

Ag⁺-Chitosan Complex Membranes for Propylene/Propane Separation

Jeong-Hoon Kim[†], Soo-Bok Lee, and Xianshe-Feng*

Interface Materials and Engineering Lab, Division of Chemical Technology, Korea Research Institute of Chemical Technology,
Yusong-Gu, Taejeon, 305-333, Korea

*Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

(Received October 24, 2006, Accepted December 6, 2006)

Abstract: We have prepared new water-swollen chitosan-Ag⁺ complex membranes and studied their permeation and separation behavior for propylene and propane gases. The Ag⁺ containing chitosan complex membranes were prepared from chitosan and AgNO₃ aqueous solution. The AgNO₃ and water content in the membrane were controlled by adjusting AgNO₃ concentration of casting solution. The permeation properties of propylene and propane were investigated as a function of AgNO₃ concentration, and various operation conditions. High permeability of above 17 barrer and high selectivity of above 170 could be obtained with the membranes prepared from 3 M AgNO₃ aqueous solution. Periodic regeneration test confirmed these membranes could be very useful for the separation of propylene/propane and other olefin/paraffin separation.

Keywords: chitosan-Ag⁺ complex, membranes, propylene, propane facilitated transport

1. Introduction

The separation of light olefin/paraffin is an important process in petrochemical refining industries. Traditionally, cryogenic distillation process has been used for a long time. But due to their similar size and condensability (or volatility), this process has been carried out under the energy-consuming conditions - low temperature, high pressure and large distillation column in separation trains. Many researchers have investigated the alternative processes. Among them, the most attractive technology is a facilitated or carrier-mediated transport membrane using the reversible π -complex formation between transition metal ions and double bond of olefin compounds[1]. Facilitated transport (FT) mechanism for olefin/paraffin separation has been explained clearly in the literature[2-4]. In this membrane, olefins are complexed with facilitating agent (i.e., Ag⁺

or Cu⁺ etc.)- at high pressure of feed side. The complexed olefin transports across the membrane from high- to low-pressure side by diffusion of complex or by re-complexation with adjacent metal ion because of its concentration difference, i.e., metal ion acts as a carrier for olefin. The complex in the low-pressure side can release olefin through de-complexation and be regenerated to free metal ions. The regenerated metal ion diffuses backward to the high-pressure side. This makes one cycle of FT mechanism, which occurs repeatedly. If the concentration of facilitating agent increases, the complexation or solubility of olefin in the membrane can be increased, and thus, the transport of olefin is facilitated markedly. But, paraffin without double bond cannot complex with complexing agent and thus, they cannot transport easily through the membrane. Therefore, FT membranes can show high olefin permeability and high olefin/paraffin selectivity.

The literature survey shows that the experimental studies have focused mainly on how the facilitating agent is trapped effectively in the membranes without

[†] Author for all correspondences
(e-mail : jhoonkim@kRICT.re.kr)

deteriorating the reversible complexation and diffusion capacity. These FT membrane materials can be divided into three classes – 1) supported liquid membrane using porous supports[4-7], 2) water-swollen polymer membrane using cross-linked hydrophilic polymer or ion-exchange membranes[8-13] and 3) solid-state polymer membranes using polymer electrolyte and conducting polymer[14-18].

In this paper, Ag⁺-containing chitosan chelate membrane was prepared as a new water-swollen membrane material with facilitated transport property. AgNO₃ is chosen as a facilitation agent because Ag⁺ is known to be the most non-toxic among transition metal ions. Chitosan is also chosen because it can form easily water-swollen chitosan chelate membranes containing high Ag⁺ content due to its abundant amino groups to make the coordinated sites toward the transition metal ions.

2. Experimental Section

2.1. Materials

Chitosan with molecular weight (MW) = 100,000 and 99% *N*-deacetylation degree was kindly supplied from Kyowa Technos Inc., Japan. Silver nitrate (99.5 wt%) was purchased from Aldrich Co. and used without further purification. Acetic acid was purchased from BDH Co. Propylene and propane with 99.5% purity were purchased from Praxair company in Canada.

