New Insights into the Coordination Mode of Silver Ions Dissolved in Poly(2-ethyl-2-oxazoline) and Its Relation to Facilitated Olefin Transport[†]

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ABSTRACT: The coordination behavior of silver ions dissolved in a polymer solvent is investigated to elucidate the facilitated transport phenomena in solid-state membranes. Silver polymer electrolyte membranes were prepared by dissolving $AgCF_3SO_3$ in poly(2-ethyl-2-oxazoline) (POZ) or poly(*N*-vinylpyrrolidone) (PVP). The permeance and solubility of propylene in the silver polymer electrolyte increased slowly with silver ion concentration up to the silver mole fraction of 0.25 ([C═O]:[Ag] = 3:1), after which the permeance and solubility of propylene abruptly increased. Other properties such as the Bragg *d* spacing, glass transition temperature (T_g), and propane permeance also showed marked changes at a silver mole fraction of 0.25. The existence of this threshold concentration is attributed to the following observations: (1) the most favorable coordination number for silver ions in polymer electrolytes under a propylene environment is 3, and (2) the coordination bond strength between silver ion and carbonyl oxygen is marginally stronger than that between silver ion and olefin molecule. As a result, it is proposed that silver ions can act as olefin carriers only when they have vacant coordination sites, i.e., only when the coordination number of silver ion for carbonyl oxygens is less than 3. Therefore, the silver ion coordination number is shown to have a strong bearing both on the activity of the silver ion as an olefin carrier and on the structure of polymer electrolytes.

Introduction

Polymer electrolytes comprise metal salts of low lattice energy dissolved in a polymer matrix containing polar moieties such as ether, carbonyl, or amide. Metal salts can dissolve into such polymer matrixes by virtue of the coordinative interaction between the metal ion and the polar groups. The conductive properties of polymer electrolytes have led them to be intensively studied for potential applications in lithium polymer batteries and electrochromic devices.[1−5] Recently, polymer electrolyte membranes containing silver salts *in the solid state* were shown to have properties that make them potentially very useful for separating olefin/paraffin mixtures.[6−12] For example, the dissolution of $AgBF_4$ into poly(2-ethyl-2-oxazoline) (POZ) or $AgCF_3SO_3$ into poly(*N*-vinylpyrrolidone) (PVP) produced polymeric materials with propylene permeances almost 900-fold greater than those of the corresponding pure polymer matrixes, whereas the permeance of propane through POZ and PVP decreased on addition of the silver salt. Thus, dissolution of silver salt into POZ and PVP results in membranes with extremely high selectivity of propylene over propane (more than 10 000).[8] Membrane processes utilizing facilitated transport in the solid state to separate olefin/paraffin mixtures may therefore offer an intriguing alternative to the energy-intensive method of cryogenic distillation.[13−15]

The dissolution of silver salts into a polymer matrix is stabilized by the coordinative interaction between the silver ions and the polar groups of the matrix. In an olefin environment, the silver ions also coordinatively interact with olefin molecules. The coordination behavior of silver ions may therefore play an important role in determining the structure and carrier activity of polymer electrolyte membranes, properties which in turn dictate the facilitated transport phenomena. The basis of facilitated transport in the *solid state* is the concentration fluctuation arisen from the reversible interaction of olefins with silver ions dissolved in a polymer matrix to make silver cation−olefin complexes.[16]

In the present study, the effect of $AgCF_3SO_3$ incorporation on the structural properties of polymer electrolytes was characterized by monitoring the Bragg *d* spacing, glass transition temperature (T_g), and propane permeance. The propane permeance is of particular interest because propane does not interact with silver ions, and its transport properties are very sensitive to the structure of the polymer electrolyte. In addition, the solubility of propylene in the polymer electrolytes, along with its permeance through polymer electrolyte membranes, was investigated to elucidate the coordinative interaction between the silver ions and propylene molecules, thereby clarifying the role of this interaction in facilitated olefin transport. The results of these experiments give the most probable coordination number of silver ions dissolved in a polymer matrix under an olefin environment. In light of these results, the activity of silver as an olefin carrier is evaluated with the support of theoretical calculations.

