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Enhancement of facilitated olefin transport by amino acid in silver–polymer complex membranes

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Silver ions dissolved in a polymer matrix are additionally coordinated by carbonyl oxygens of asparagines and their counter anions interact with cationic sites, resulting in the enhanced activity of the silver ion as an olefin carrier for facilitated olefin transport.

Olefin/paraffin separation, one of the most important processes in the petrochemical industry, has typically been performed by highly energy-intensive distillation.[1] Among various alternative energy saving separation processes,[2] the facilitated transport membranes based upon silver polymer electrolytes have attracted significant interest because of the remarkable separation performance for olefin/paraffin in the solid state.[3–5] For example, when silver salts such as $AgBF_4$ or $AgCF_3SO_3$ are dissolved in polymer matrices such as poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (POZ) or poly(*N*-vinyl pyrrolidone) (PVP), the silver ions are active as olefin carriers, resulting in facilitated olefin transport through the membranes.

To enhance the separation performance and the membrane stability for gaseous mixtures, the introduction of a third component has been commonly employed.[6] The idea of using amino acids stems from the fact that they are quite reactive with chemical substances involving metal ions such as silver ions.[7] In particular, asparagines containing $-NH_3^+$, $-C{=}O$ and $-COOH$ in acidic conditions are expected to interact with silver ions as well as counter anions of the salt.

The complex formation of silver ions with an olefin molecule is known to be quite sensitive to the type of silver salt, *i.e.* its counter anion.[8] Large, low electronegativity anions such as BF_4^-, $CF_3SO_3^-$ and ClO_4^- form silver salts with low lattice energy and act as effective olefin carriers when dissolved in polymer matrices.[8a] In contrast, small and highly electronegative anions such as F^-, Cl^- and NO_3^- form salts with high lattice energy and hinder complexation of the silver ion with an olefin molecule.[8a] It is furthermore found that silver–polymer complex membranes with strong silver ion–polymer and weak silver ion–anion interactions exhibit more favorable silver ion complexation with olefins, resulting in higher olefin solubility and improved permeation.[8b]

Asparagine contains $-NH_3^+$ cations because the silver polymer electrolyte solutions, *e.g.* POZ/$AgBF_4$ in water, are measured to be strong acids ranging from pH 3–4 (Suntex Industries Inc., Taiwan). The positive charge of NH_3^+ may interact with the counter anion of the silver salt in silver–polymer complexes. Thus, the interaction between the silver ion and the counter anion will be reduced upon the addition of asparagines and consequently causes the silver ions to be more active for olefin coordination. Moreover, the asparagine possesses the carbonyl group which can coordinate to the silver ion. Therefore, the silver ion can interact with both carbonyl oxygens of POZ and asparagines, and becomes more free from its counter anion in the silver–polymer complexes. Based on this concept, we introduced asparagines into two systems of POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes. The former exhibits very high separation performance for olefin/paraffin mixtures whereas the latter shows almost no separation.[3,8] Thus the effect of asparagines on the complexation behavior of silver ions with propylene and the facilitated propylene transport through the membranes has been investigated in the present study.

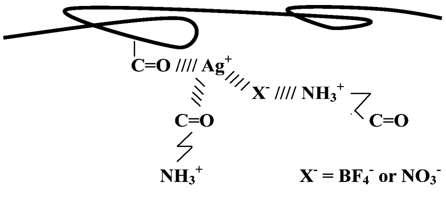
The POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes were prepared by dissolving $AgBF_4$ or $AgNO_3$ and asparagine in water solutions containing 20 wt% of POZ. The molar ratio of carbonyl oxygen of POZ to silver ion was fixed at 1 : 1 and the amount of the asparagine was varied depending on the molar ratio. The permeation experiment and FT-IR spectroscopy were carried out as described in our previous papers.[3,4]

The separation experiment of the propylene/propane mixture was conducted to evaluate the effect of the asparagine on the separation performance of POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes. The molar ratio of asparagine to silver ion for the best separation performance was 0.01. As shown in Table 1, the addition of the asparagines clearly improves the separation performance of both POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes. The selectivity of propylene/propane and the mixed gas permeance are increased up to 65.5 and 18.0 GPU, respectively, for the POZ/$AgBF_4$/asparagine membrane, and the corresponding values are remarkably increased up to 34.0 and 1.4 GPU†, respectively, for the POZ/$AgNO_3$/asparagine membrane.

Table 1 Effect of asparagine on the mixed gas permeance and the selectivity of propylene/propane for 1 : 1 POZ/$AgBF_4$ and POZ/$AgNO_3$ membranes

Membrane	Permeance/GPU	Selectivity
POZ/$AgBF_4$	12.5	45.2
POZ/$AgBF_4$/asparagine	18.0	65.5
POZ/$AgNO_3$	0.1	0.95
POZ/$AgNO_3$/asparagine	1.4	34.0

The remarkable improvement in the membrane separation performance shows that the addition of the asparagine has a strong bearing on the complex formation of the silver ion with propylene and the facilitated propylene transport. The enhancement of facilitated propylene transport could be explained by the increased interaction between propylene and silver ions. This is attributable to the weakened interaction between Ag^+ and the counter anion X^- (BF_4^- or NO_3^-), caused by the electrostatic interaction between the positively charged NH_3^+ of asparagines and X^- (BF_4^- or NO_3^-) as well as the coordinative interaction between silver ions and carbonyl oxygens of asparagine as depicted in Scheme 1.