2.2. Membrane Preparation

A homogeneous chitosan aqueous solution consisting 1.1 wt% chitosan and 2 wt% acetic acid was prepared and filtered to remove undissolved chitosan and impurities. The chitosan solution was cast onto the glass plate with the aid of adhesive tapes and dried for 2 days in vacuum to make thin membranes. The protonated (-NH₃⁺) chitosan membrane was immersed into 0.8 M of NaOH in 50/50(v/v) EtOH/H₂O solution for 2 days to give water-insoluble chitosan membranes with amino group. 50/50 (v/v) EtOH/H₂O mixture was chosen to control water content of chitosan mem-

branes. The membranes were washed thoroughly with a large amount of pure water for 3 days to remove trace NaOH. The membrane was dipped into AgNO₃ aqueous solution with various concentrations ranging from 0.2 to 5 M to prepare Ag⁺ containing chitosan chelate membranes for 48 hrs in a light- and oxygen-protected environment. After wiping out the water on the membrane surface with filter paper, the wet membrane was tested in the permeation cell. The thickness of the wet membranes was about 70±10 μm.

2.3. Membrane Characterization

AgNO₃ content and water content in Ag⁺ containing chitosan chelate membranes were measured as follows. After measuring the initial weight of dried chitosan membrane, M_0 , it was immersed into AgNO₃ aqueous solution for a predetermined time. The water on the membrane surface was wiped with filter papers and weighed to give the weight of wet chitosan chelate membrane, M_{1W} . Then, it was dried using vacuum pump and weighed again to measure the weight of dried chelate membrane, M_{1D} . AgNO₃ content, C_{AgNO_3} , and water content, C_{H_2O} , were calculated with the following equations:

$$C_{AgNO_3} = \frac{M_{1W} - M_0}{M_{1W}} \quad (1)$$

$$C_{H_2O} = \frac{M_{1W} - M_{1D}}{M_{1W}} \quad (2)$$

2.4. Gas Permeation Test

Propylene and propane gases were used for permeation test. The gas permeation properties were measured by bubble flowmeter. The permeability, P (barrer: $10^{-10} \times \text{cm}^3 \text{ (STP)} \cdot \text{cm} / \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$) and propylene/propane selectivity, α , were calculated using the following equation :

$$P = \frac{Q \cdot l}{A \cdot t \cdot (p_1 - p_2)} \quad (1)$$

$$\alpha = \frac{P_{propylene}}{P_{propane}} \quad (2)$$

where Q is the quantity of the gas permeated at STP in time interval t , A is effective membrane area, l membrane thickness, and p_1 and p_2 are upstream and downstream pressures, respectively. In this study, p_1 values of propylene and propane are 136 psi and 109 psi, respectively and p_2 is assumed 1 atm (atmosphere) in calculating their permeability. The two membrane areas of 10.8 and 104.3 cm² were used, respectively.

2.5. Regeneration Test

The regeneration test was done with the chitosan chelate membranes which were prepared from 3 M AgNO₃ casting solution. After immersing the membranes in the 3 M AgNO₃ aqueous solutions for 10min, the membrane was re-installed and its permeability was measured again. Periodic regeneration was done everyday for 7 days of operation time.

3. Results and Discussion

3.1. AgNO₃ Content in the Membranes

The contents of three components (water, AgNO₃ and chitosan) forming Ag⁺ containing chitosan chelate membranes were measured as a function of AgNO₃ concentration in casting solutions. The obtained results are shown in Table 1, where total wt% of three components is 100. As AgNO₃ concentration increases from 0.0 M to 5.0 M, the content of AgNO₃ in the membrane increases highly from 0 wt% to 50.8 wt%. This means propylene permeation can be maximized by increasing AgNO₃ concentration in casting solution. There are two Ag⁺ forms in the membranes. One is Ag⁺ forming chelate with amino group (NH₂) of chitosan and the other is Ag⁺ dissociated in water in the membrane. But, the exact ratio was not measured in this study. With increasing AgNO₃ concentration, water content decreases from 55 to 20.2 wt%. The content of chitosan decreases from 45 to 29 wt%. The initial increase of chitosan content at 0.2 M AgNO₃ solution seems to be attributed to the shrinkage of water-swollen chitosan membrane due to chelate formation be-