[†] This is dedicated to respectable Professor Jung-Il Jin of Korea University on the occasion of his 60th birthday.

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Experimental Section

Sample Preparation. Poly(2-ethyl-2-oxazoline) (POZ) (M_w = 5×10^5) and silver trifluoromethanesulfonate (silver triflate, $AgCF_3SO_3$) were purchased from Aldrich Chemical Co. and poly(*N*-vinylpyrrolidone) (PVP) (M_w = 1×10^6) from Polysciences. All chemicals were used as received. The silver salts were dissolved in 20 wt % polymer solution in methanol; the amount of added salt was chosen so as to achieve the desired mole ratio of [C=O]:[Ag]. The solution was then cast on a Teflon glass plate and dried under nitrogen. The resulting films were further dried in a vacuum oven for 2 days at room temperature to remove residual solvent.

Gas Permeance. Gas permeation experiments were carried out using a constant pressure/variable volume method. In cases characterized by very low gas permeance, such as that of propane, a constant volume/time lag method was also employed. For the gas permeation test, the polymer solution was coated onto a microporous polysulfone substrate (Seahan Industries Inc., Seoul, Korea) using an RK Control Coater. After evaporation of the solvent in a convection oven at room temperature under nitrogen, the membrane was dried completely in a vacuum oven for 2 days at room temperature. The thickness of the top polymer electrolyte layer was ca. 1 μm, and the pressure difference was 413.5 kPa. The unit of gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg).

Propylene Solubility. The solubility of propylene in the solid polymer electrolyte was measured using a barometric (pressure-decay) sorption apparatus. The system temperature was controlled to 25 ± 0.1 °C using a heating element. Initially, the polymer electrolyte film was placed in a sample chamber, which was then evacuated for more than 12 h. After evacuation, propylene gas was introduced into the chamber and allowed to equilibrate. The difference between the initial pressure and the pressure after equilibration was measured; the gas solubility at a given pressure was calculated from this pressure difference. When the chamber pressure reached a constant value, additional propylene gas was introduced, and the measurement process was repeated. In this way the propylene solubility was obtained as a function of propylene pressure.

Calculations

The electronic energy (i.e., dissociation enthalpy) was calculated by full optimization, without any geometrical constraint, of Becke's three-parameter hybrid functional[17] using the Lee, Yang, and Parr correlation functional[18] with the 6-31+G(d) basis set,[19] except for the transition metal element, Ag, which was modeled using effective core potential (ECP) basis sets of type LANL2DZ.[20] 6D-Cartesian functions were used for the d-orbitals to obtain more accurate energies. The nature of all stationary species was verified by the vibrational frequencies.[21] The program package Gaussian 98 was used throughout the work.[22]

Results and Discussion

Structure of the Silver Polymer Electrolytes. Bragg *d* Spacing. The wide-angle X-ray scattering spectra of pure POZ and POZ:silver salt complexes exhibit two peaks.[23-25] These peaks, which correspond to spacings of approximately 9.5 and 4.9 Å (calculated using the Bragg equation), have been assigned to the interchain distance and the distance between the pendant groups in POZ, respectively.[25] Figure 1 shows the Bragg *d* spacings for these two peaks as a function of the mole fraction of silver, i.e., [Ag]/([C=O] + [Ag]). The Bragg *d* spacings corresponding to both peaks decrease with increasing silver mole fraction of 0.25 ([C=O]:[Ag] = 3:1), which may result from the formation of transient cross-links between polymer chains due to coordinative interactions between the silver cations and the carbonyl oxygens of POZ. Interestingly, when the silver concentration was raised to higher than the silver mole fraction of 0.25, the interchain distance calculated from the first peak increased whereas the *d* spacing from the second peak showed only a gradual decrease. This increase of the interchain distance at high silver concentrations may be due to electrostatic repulsion between the large free anions pushing the polymer chains apart,[26,27] which is spectroscopically free anions as evidenced by IR or Raman spectroscopy.[1-5] The results therefore lead to an overall picture in which the interchain distance decreases at silver concentrations lower than the silver mole fraction of 0.25 due to the formation of transient cross-links involving the silver cations, whereas above 0.25 the interchain distance increases due to the "pushing-apart" effect of the free anions. This strongly suggests that silver polymer electrolytes undergo a significant structural change at around [C=O]:[Ag] = 3:1.

