Selective Transport of Propylene by Silver Ion Complex Through an Immobilized Liquid Membrane

M. Takht Ravanchi[1,2], T. Kaghazchi[1], A. Kargari[3]*

1- Center of Excellence for Petrochemical Engineering, Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran.
2- National Petrochemical Company, Research and Technology Co., Tehran, Iran.
3- Petrochemical Engineering Department, Amirkabir University of Technology (Tehran Polytechnic), Mahshahr Campus, Mahshahr, Iran

Abstract

The separation of hydrocarbon mixture using facilitated transport membrane (an immobilized liquid membrane type) was investigated. A 50:50 (vol. %) propylene-propane mixture was used as a sample of the hydrocarbon mixture. The effect of trans-membrane pressure (in the range of 50-120 kPa) and carrier concentration (in the range of 0-20 wt.% $AgNO_3$) on separation performance was studied experimentally and mathematically. It was observed that increasing trans-membrane pressure and carrier concentration supports the separation factor and propylene permeation rate. On the other hand, increasing trans-membrane pressure and decreasing carrier concentration supports the propane permeation rate. Hence, the greater the trans-membrane pressure and carrier concentration, the more purified the product obtained. It was found that at trans-membrane pressure of 120kPa and carrier concentration of 20wt. %, the highest separation factor (270) and propylene permeation rate ($7*10^{-7}mol/s$) was obtained. The average deviation between the experimental and modeling results was found to be 5.3% for propylene permeation rate and 0.03% for propane permeation rate.

Keywords: *Facilitated Transport, Immobilized Liquid Membrane, Modeling, Propylene, Propane, Silver Nitrate*

1. Introduction

In the petrochemical industry, propylene is one of the most important chemicals used for the production of polypropylene, acrylonitrile, propylene oxide, oxo alcohols, cumene, acrylic acid and isopropyl alcohol. In 2006, 69.577million tons of propylene per year were produced in the world from which 0.454million ton per year were produced in Iran.

Various petrochemical streams contain propylene and propane. An important step in their manufacture is the large scale separation of propylene from propane. Over the years, different processes have been used for the separation of olefin-paraffin mixtures, such as low-temperature distillation, extractive distillation, physical or chemical adsorption and physical or chemical absorption [1, 2].

∗ Corresponding author: kaghazchi@aut.ac.ir

Industrially, this separation is carried out by cryogenic distillation, which is highly energy-intensive due to the cryogenic temperatures required for the process and the low relative volatilities of the components. Due to the large capital expense and energy cost required for cryogenic distillation, researchers have tried to propose a substitute separation process [3].

Membrane technologies have recently emerged as an additional category of separation processes to the well-established mass transport processes. Membrane separation technologies offer advantages over existing mass transfer processes, such as high selectivity, low energy consumption, moderate cost to performance ratio and compact and modular design [4-8].

The separation of propylene-propane mixtures using conventional polymeric membranes has not been effective because the physico-chemical properties of propylene and propane such as their molecular size and solubility are largely indistinguishable [9, 10]. Results obtained by Krol and co-workers [11], Bai and co-workers [12], Sridhar and Khan [13], Staud-Bickel and Koros [14], Burns and Koros [15], and Tanaka and co-workers [16] show that the application of such membranes is not attractive for industrial purposes because of the relatively low separation factors (less than 10) obtained.

Facilitated transport membranes are another type of membrane in which some carriers were incorporated that can selectively transport a special carrier along the membrane thickness. "Solid polymer electrolyte (SPE) membrane" and "immobilized liquid membrane (ILM)" are two categories of facilitated transport membranes that can be used for propylene-propane separation. ILMs are made by impregnating a microporous membrane with a solution containing the carrier. The carrier solution is held within the pores of the membrane by capillary forces. In solid polymer electrolyte membrane, carrier ion is incorporated in the membrane matrix in the membrane preparation procedure.

SPE membranes containing silver salt as the carrier have inherent disadvantages. One disadvantage is that their separation performance may decrease with time. Another problem is that if feed gas contains impurities, such as H_2S or the like, the membrane will become poisonous and must be replaced. But in the case of impurities for immobilized liquid membrane system, by implementing a circulation line for the carrier solution this problem can be overcome, the liquid phase inside the pores of the membrane will be replaced, the membrane filter can be used, and there is no need for its replacement.

Results obtained by Kim and co-workers [17-19], Yoon and co-workers [20] and Park and co-workers [21] show that facilitated transport membrane (solid polymer electrolyte type) has a better performance for propylene-propane separation.

In most of the previous studies researchers used solid polymer electrolyte membranes for the separation of propylene-propane mixture. As preparation of ILM is simpler than SPE membrane, and because of its operational advantages, in the present study, an immobilized liquid membrane was used for the separation of 50:50 (vol. %) propylene-propane mixture. The influence of

trans-membrane pressure and carrier concentration on the separation performance was studied experimentally and theoretically. As most of the petrochemical propylene-propane mixtures are 50:50 (vol. %), in this study, this mixture was used as the feed gas.

2- Facilitated Transport in Membrane

It is well known that some transition metals react reversibly with alkenes in the solution. The ability of the transition metal ion as a carrier is largely dependent on the intensity of the π-complexation with alkenes. The intensity of the π-complexation with alkenes is determined primarily by the electronegativity, which is a measure of the relative strength of an atom in a molecule to attract bonding electrons to itself. The electronegativity values of transition metals are presented in Table 1 [22].

The greater the electronegativity, the more strongly metal atoms draw binding electrons. If the electronegativity of the metal is excessively high, the metal is not suitable for the facilitated carrier because it is susceptible to irreversible reaction with the π electrons of the alkene; otherwise, if the electronegativity is too low, the metal is also impractical as a carrier due to its weak interaction with the alkene. For reversible reaction between the transition metal ion and the alkene, the electronegativity of the metal is preferably in the range of 1.6 to 2.3 [22].