Table 1. Effect of AgNO₃ Concentration of Casting Solution on the AgNO₃ Content in Ag⁺-Chitosan Complex Membranes

AgNO ₃ Concentration in casting solution (M)	Content of water-swollen Ag ⁺ chitosan complex membrane (wt%)		
	Chitosan	Water	AgNO ₃
0.0	45.0	55.0	0.0
0.2	51.5	36.0	12.5
0.8	47.0	30.6	22.4
3.0	32.9	25.8	41.3
5.0	29.0	20.2	50.8

tween AgNO₃ and amino groups (NH₂) of chitosan.

3.2. Effect of AgNO₃ Content on Permeation Properties

To understand the concentration effect of facilitating agent, AgNO₃ on the transport properties, permeation experiment was done for the membranes with various casting solution concentrations from 0.2 to 5.0 M AgNO₃ and the obtained results are shown in Fig. 1. The decreasing trends of propylene permeabilities during 2 days are observed with all the membranes, which seemed to be due to water vapor loss in the membrane arising from high permeation of gases.

As the concentration of AgNO₃ in casting solution increases from 2 to 5.0 M, the propylene permeabilities increase from 3.4 to 55 barrer. Remarkable increase of propylene permeability is caused by the increase of Ag⁺ content at the higher AgNO₃ concentrations increase in AgNO₃ content enhances propylene-Ag⁺ complex formation to facilitate propylene permeation by facilitated transport mechanism, i.e., complexation-diffusion-decomplexation.

To obtain the propylene/propane selectivity, permeation experiments were done for propylene and propane gases for the membranes with various casting solution concentrations from 0.2 to 5.0 M AgNO₃ and the obtained results are shown in Table 2. In order to minimize the permeability change during the measuring time, the test was done in 1 day after the test was started. As the concentration of AgNO₃ in casting sol-

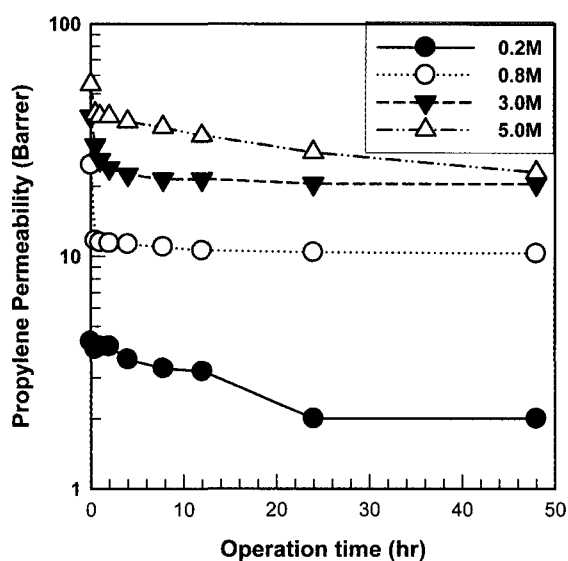


Fig. 1. Effect of AgNO₃ concentration of casting solution on the permeation properties of Ag⁺ - chitosan complex membranes.

Table 2. Effect of AgNO₃ Concentration of Casting Solution on the Permeabilities and Selectivities of Ag⁺ - Chitosan Complex Membranes

AgNO ₃ concentration (M)	0.2	0.8	3.0	5.0
Propylene permeability, P _{propylene} (Barrer)	3	10.4	20.5	28
Propane permeability, P _{propane} (Barrer)	0.6	0.1	<<0.1	<<0.1
Selectivity, (P _{propylene} /P _{propane})	49	104	<<20.5	<<280

tion increases from 0.2 to 5.0 M, the resulting showed propylene permeabilities ranging from 3 to 28 barrer. But propane permeability decreases very steeply from 0.6 to below 0.1 barrer (i.e., less than measuring limit in this study) for the membranes prepared from 0.2~5.0 M AgNO₃ solution. Thus, the propylene/propane selectivity increases highly from 3 to >> 280. The increase in propylene permeability is explained by increase AgNO₃ contents in the water-swollen membrane. But, the decreasing trend of propane is observed with increasing AgNO₃ content. The opposite permeation behaviors for two gases against AgNO₃ con-