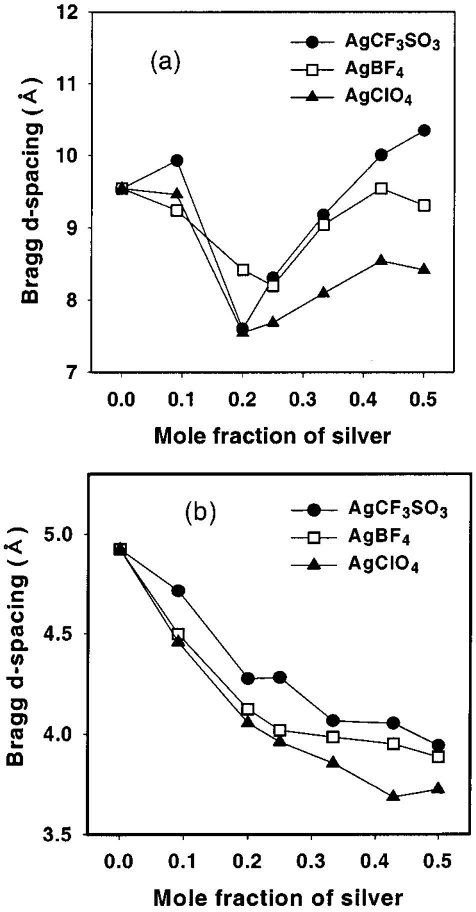


Figure 1. Bragg *d* spacings calculated from the positions of both peaks in POZ:Ag salt complexes with various silver concentration: (a) first peak, (b) second peak.[25]

Glass Transition Temperature. The glass transition temperatures (T_g) for pure POZ and POZ:Ag salt complexes are presented in Figure 2 as a function of the silver salt concentration.[25] The symbols and solid lines in this figure represent the experimental data and theoretical curves calculated from the configurational entropy,[28] respectively. The value of T_g initially increases with increasing silver concentration before reaching a broad maximum at the silver mole fraction of 0.25, after which it decreases slightly. The increase in T_g at lower silver concentrations is due to the

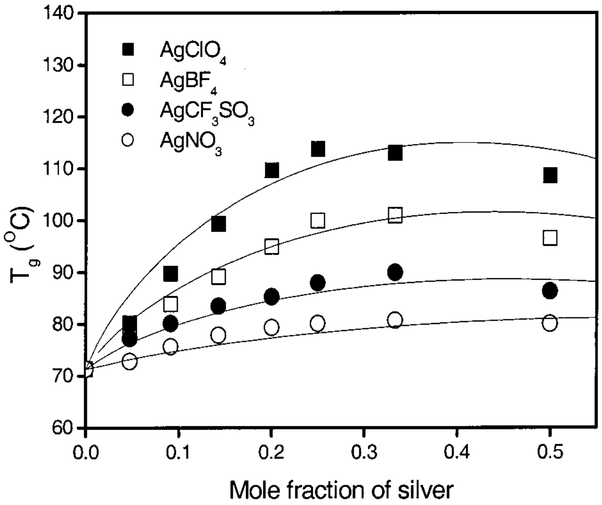


Figure 2. Glass transition temperatures of pure POZ and POZ:Ag salt complexes as a function of silver concentration.[25] The solid lines are calculated curves from theoretical T_g equation.[28]

