아미노산을 이용한 올레핀 촉진수송 분리막의 성능향상

강상욱, 김종학*, 원종옥**, 차국헌, 강용수*

서울대학교 응용화학
* 한국과학기술연구원 촉진수송분리막연구단
** 세종대학교 응용화학

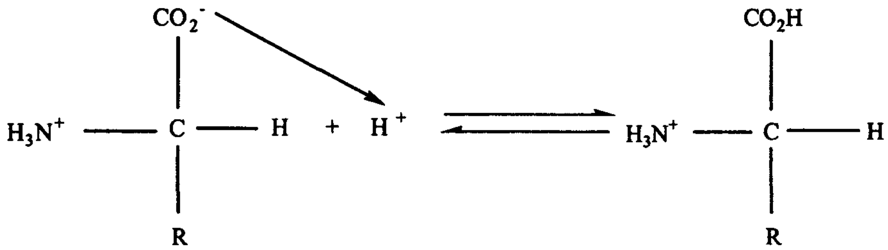
Enhancement of Facilitated Olefin Transport by Amino acid in Silver Polymer Complexes

Sang Wook Kang, Jong Hak Kim*, Jongok Won**, Kookheon Char and Yong Soo Kang*

School of Chemical Engineering and Institute of Chemical Processes, Seoul National University, Seoul
* Center for Facilitated Transport Membranes, KIST, Seoul
** Department of Applied Chemistry, Sejong University, Seoul

Introduction

Polymer electrolytes containing silver ions have attracted much interest due to their potential application to separate olefin/paraffin mixture using the reversible silver-olefin complexes as a carrier for a facilitated transport [1-3]. However in recent days, to adjust silver polymer electrolytes membranes to the commercialization of separation process, it is required to enhance the performance such as selectivity and permeance further. The idea of using amino acids stems from the fact that amino acids are very reactive with different chemical substances including metal ions such as silver ion. Since the amino acid is amphoteric, it is possible to happen the interaction between Ag^+ and COO^- of amino acid, and as the result undesirable coordination between them can occur. However since the polymer electrolyte of POZ/$AgBF_4$ is a strong acid as pH 3 (this polymer electrolytes have many H^+ because the complexation between Ag^+ and OH^- of water happen), the reaction will predominantly proceed to forward direction and thus the amino acid will exist mainly as right form of Scheme 1. Therefore the solubility of silver salt in polymer and the complexation behavior between silver ion and polymer complexes are manipulated by the complex formation between silver ion and the NH_3^+ of amino acid. The positive charge of amino acid serve as a coordinating site to interact with the counter anion of silver salt in silver polymer electrolytes. Furthermore, since the asparagine possesses the group of C=O, there would be the interaction between Ag^+ and C=O of asparagine as well as the interaction between Ag^+ and C=O of POZ. Due to the simultaneous interaction of silver ion with both C=O of POZ and C=O of asparagine, Ag+ will be more stable and will be more free from the anion of silver salts. The stronger an interaction between Ag+ and C=O is by being set free from anion of Ag salts, the higher the olefin complexation with silver ion [4].



Scheme 1

Experimental

Poly (2-ethyl-2-oxazoline) (POZ), $AgBF_4$ and asparagine were purchased from Aldrich Chemical Co. and were used without further purification. The appropriated amounts of POZ and silver salts were dissolved in water. Then, 0.01 mol of asparagine is incorporated into this solution. The solution was then cast on a polysulfone microporous membrane support (SEAHAN Industies Inc., Seoul, Korea) using an RK Control Coater and dried under N_2 environment. The films were further dried in a vacuum oven for at least two days at room temperature. The thickness of the top polymer electrolyte layer was ca. $1 \mu m$ as determined by SEM. Gas flow rates represented by gas permeance were measured by a soup bubble flow meter. The unit of the gas permeance is GPU, where 1 GPU = 1 * 10-6 cm3 (STP)/(cm2 sec cmHg). The mixed gas (50:50 vol % of a propylene/propane mixture) separation properties of the membranes were evaluated using gas chromatography (Gow-Mac) equipped with a TCD and a unibead 2S 60/80 packed column.

Results and discussion

The separation experiment of propylene/propane mixture was conducted to evaluate the effect of asparagine on the performance of the POZ/AgBF4 and POZ/ AgNO3 membranes. The molar ratio of asparagine to silver ion is 0.01, where the best separation performance is achieved. The selectivity of propylene over propane for POZ/AgBF4 membrane without asparagine is about 45 and the permeance for POZ/AgBF4 is about 12.5 GPU while for POZ/AgNO3 the selectivity is about 0.95 and the permeance is less than 0.1 GPU. On the other hand, the addition of asparagine significantly improves the separation performance of the POZ/AgBF4 and the POZ/AgNO3 membranes. The selectivity of propylene/propane mixture is increased by 20-25 and the mixed gas permeance is increased by 5-6 GPU for the POZ/AgBF4 membranes while for the POZ/AgNO3 membranes the selectivity is increased by 35 and the mixed gas permeance is increased by 1.5 GPU.