centration show two gases permeate through membranes by different transport mechanisms. Propane permeates through simple solution-diffusion mechanism while propylene permeates through facilitated transport mechanism. The reason for the decrease in propane with AgNO₃ content can be explained in terms of the viscosity of AgNO₃ solution in the membranes and salting out effect for propane solubility. Increasing AgNO₃ concentration not only enhances dominantly propylene permeation by complex formation but also disturbs propane permeation by salting out effect. Therefore, the membrane with higher AgNO₃ concentration of 5.0 M gave extremely high propylene/propane selectivity (>> 280) and high propylene permeability of 28 barrer. The excellent permeation and separation properties of these chitosan-Ag⁺ complex membranes are superior to the other water-swollen membranes and polymeric membranes reported in the literature[8-13].

3.3. Effect of Operation Pressure and Temperature on Propylene Permeability

The effect of operation pressure and temperature on the permeation flux and permeability of two gases were investigated for the membranes prepared from 3 M AgNO₃ solution and the results are shown in Table 3. In order to minimize the permeability change due to measuring time, the tests were done in 1 day after the test started.

In Table 3, as the operation pressure of propylene increases from 20 to 136 psi, the permeation flux increases gradually but the permeability decreases from 45.9 to 20.5 barrer, unlike the case of polymeric membranes. Though some deviations in flux are observed, this behavior is a typical behavior in FT membranes. The deviations seem to be originated from water loss with measuring time. In FT membranes, the solubility of propylene is controlled by the complexation reaction of propylene with Ag⁺. Even though feed pressure of propylene increases highly, the concentration of complex (or solubility of propylene) cannot be increased

Table 3. Effect of Operation Pressure on Propylene Permeability of Ag⁺-chitosan Complex Membranes

Operation Pressure (psi)	Propylene Permeability P _{propylene} (Barrer)
0	0
20	45.9
40	41.2
60	30.6
80	27.3
100	23.4
120	21.4
136	20.5

because of the constant number of complexation sites, Ag⁺ in the membrane. Ag⁺ sites are already used up in lower pressure, like Langmuir-type adsorption. Thus, permeability decreases against pressure is observed in Table 3.

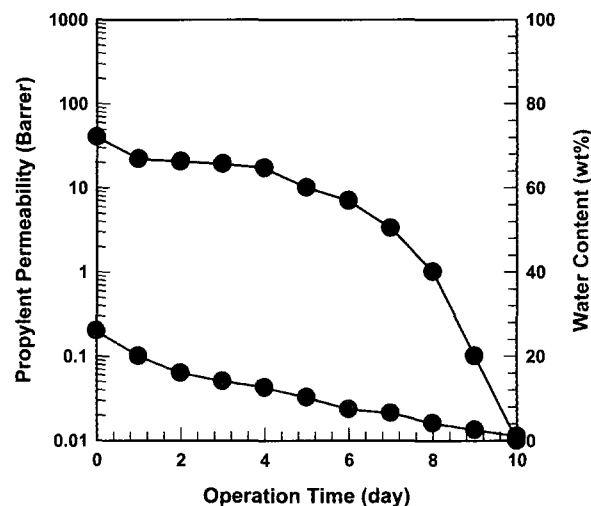
In order to obtain the effect of operation temperature on propylene permeability, two membranes obtained from 0.8 and 3.0 M AgNO₃ casting solutions were tested and the obtained results are shown in Table 4. In the case of 0.8 M and 3.0 M AgNO₃, the propylene permeability increases with operation temperature. It was reported that olefin solubility decreases with increasing temperature in FT membrane[9,10]. The increase of permeability of propylene with temperature is mainly due to the increase of mobility of membrane matrix (or diffusivity of complex) with temperature.