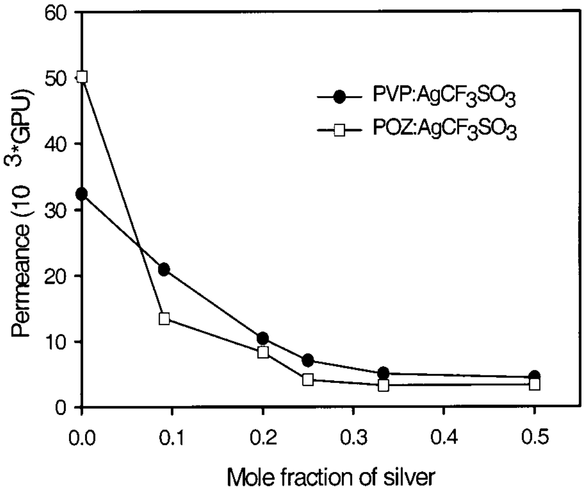


Figure 3. Permeances of propane through polymer electrolyte membranes containing $AgCF_3SO_3$ as a function of silver concentration.

restriction of the chain mobility caused by transient cross-links involving the cations and/or by dangling heavy ions onto polymeric chains. On the other hand, the decrease in T_g at the silver mole fraction of 0.25 may result from the increase in interchain distance over this range of silver concentration. As a result, the T_g values for the POZ:Ag salt complexes initially increase with the salt concentration but reach a maximum at around [C═O]:[Ag] = 3:1.

Propane Permeance. Paraffins such as propane do not have any specific interaction with silver ions and thus permeate only via Fickian transport. The permeance behavior of propane is therefore strongly associated with the structure of the polymer electrolyte through which it passes. Figure 3 shows the propane permeance through pure POZ and PVP and their complexes with $AgCF_3SO_3$ at 25 °C. The propane permeances of the POZ and PVP systems decrease rapidly up to the silver mole fraction of 0.25, after which they decrease very slowly before reaching an almost constant value.

The coordination of silver ions to the carbonyl oxygens of PVP or POZ causes the polymer chains to become more rigid owing to transient cross-links between chains, resulting in an increased packing density of polymer and a consequent reduction in the propane permeance. This effect dominates up to the silver mole fraction of 0.25. However, at silver concentrations higher than the silver mole fraction of 0.25, the "pushing-apart" effect due to the free anions compensates for the effects of silver ion coordination, leading to a gradual decrease in the propane permeance. The dependence of the propane permeance on silver ion concentration is consistent with the changes in structural properties (*d* spacings and glass transition temperatures) with increasing silver ion concentration, which indicates a structural change at around a ratio of 3:1. Thus, we conclude that the structure of the polymer electrolytes largely depends on the combination of the interaction of the silver ions with the carbonyl oxygens of POZ or PVP and the repulsion of the anions, which in turn affects the gas transport.

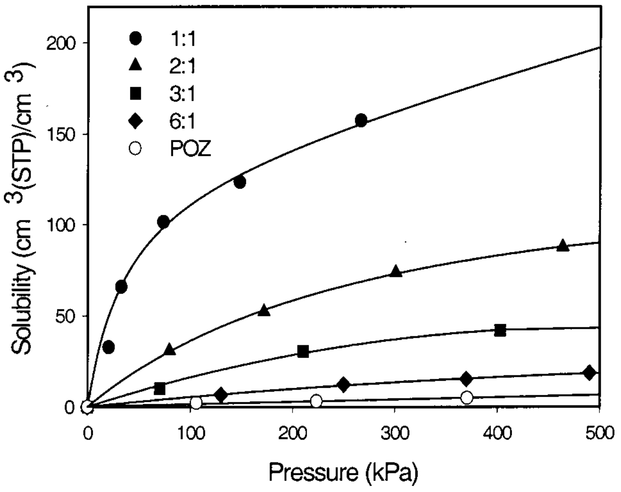


Figure 4. Solubility of propylene in pure POZ and POZ: $AgCF_3SO_3$ complexes against propylene pressure.

