

Ionic Liquid as a solvent and Long-Term Separation Performance in Polymer/Silver Salt Complex Membrane

Sang Wook Kang¹, Jong Hak Kim², Kookheon Char¹,
Yong Soo Kang³*

¹ School of Chemical & Biological Engineering, Seoul National University, Seoul, Korea

² Department of Chemical Engineering, Yonsei University, Seoul, Korea,

³ Department of Chemical Engineering, Hanyang University, Seoul, Korea
kangys@hanyang.ac.kr

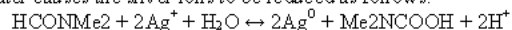
Introduction

Ionic liquids (ILs) are molten salts that are fluid over a wide temperature range, with higher viscosities (10^{-2} to 10^0 Pa s) than either aqueous ($<10^{-3}$ Pa s) or organic ($\sim 6 \times 10^{-3}$ Pa s) electrolytes at room temperature. Their potential for recyclability, ability to dissolve a variety of materials, and negligible vapor pressure are some of their unique attributes responsible for newly found popularity. Recently, ionic liquids have explosively been researched as environmentally benign solvent substitutes for conventional volatile solvents in a variety of applications such as chemical synthesis,¹ extractions,^{2,3} dissolution,⁴ polymerization⁵ and catalysis.⁶ Very recently we also found a new, effective application of IL to facilitated olefin transport membranes by controlling the strength of ionic interaction in polymer/silver salt complexes.⁷

The facilitated olefin transport membranes consist of polymer having the functional group and silver salt capable of reacting with olefin molecules reversibly.⁸ Silver polymer electrolyte membranes consisting of AgBF_4 or AgCF_3SO_3 dissolved in either poly(2-ethyl-2-oxazoline) (POZ), poly(N-vinyl pyrrolidone) (PVP) or poly(ethylene oxide) (PEO) showed that the mixed gas selectivity of propylene over propane reached 45 and the mixed gas permeance up to 12 GPU (1 GPU = 1×10^{-6} cm³ (STP)/cm² s cmHg).⁸ However, the membranes containing AgNO_3 was not effectively used to separate propylene/propane mixtures because of the high lattice energy of salt. In previous paper, we reported on the successful use of IL in controlling the interaction between Ag^+ and NO_3^- , thus making Ag^+ more active in silver-olefin complexation. The permeance increased from 0.1 to 5.5 GPU and the mixed gas selectivity did from 1.0 to 32.0.⁷

Maintaining the long-term stability of separation performance through the membranes is also significantly important issues in facilitated olefin transport membranes. The gradual decrease in separation performance with time through the silver polymer electrolyte membranes have been frequently observed,⁹ mostly because of the loss of carrier activity by the reduction of silver ions to silver nanoparticles. This reduction is originated from the fact that the polymer matrices such as POZ, PVP or PEO play a significant role as a reducing agent for silver ions.^{10,11}

Isabel and Luis explained that *N,N*-dimethylformamide (DMF) in water causes the silver ions to be reduced as follows:¹²



Because the structure of PVP having amide group is similar to DMF, the similar reduction behavior is expected under the existence of water. Therefore, if other solvents are used for the preparation of polymer/silver salt membrane, the reduction of silver ions might be prohibited for a long time. It has been also reported that alcohols participate in the reduction reaction of silver ions.¹³ Thus, the use of alternative solvent other than water or alcohols are seemingly desirable. In this paper, therefore, we introduced IL and acetonitrile (ACN) as a solvent to prepare polymer/silver salt complex membranes and investigated the separation performance of facilitated transport membranes for propylene/propane mixtures.

Experimental

Silver tetrafluoroborate (AgBF_4 , 99%), poly(N-vinyl pyrrolidone) (PVP, $M_w = 1.3 \times 10^5$ g/mol) were purchased from Aldrich Chemical Co. 1-butyl-3-methylimidazolium nitrate ($\text{BMIM}^+\text{NO}_3^-$) as an ionic liquid was purchased from C-TRI Co.

Results and discussion

The mole ratio of silver ions to the monomeric units of polymer was fixed at 1:1. Initially, (PVP in water)/ AgBF_4 membrane showed the selectivity of 46 and the permeance of 12 GPU at $[\text{C}=\text{O}]:[\text{Ag}]=1:1$. (PVP in ACN)/ AgBF_4 membrane showed the selectivity of 41.2 and the permeance of 12.3 GPU at $[\text{C}=\text{O}]:[\text{Ag}]=1:1$. On the other hand, for the (PVP in IL)/ AgBF_4 membranes the selectivity of propylene over propane was 7.2 and the permeance was 3.6 GPU, respectively.