Scheme 1

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However, if only the electrostatic interaction is effective, the separation performance of the POZ/AgBF$_4$ membranes would not be significantly enhanced because the interaction between Ag$^+$ and BF$_4^-$ is originally weak according to Raman spectroscopy.[8b] It should also be noted at this point that there is no significant difference in both selectivity and permeance when a positively charged polypyrrole, not containing the C=O group, is introduced into the POZ/AgBF$_4$ membranes.[9]

In addition to the electrostatic interaction between X$^-$ (BF$_4^-$ or NO$_3^-$) and NH$_3^+$, the coordinative interaction between Ag$^+$ and the C=O moiety of the asparagine was investigated using FT-IR spectroscopy. FT-IR spectra for pure POZ, pure asparagine, asparagine/AgBF$_4$ and the 1 : 1 POZ/AgBF$_4$ complex with and without asparagine are given in Fig. 1. Upon incorporation of AgBF$_4$ into POZ, the C=O stretching band shifted from 1641 cm^{-1} to a lower wavenumber at 1595 cm^{-1}, which is presumably due to the reduced C=O double bond strength caused by the coordinative interaction between the silver cation and the carbonyl oxygen of POZ. Pure asparagine exhibits slightly overlapped bands of the carboxylic C=O stretching at 1658 cm^{-1}, the amide C=O stretching at 1644 cm^{-1} and the NH$_2$ bending at around 1600 cm^{-1}, as shown in Fig. 1c. When AgBF$_4$ was dissolved in asparagine, the relative intensity of the amide C=O stretching band at 1644 cm^{-1} was decreased in comparison with the carboxylic C=O stretch and a new band at 1608 cm^{-1} became prominent (Fig. 1d). Thus this new band can be assigned to the amide C=O of asparagine complexed with silver ions. When a small amount of asparagine was added to the POZ/AgBF$_4$ complex, the position of the C=O stretching band was further changed from 1595 to 1577 cm^{-1}, demonstrating that the interaction between the C=O of POZ and the silver ion became stronger (Fig. 1e). This result implies that the BF$_4^-$ anions are rather pulled out from the silver ions by the positive charge of the protonated asparagines and thereby the interaction between the silver cations and the counter BF$_4^-$ anions becomes weak.

To analyze in detail the C=O band in the POZ/AgBF$_4$ complex containing a small amount of asparagine, the FT-IR spectrum was deconvoluted as shown in Fig. 2. A carbonyl band of POZ shifted from 1595 to 1577 cm^{-1}, and two new shoulder bands at 1658 cm^{-1} and 1608 cm^{-1} appeared concurrently. These shoulder peaks at 1658 cm^{-1} and 1608 cm^{-1} are attributed to the free carboxylic C=O of the asparagine and the amide C=O of the asparagine complexed with the silver ion, respectively. This assignment is supported by the FT-IR spectrum of asparagine/AgBF$_4$ shown in Fig. 1d. Consequently, the FT-IR data suggest that the silver ions are coordinated by both the C=O of the asparagine and C=O of POZ.

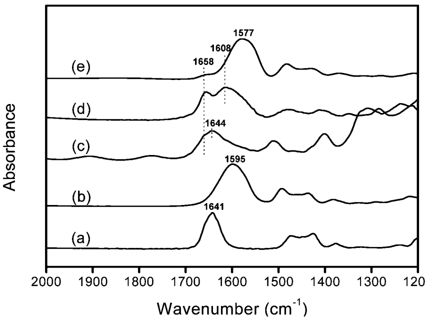

Fig. 1 FT-IR spectra of (a) pure POZ, (b) POZ/AgBF$_4$, (c) asparagine, (d) asparagine/AgBF$_4$ and (e) POZ/AgBF$_4$/asparagine complexes.

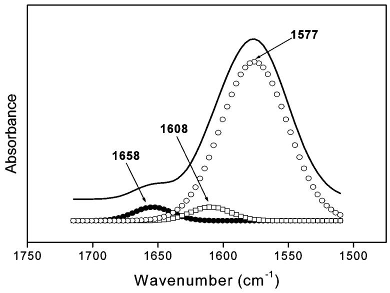

Fig. 2 Deconvoluted FT-IR spectra for POZ/AgBF$_4$/asparagine complexes from Fig. 1e. Open circles are for the shifted C=O stretch of POZ, filled circles are for the free carboxylic C=O stretch of asparagine and open squares are for the amide C=O stretch of asparagine complexed with silver ions.

In summary, the introduction of asparagine into POZ/AgBF$_4$ or POZ/AgNO$_3$ complex membranes caused the enhanced separation performance of propylene/propane mixtures due to facilitated propylene transport by the silver ion. In particular we are successful in making inactive AgNO$_3$ as an active olefin carrier upon the incorporation of asparagine into silver–polymer complex membranes. These results are believed to be obtained by the diminished interaction of silver cations with counter anions from both (1) the electrostatic interaction of the counter anion with NH$_3^+$ of the asparagine and (2) the coordinative interaction of C=O in asparagine with the silver ion.

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† 1 GPU = 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1}.

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