In summary, silver salts dissolve in solutions of PVP and POZ to create homogeneous solid solutions of polymer electrolytes due to the coordinative interaction between silver ions and the carbonyl oxygens on the polymer chains. The structure of the polymer electrolytes and consequently their gas transport properties depend on the concentration of the silver salt in the system. The *d* spacing, glass transition temperature, and propane permeance change distinctively at a threshold silver concentration ([C═O]:[Ag] = 3:1). Below the threshold concentration, the structure becomes more compact and rigid with increasing silver concentration, resulting in a lower propane permeance. Above the threshold, however, the changes of structure and properties become much less prominent, demonstrating the existence of the threshold concentration for structural change.

Olefin Coordination to Silver Ions. Propylene Solubility. The solubility of propylene in pure POZ and $POZ:AgCF_3SO_3$ electrolytes was measured against propylene pressure over a range of silver concentrations using the pressure decay method; the results are presented in Figure 4. The propylene solubility in pure glassy POZ increases linearly with propylene pressure, demonstrating that the hole-filling/or Langmuir mode is hardly apparent. Thus, the solubility of propylene in POZ can be readily described by a simple Henry's mode ($C = k_D P_0$). The curves of the propylene solubility in

Table 1. Parameters Used in Correlation of Propylene Solubility in POZ:AgCF$_3$SO$_3$ with Varying Mole Ratio of [C=O]:[Ag]

[C=O]:[Ag]	$k_D \times 10^5$ (cm^3(STP)/(cm^3 cmHg))	$K \times 10^3$ (1/cmHg)	$C_c' \times 10^3$ (mol/cm^3)
pure POZ	3.29		
6:1	3.34	1.79	1.88
3:1	3.35	2.89	3.75
2:1	3.54	5.44	5.24
1:1	13.35	17.32	8.15

silver polymer electrolytes become concave to the ordinate with increasing silver concentration, indicating the presence of the second mode sorption. The second mode sorption is evidently due to the interaction between silver ions and propylene molecules and can be described by a simple Langmuir model. Thus, the propylene solubility in silver polymer electrolytes was analyzed using the dual sorption model:[29,30]

$$C = k_D P_0 + \frac{C_c' K P_0}{1 + K P_0} \tag{1}$$

where C is the concentration of propylene in the membrane, P_0 is the applied propylene pressure, k_D is the solubility coefficient of propylene for Henry's law, K is the equilibrium constant, and C_c' is the saturated amount of propylene coordinated to the silver ions. The values of k_D, K, and C_c' estimated by nonlinear least-squares regression of the curves in Figure 4 are summarized in Table 1.

The value of k_D is constant for silver concentrations below 2:1, showing that the propylene solubility in POZ is not greatly affected by the silver concentration. However, the value of k_D increases substantially when the mole ratio is changed from 2:1 to 1:1, indicating an enormous enhancement of the propylene solubility in the POZ matrix. This change in solubility corresponds to a structural change of the polymer matrix caused by the coordination of propylene molecules to silver cations. Although the in-situ T_g of the POZ:silver salt complex containing dissolved propylene gas was not quantitatively determined, we visually observed that 1:1 POZ:AgCF$_3$SO$_3$ became rubbery in the environment of more than 1 atm propylene and room temperature, although its T_g is approximately 85 °C. As expected, the K value, which represents the amount of propylene coordinated to silver ions, gradually increases with silver concentration before increasing sharply at [C=O]:[Ag] = 1:1, thereby demonstrating the proportional relationship between K and silver concentration.

