

Table 1: Gas permeance and separation factor of propylene and propane through PU membranes.

Membrane	Gas Permeance (Barrer)		$\alpha_{C3H6/C3H8}$
	Propylene	Propane	
Pure PU	191.5	91.6	2.1
PU/$AgCF_3SO_3$ (20 % w/w)	188.1	18.0	10.4
PU/$AgSbF_6$ (20 % w/w)	50.1	7.7	6.5

CONCLUSIONS

Silver salts are well solvated by the PU matrix in the PU/ $AgCF_3SO_3$ and PU/ $AgSbF_6$ membranes, since no crystalline structure peaks are observed in the related XRD spectra. The FTIR results showed that the coordination of silver ions occurs with the ester oxygen of the polyurethane, verified through the wavenumber shifts of hydrogen bonded –NH and ester oxygen regions. Another evidence of complete solvation of the silver salt in the polymeric matrix was the presence of the free triflate ion bands and the non-occurrence of ion pair bands in the FTIR spectrum of PU/$AgCF_3SO_3$.

The TD characterization method was successfully used to validate the complexation between silver ions and propylene molecules. Ionic conductivity and permeance tests showed that the triflate salt is the most efficient carrier agent for facilitated propylene transport, as the larger anion size leaves the silver ion more available for complexation with propylene. The PU membranes containing the silver triflate salt showed the best performance for the separation of propylene/propane mixtures, reaching an ideal selectivity of 10 and propylene permeability of 188 Barrer.

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