The relatively lower separation performances of (PVP in IL)/ AgBF_4 membranes might be explained as follows. First, (PVP in IL)/ AgBF_4 membranes has much higher thickness than other two membranes, because IL is hardly volatile and thus mostly ($\sim 95\%$) in the total membrane) remains in the membranes. Second, since the concentration of IL in the membranes is higher, the relative concentration of silver ions in the total membrane becomes lower even at the same $[\text{C}=\text{O}]:[\text{Ag}]$. Thus the activity of silver ions in (PVP in IL)/ AgBF_4 membranes becomes lower, leading to lower separation performance of the membranes.

The (PVP in water)/ AgBF_4 membrane showed the rapid decrease of separation performance with time. On the other hand, the 1:1 (PVP in ACN)/ AgBF_4 membrane showed the long-term stability for 100 hours, after which the deterioration of separation performance was gradually observed. However, the selectivity and the permeance of the (PVP in IL)/ AgBF_4 membrane were nearly constant for the duration of the experiment up to 160 h, implying the activity of silver ions as olefin carriers is very stable in this system. The detailed mechanism of the long term stability of silver ions in (PVP in IL)/ AgBF_4 membrane will be discussed in next section.

Conclusions

The effect of solvent, i.e. IL, ACN and water was investigated on the long-term stability of polymer/silver salt complex membranes together with the correlation with the reduction behavior of silver ions to silver nanoparticles. It was found that the 1:1 (PVP in ACN)/ AgBF_4 and 1:1 (PVP in IL)/ AgBF_4 complex membranes are more stable with time in separation of propylene/propane mixtures than 1:1 (PVP in water)/ AgBF_4 complex membrane. It is believed that the deterioration of long-term stability in (PVP in water)/ AgBF_4 membrane with time is attributable to the role of water trace remained in the membranes as a reducing agent. Furthermore, the higher stability of 1:1 (PVP in IL)/ AgBF_4 complex membranes could be explained by the fact that the silver ions coordinated with IL are more stable than those coordinated with carbonyl oxygens, confirmed by FT-IR spectroscopy. Therefore we succeeded in preparing the long-term stable membrane for olefin/paraffin separation by using ionic liquid as an alternative solvent.

References

- [1] T. Welton, Chem. Rev. 99 (1999) 2071.
- [2] L. A. Blanchard, D. Hancu, E. J. Beckmann, J. F. Brennecke, Nature 399 (1999) 28.
- [3] J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, Chem. Commun. (1998) 1765.
- [4] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, J. Am. Chem. Soc. 124 (2002) 4974.
- [5] A. J. Carmichael, D. M. Haddleton, S. A. F. Bon, K. R. Seddon, Chem. Commun. (2000) 1237.
- [6] A. C. Cole, J. L. Jensen, I. Ntai, K. Loan, K. L. Tran, T. K. J. Weaver, D. C. Forbes, J. H. Davis Jr., J. Am. Chem. Soc. 124 (2002) 5962.
- [7] S. W. Kang, K. Char, J. H. Kim, C. K. Kim, Y. S. Kang, Chem. Mater. 18 (2006) 1789.
- [8] S. U. Hong, J. Won, Y. S. Kang, Adv. Mater. 12 (2000) 968.
- [9] S. W. Kang, J. H. Kim, K. S. Oh, J. Won, K. Char, H. S. Kim, Y. S. Kang, J. Membr. Sci. 236 (2004) 163.
- [10] H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Deng, G. Q. Xu, Langmuir 12 (1996) 909.
- [11] H. Henglein, Chem. Mater. 10 (1998) 444.
- [12] P.-S. Isabel, M. L. -M. Luis, Langmuir 15 (1999) 948.
- [13] L. Sun, Z. Zhang, H. Dang, Materials Letters 57 (2003) 3874.
- [14] J. H. Kim, B. R. Min, H. S. Kim, J. Won, Y. S. Kang, J. Membr. Sci. 212 (2003) 283.
- [15] A. Faik Demirors, Bekir E. Eser, and Omer Dag, Langmuir 21 (2005) 4156.
- [16] T. Itakura, K. Torio, and K. Esumi, Langmuir 11 (1995) 4129.