Figure 5 depicts the solubility of propylene in POZ:AgCF$_3$SO$_3$ electrolytes as a function of the mole fraction of silver at three pressures. The propylene solubility increases abruptly at the silver mole fraction of approximately 0.25, which corresponds to [C=O]:[Ag] = 3:1, irrespective of propylene pressure. The change in slope at around a ratio of 3:1 may be related to the activity of the silver ion for olefin complexation. In the next section this point will be discussed in terms of the coordination number of the silver ion in the polymer electrolytes under an olefin environment.

Facilitated Olefin Transport. Measurements of the propylene permeance through silver polymer electrolyte membranes below 0.5 mole fraction of silver have been recently reported for systems in which either AgBF$_4$ or AgCF$_3$SO$_3$ was dissolved in a POZ or PVP matrix.[7] Here, the permeances of propylene through polymer electrolyte membranes containing AgCF$_3$SO$_3$ are measured up to much higher concentrations of silver salts and plotted in Figure 6. The propylene permeances are extremely low up to a mole fraction of silver ions of approximately 0.25 ([C=O]:[Ag] = 3:1). However, at higher mole fractions the propylene permeances increase almost linearly with silver concentration. Concentration fluctuation theory predicts an almost linear relationship between the permeability through a facilitated transport membrane and the carrier concentration:[16]

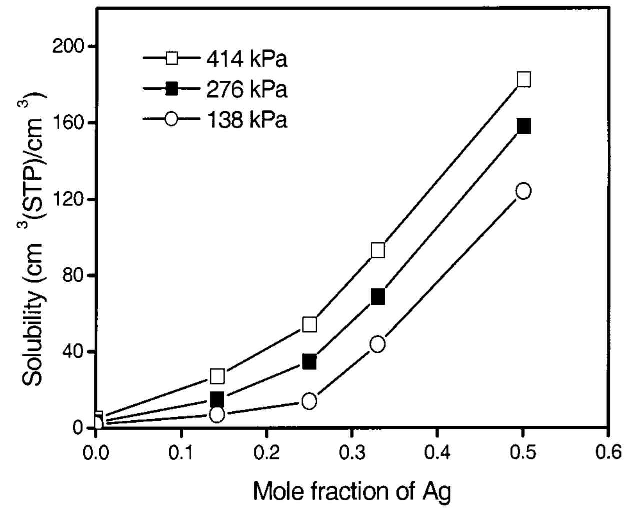


Figure 5. Solubility of propylene in pure POZ and POZ:AgCF$_3$SO$_3$ complexes against silver concentration.

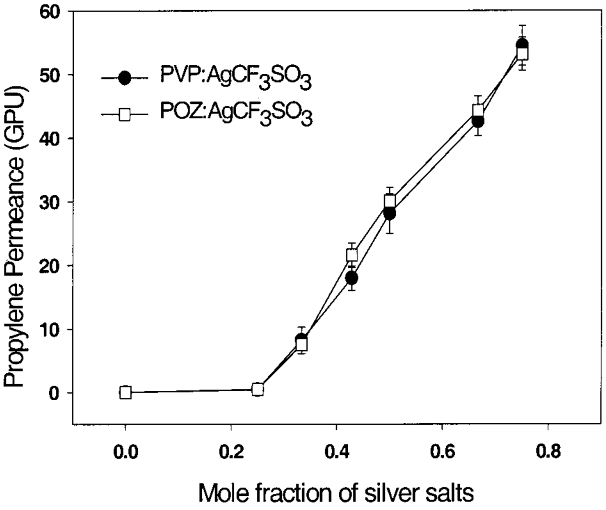


Figure 6. Permeances of propylene through polymer electrolyte membranes containing AgCF$_3$SO$_3$ as a function of silver concentration.

$$\frac{\overline{P_f}}{\bar{P}} = 1 + \left(\frac{p_d}{p_0}\right)\sqrt{n^2 + \left\{\frac{2\pi k_2 L^2 C_B^0}{\bar{P}} \frac{\ln(1 + Kp_0)}{p_0}\right\}^2}$$

where $\overline{P_f}$ and $\bar{P}$ are the permeabilities of the facilitated transport membrane and membrane matrix, respectively; p_0 and p_d are the applied pressure and pressure fluctuation due to the reversible reaction, respectively; $n = N_A C_B^0(\pi r_s^2 L)$, where L is the membrane thickness, r_s is the permeant radius, and C_B^0 is the carrier concentration; and k_2 and K are the backward reaction