3.4. Effect of Operation Time on Propylene Permeability and Water Content

In order to understand the relationship of operation time with water content and propylene permeability, permeation test was done for 10 days with the membrane with 3 M AgNO₃ solution. The obtained results are shown in Fig. 2. As operation time increases, propylene permeability decreases smoothly from 40 to 17.1 barrer for early 4 days, but decreases very steeply for 4~10 days. Water content in the membrane decreases smoothly with operation time. The propane permeability within testing period shows extremely low propane permeability (<< 0.1 barrer).

Table 4. Effect of Operation Pressure on Permeation Flux and Permeability of Propylene of Ag⁺-chitosan Complex Membranes

Propylene Permeability (Barrer)	Operation Temperature (°C)		
	20	30	40
0.8 M AgNO ₃	10.1	11.7	13.7
3.0 M AgNO ₃	16.9	21.5	28.0

**Fig. 2.** Effect of operation Time on water content and propylene permeability of Ag⁺-chitosan complex membranes.

3.5. Long-term Test Through Periodic Regeneration

In the FT membranes, propylene permeability decreases with operation time due to water loss and thus, regeneration could be important for practical application. Three times of regeneration test were done with the membranes prepared from 3.0 M AgNO₃ solutions. Regeneration was repeated every 3 day for 10 min. The obtained results are shown in Fig. 3. When the membranes were regenerated three times, propylene permeability of above 17 barrer were maintained and propane permeability measured was below 0.1 barrer and high selectivity of above 170 were maintained, which means that it is possible to maintain the performances through periodic regeneration for long-term period. These indicate that this membrane could be useful for the separation of propylene/propane and oth-

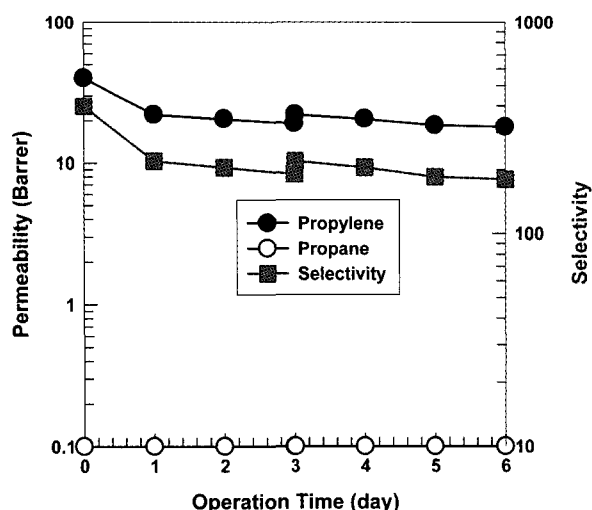


Fig. 3. Long-term test through periodic regeneration with 3M AgNO₃ aqueous solutions.

er olefin/paraffin system in petroleum industry by periodic regeneration. This simple periodic regeneration would be a good advantage of this water-swollen membranes compared to the other facilitated transport membranes, because the water-swollen thin layer with facilitated agent can be recovered easily even if the membranes are deteriorated with trace H₂ and H₂S - catalyst poisoning agent-involved in the streams of refinery process.

4. Conclusions

Ag⁺ containing chitosan complex membranes were prepared from chitosan and AgNO₃ aqueous solution and their permeation properties of propylene and propane were investigated against membrane preparation and operation conditions. With increasing AgNO₃ concentration of casting solution, propylene permeability increases highly and propane permeability decreases and thus high propylene/propane selectivity is observed. As the operation temperature increases or operation pressure decrease, propylene permeability increases. As operation time increases, both propylene permeability decrease due to loss of water in the membranes. These behaviors are explained in terms of the following three factors - 1) facilitating agent, AgNO₃ -

enhancing propylene permeation preferentially, 2) salting out effect - decreasing propane permeation and 3) water loss (i.e., mobility loss) - decreasing the permeability. High permeability of above 17 barrer and high selectivity of above 170 was maintained with the membranes through periodic regeneration 3 M AgNO₃ aqueous solution.