This result obviously represents that the asparagine takes part in the formation of the complex between the silver ion and propylene and resulting facilitated propylene transport. The enhanced propylene permeance may be explained by the favorable interactions of propylene with silver ions. This is due to the weakened interaction of Ag^+ and X-(BF_4^- or NO_3^-) compensated by the electrostatic interaction between the positive-charged asparagine and X- (BF_4^- or NO_3^-).

However if the interaction exists simply between X- and Ag^+, separation performance of the POZ/$AgBF_4$ membranes would not be enhanced because the interaction between Ag^+ and BF_4^- is originally weak according to the Raman spectroscopy [4].

It should be noted that there was no difference in selectivity and permeance when the positive-charged Polypyrrole which used as a anion complexation agent is introduced into the POZ/$AgBF_4$ membranes.

In this experiment, in addition to the interaction between X- (BF_4^- or NO_3^-) and NH_3^+, the interaction between Ag^+ and C=O of asparagine was investigated by using the FT-IR spectroscopy. FT-IR spectra for pure POZ, asparagine/$AgBF_4$ and 1:1 POZ/$AgBF_4$ complex with and without asparagine are given in Figure 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 a loosened C=O double bond by the coordination interaction between silver cation and carbonyl oxygen of POZ. The slight position change of the C=O stretching band from 1595 to 1588 cm^{-1} was observed when asparagine was added in the POZ/$AgBF_4$ complex. The interaction changes between carbonyl oxygen and silver cation may result from the fact that the BF_4^-anions are pulled up by the positive charge of protonated asparagine and Ag^+ cations are pulled up by C=O of asparagine as well as C=O of POZ. Thereby the interaction between silver cation and the counter anion becomes weak.

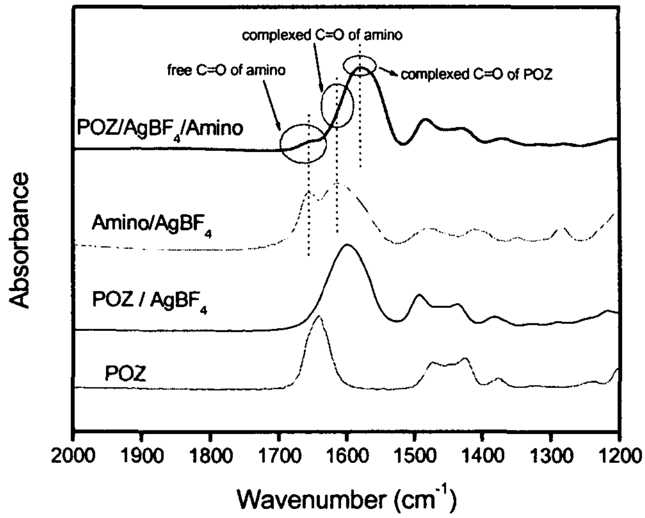


Figure 1. FT-IR spectra of pure POZ, POZ/AgBF4, Asparagine(Amino)/AgBF4 and 1:1:0.01 POZ:AgBF4:Asparagine(Amino) complexes.

In summary, the incorporation of asparagine into POZ/AgBF4 or POZ/AgNO3 complex membranes induced the enhanced performance of facilitated propylene transport. These results may be predominantly attributed to the pulling up of NO3- or BF4- anions from silver cations by the complexation of NO3- and BF4- with NH3+ of asparagine as well as the interaction between C=O of asparagine. The propylene permeance and the selectivity of propylene/propane increased from ca. 12.5 to 18 GPU and about 45 to 65 in POZ/AgBF4 membranes whereas in POZ/AgNO3 membranes the corresponding values increased from ca. 0.1 to 1.5 GPU and about 0.95 to 35, respectively, when 0.01 mole ratio of [asparagine]/[Ag] was added.

References

1. J. H. Kim, B. R. Min, J. Won, Y. S. Kang, *Chem. Eur. J.* 2002, **8**, 650 J. H. Kim, B. R. Min, C. K. Kim, J. Won, Y. S. *Marcomolecules*, 2001, **34**, 6052 J. H. Kim. B. R. Min, C. K. Kim, J. Won, Y. S. Kang. *Macromolecule* , 2002, **35**, 5250 S. U. Hong, J. Won and Y. S. Kang, *Adv. Material.*, 2000, 12, 968.
2. H. S. Kim, J. H. Ryu, H. Kim, B. S. Ahn and Y. S. Kang, *Chem.Commun.*,2000, 1261: J. H. Ryu, H. Lee, Y. J. Kim, Y. S. Kang and H. S. Kim, *Chem. Eur. J.*, 2001, 7, 1525
3. Pinnau, I.; Toy, L. G.; Casillas, C. U.S. Patent 5, 670, 051, 1997; S. Sunderrajan, B.D. Freeman, C.K. Hall, I. Pinnau, *J. Membr. Sci.*, 2001, **182**, 1.
4. J. H. Kim, B. R.Min, C. K. Kim, J. Won, Y. S.*J. Phys. Chem. B*, 2002, 106, 2786.