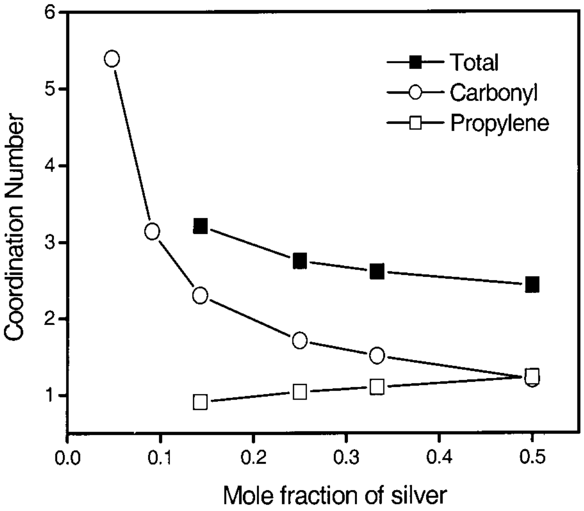


Figure 7. Coordination number of silver for carbonyl oxygen or propylene in POZ:$AgCF_3SO_3$ as a function of silver concentration.

Table 2. Dissociation Enthalpy (ΔH) at B3LYP[a] Level for POZ−Ag−X and C_2H_4−Ag−X at 298 K (kcal/mol)

X	to POZ + AgX	to C_2H_4 + AgX
BF_4	25.33	22.75
CF_3SO_3	24.71	21.71
ClO_4	25.11	22.35
NO_3	23.41	22.15

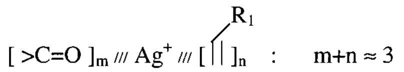
[a] Calculations were carried out using the general basis set method, i.e., 6-31+G(d) for the first- and second-row elements and the LANL2DZ basis set for Ag.

rate constant and the equilibrium constant of the solute−carrier reaction, respectively. Therefore, the linear dependence between the propylene permeance and the silver concentration evident in the experimental results is consistent with the concentration fluctuation theory. In addition, the occurrence of facilitated propylene transport only above silver mole fraction of 0.25 may be strongly associated with the chemical environment, i.e, the coordination behavior of the silver ion as an olefin carrier.

Coordination Behavior of Silver Ions. The results presented above show that the values of the *d* spacing and T_g of the polymer electrolyte, along with the permeance of propane and propylene through the polymer matrix, undergo a distinctive change at a threshold silver concentration ([C=O]:[Ag] = 3:1). Such changes in the structure and properties of silver polymer electrolytes are expected to be strongly associated with the coordination of the silver cations with both carbonyl oxygens and olefin molecules. The coordination of a silver cation depends strongly upon its environment. For example, X-ray absorption fine structure (XAFS) studies have demonstrated that silver ions in aqueous solution are coordinated to four water molecules, while those in gel-type membranes are coordinated to three oxygen atoms.[31]

In the case of silver polymer electrolytes in a propylene environment, the silver cations are coordinated to both carbonyl oxygens and olefin molecules. The coordination number of the silver ion for *carbonyl oxygens* can be obtained simply from the concentration ratio of complexed C=O to silver cation, which can be determined by IR and Raman spectroscopies.[10] The coordination number of the silver ion for *olefin molecules* is obtained by analyzing the dual sorption model for the propylene solubility. The concentration ratio of propylene molecules coordinating silver cations is represented by C_c' in eq 1. The coordination numbers of carbonyl oxygen and propylene in POZ:$AgCF_3SO_3$ are plotted against the mole fraction of silver cation in Figure 7.