References

1. R. B. Eldridge, Olefin/Paraffin Separation Technology: Review, *Ind. Eng. Chem. Res.*, **32**, 2208-2212 (1993).
2. J. D. Way and R. D. Noble, Facilitated transport, in: W. S. Ho, S. S. Sirkar (Eds), *Membrane Handbook*, Van Nostrand, New York (1992).
3. E. L. Cusser, Facilitated and active transport, in: D. R. Paul, Y. P. Yanpol'skii (Eds), *Polymeric Gas Separation Membranes*, CRC Press, Boca Raton, FL, 1994 pp. 274-300.
4. M. Teramoto, H. Matsuyama, T. Yamashiro, and Y. Katayama, Separation of ethylene from ethane by supported liquid membranes containing silver nitrate as a carrier, *J. Chem. Eng. Jpn.*, **19**, 419 (1986).
5. J. C. Davis, R. J. Valus, R. Eshraghi, and A. E. Velikoff, Facilitated transport membrane hybrid systems for olefin purification, *Sep. Sci. Technol.*, **28**, 463 (1993).
6. Mitsuyasu Kwaskami, Masaru Tatkeshi, Masakazu Iwamoto and Shuichi Kagawa, Selective permeation of ethylene and propylene through Rh⁺-polyethylene glycol liquid membranes, *J. Memb. Sci.*, **30**, 105 (1987).
7. R. D. Hughes, J. A. Mahoney, and E. F. Steigelmann, Olefin separation by facilitated transport membranes, in N > N Li and J. M. Calo (Eds.), *Recent Developments in Separation Science*, Vol. IX, CRC, Boca Raton, FL, pp. 173 (1986).
8. W. S. Ho and D. C. Dalrymple, Facilitated transport of olefins in Ag⁺-containing polymer mem-

- branes, *J. Memb. Sci.*, **91**, 13-25 (1994).
9. J.-S. Yang and G.-H. Hsiue, Swollen polymeric complex membranes for olefin/paraffin separation, *J. Memb. Sci.*, **138**, 203-211 (1998).
 10. James C. Davis, Ronald, and J. Valus, Reza Eshraghi and Alex E. Velikoff, Facilitated transport membrane hybrid systems for olefin purification, *Sep. Sci. and Technol.*, **28**(1-3), 463-476 (1993).
 11. Hans H. Funke, Richard D. Noble, and Carl a. Koval, Separation of gases olefin isomers using facilitated transport membranes, *J. Memb. Sci.*, **82** (1993).
 12. Odd I. Eriksen, Elin Akkxnes, and Ivar M. Dahl, Facilitated transport of ethane through Nafion membranes. Part I. Water swollen membranes, *J. Memb. Sci.*, **85**, 89-97 (1993), Part II. Glycerine treated, water swollen membranes, *J. Memb. Sci.*, **85**, 99-106 (1993).
 13. Takeo Yamaguchi, Chelsey Baertsch, Carl A. Koval, Richard D. Noble, and Christopher N. Bowman, Olefin separation using silver impregnated ion exchange membranes and silver salt/polymer blend membranes, *J. Memb. Sci.*, **117**, 151-161 (1996).
 14. I. Pinnau, L. G. Yoy, S. Sunderrajan, and B. D. Freeman, solid polymer electrolyte membranes for olefin/paraffin separation, *Polym. Mater. Sci. Eng.*, **77**, 269 (1997).
 15. Yosang Yoon, Jongok Won, and Yong Soo Kang, Polymer electrolyte membranes containing silver ion for facilitated olefin transport, *Macromolecules*, **33**(9), 3185 (2000).
 16. Dongkyum Ko, Jonghak Kim, Sung Taik Chung, and Yong Soo Kang, Analysis of facilitated olefin transport through polymer electrolyte membranes containing silver salts, *Membrane J.*, **13**(4), 239-245 (2003).
 17. Ingo Pinnau and Lora G. Toy, Solid polymer electrolyte composite membranes for olefin/paraffin separation, *J. Memb. Sci.*, **184**, 39-48 (2001).
 18. Silver doped Nafion-poly(pyrrole)membranes for facilitated permeation of liquid-phase olefins, A. Sungpet, J. D. Way, A. A. Koval and M. E. Eberhart, *J. Memb. Sci.*, **189**, 271-279 (2001).