The coordination number for *carbonyl oxygens* decreases exponentially whereas that for *propylene molecules* increases almost linearly. Surprisingly, the total coordination number maintains a value of around 3 for mole fractions of the silver cation ranging from 0.15 to 0.5. This result strongly suggests that the most favorable coordination number of silver ions dissolved in polymer matrix under a propylene environment is close to 3. However, the actual coordination number is expected to be slightly lower than 3 because the rather rigid polymeric chains limit the access of the propylene molecules to the silver ions.



$$[\,{>}C{=}O\,]_m \,///\, Ag^+ \,///\, [\,\|\,]_n \quad : \quad m+n \approx 3$$

In addition, ab initio calculations were carried out to compare the coordination bond strengths of silver−carbonyl oxygen and silver−olefin. Table 2 shows the dissociation enthalpy change (ΔH) in going from POZ−Ag−X or C_2H_4−Ag−X to POZ + AgX or C_2H_4 + AgX, respectively, in four complexes (X = BF_4, CF_3SO_3, ClO_4, NO_3). A high value of ΔH represents a strong interaction between silver ion and ligand. Thus, the interaction of a silver ion with the carbonyl oxygen of POZ is stronger than that with olefin molecules, irrespective of the counteranion. However, this difference is insufficient to induce the complete replacement of the coordinated oxygen atoms with propylene molecules, as has been shown by IR spectroscopy.[32] In a propylene environment, silver cations are coordinated to both carbonyl oxygens and propylene molecules when the coordination of the silver cation to carbonyl oxygens is less than 3.

The results presented above can be used to evaluate the relationship between facilitated olefin transport and the most probable coordination number of the silver ions. When the coordination number for carbonyl oxygens is higher than 3, the coordination sites of the silver ions are already occupied by more than 3 carbonyl oxygens even before the introduction of the olefin gas. Moreover, the interaction of silver ion with carbonyl oxygen is stronger than that with olefin. Thus, silver ions do not readily interact with the surrounding olefin molecules, implying that the silver ion does not act as an olefin carrier. When the coordination number for carbonyl oxygens is less than 3, the coordination sites of the silver ion are not completely occupied, and vacant sites are available for olefin coordination. Therefore, silver ions can act as olefin carriers only when they have vacant coordination sites, that is to say, when the coordination number of the silver ion for carbonyl oxygens is less than 3.

$$[{\rangle}C{=}O]_m \;///\; Ag^+ \begin{cases} \text{when } m < 3\text{; active carrier} \\ \text{when } m \geq 3\text{: inactive} \end{cases}$$

Therefore, it is concluded that the coordination behavior of silver ions within silver polymer electrolytes is an important determinant of the structure of the polymer electrolyte as well as the activity of silver ions as olefin carriers.

Conclusions

The structure and various physicochemical properties of silver polymer electrolytes were found to change abruptly at a threshold silver mole fraction of 0.25 ($[C{=}O]:[Ag] = 3:1$). It is proposed that transient cross-linking caused by coordinative interactions between silver cations and carbonyl oxygens dominates at silver concentrations below this threshold, whereas the "pushing-apart" effect due to the free anions dominates above the threshold. Furthermore, the propylene solubility and facilitated propylene transport in the silver polymer electrolytes began to significantly increase when the silver concentration was increased above the silver mole fraction of 0.25. Such changes in the structure and physicochemical properties of polymer electrolytes are strongly associated with the coordination behavior of the silver cations. The most favorable coordination number of the silver cations dissolved in polymer electrolytes under a propylene environment was found to be 3. Therefore, silver cations are active as olefin carriers for facilitated transport only when the coordination number for *carbonyl oxygens* is less than 3, whereas they are inactive when the coordination number is greater than 3. The present study therefore provides clear evidence that the coordination behavior of silver cations plays a very important role in determining the structure and physicochemical properties of polymer electrolytes as well as the activity of silver ions as olefin carriers.

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