To increase the reversible reactivity of the transition metal ion with the alkene, the anion of the transition metal plays an important role in determining the intensity and the rate of the interaction between a carrier and alkene. The lower the lattice energy of the transition metal salt, the weaker the ionic bond between the anion and the cation in the metal salt. Therefore, it is preferable to select the anion of the transition metal salt having low lattice energy with respect to the cation. The lattice energies of the representative transition metals are presented in Table 2 [22].

In the facilitated transport membrane, the transition metal salt preferably has lattice energy of less than 2500 kJ/mol, reducing the tendency of the anion of the transition metal salt to form a strong ion pair with the cation. According to Tables 1 and 2, only Cu^+ and Ag^+ have these two criteria, i.e. their electronegativity is in the range of 1.6 - 2.3 and the lattice energy of their salts is less than 2500 kJ/mol. As can be seen in Table 2, for a specified anion, the lattice energy of Ag^+ salt is less than that of Cu^+ salt. Therefore, Ag^+ is a suitable carrier for olefin facilitation transport.

Table 1. The electronegativity values of transition metals [22]

Transition metal	Sc	TI	V	Cr	Mn	Fe	Co	Ni	Cu
Electronegativity	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9
Transition metal	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Electronegativity	1.3	1.3	1.6	2.2	1.9	2.2	2.3	2.2	1.9
Transition metal	La	Hf	Th	W	Re	Os	Ir	Pt	Au
Electronegativity	1.0	1.3	1.5	2.4	1.9	2.2	2.2	2.3	2.5

Table 2. Lattice energy of metallic salts (kJ/mole) [22]

	Li^+	Na^+	K^+	Ag^+	Cu^+	Co^{2+}	Mo^{2+}	Pd^{2+}	Ni^{2+}	Ru^{3+}
F^-	1036	923	823	967	1060	3018			3066	
Cl^-	853	786	715	915	996	2691	2733	2778	2772	5245
Br^-	807	747	682	904	979	2629	2742	2741	2709	5223
I^-	757	704	649	889	966	2545	2630	2748	2623	5222
CN^-	849	739	669	914	1035					
NO_3^-	848	756	687	822	854	2626			2709	
BF_4^-	705	619	631	658	695	2127			2136	
ClO_4^-	723	648	602	667	712					
$CF_3SO_3^-$	779	685	600	719	793					
$CF_3CO_2^-$	822	726	658	782	848					

Facilitated transport of olefin is shown in Fig. 1. Olefin is complexed with a complexing agent M^+ such as Ag^+ incorporated in the membrane at the high-pressure side. The complex diffuses owing to its concentration difference across the membrane from the high-pressure side to the low-pressure side, where decomplexation takes place to release the olefin. The complexing agent regenerated from the decomplexation diffuses back to the high-pressure side due to its concentration difference between the low- and high-pressure sides. This completes a facilitated transport cycle, and the complexing agent repeats the cycles. Because of the complexation, the concentration of the olefin in the membrane is increased, and the transport of the olefin is facilitated. On the other hand, paraffin cannot complex with the complexing agent, and the majority of the paraffin is rejected by the membrane. The concentration of the paraffin in the membrane is small by physical solubility, and its transport rate through the membrane is low. Therefore, the facilitated transport membrane can give a high olefin/paraffin

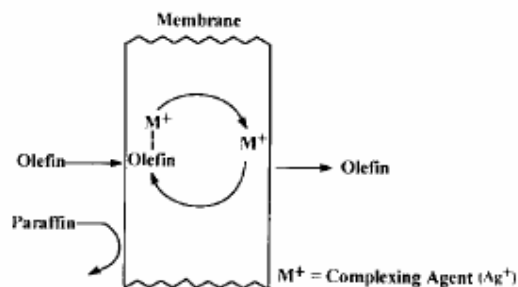selectivity to yield a permeate with high olefin purity [23, 24].

Figure 1. Facilitated transport mechanism in a membrane [24]

3. Experiments

3.1. Chemicals

Industrial grade propylene with 99.74 mol. % purity from Tabriz Petrochemical Company and industrial grade propane with 99.79mol.% purity from Tehran Refinery Complex were used as feed gases and pure nitrogen was used as the sweep gas. Silver Nitrate (AgNO₃, GR Pro Analysis) purchased from Merck Co. was used as the carrier of propylene. Polyvinilydene diflouride (PVDF) flat sheets (Durapore from Millipore) were used as the membrane.

3.2. Experimental Setup

The schematic diagram of the experimental setup is shown in Fig. 2. All tubing used to connect all parts of the setup was stainless steel (AISI 316). The experimental procedure is as follows.

Propylene and propane, after passing through mass flow controllers (Brooks Instruments, model 5850S), were mixed and entered the humidifier. The humidified feed passes through a temperature control system and enters the membrane cell. A combination of a heater and a cooler were used as the temperature control system. The feed gas was introduced to the upper compartment of the cell and the sweep gas, nitrogen, was supplied to the lower compartment. The main product, permeate, was collected from the lower compartment and the secondary product, retentate, was collected from the upper compartment. Back pressure regulators (BPR, Tescom, Germany) were used on product lines to control the pressure of the system. During all experiments, the sweep gas was controlled at atmospheric pressure. The experiments were conducted at room temperature (298±5K). All the experimental data were obtained after the system reached its steady-state condition which took as long as 4 hours.

3.3. Analysis

The gas composition was determined by a Gas Chromatograph (Agilent 6890N) equipped with a Flame Ionization Detector (FID, Agilent Technologies Inc. column, HP Al/S, 0.53 mm in diameter, and 50 m in length).
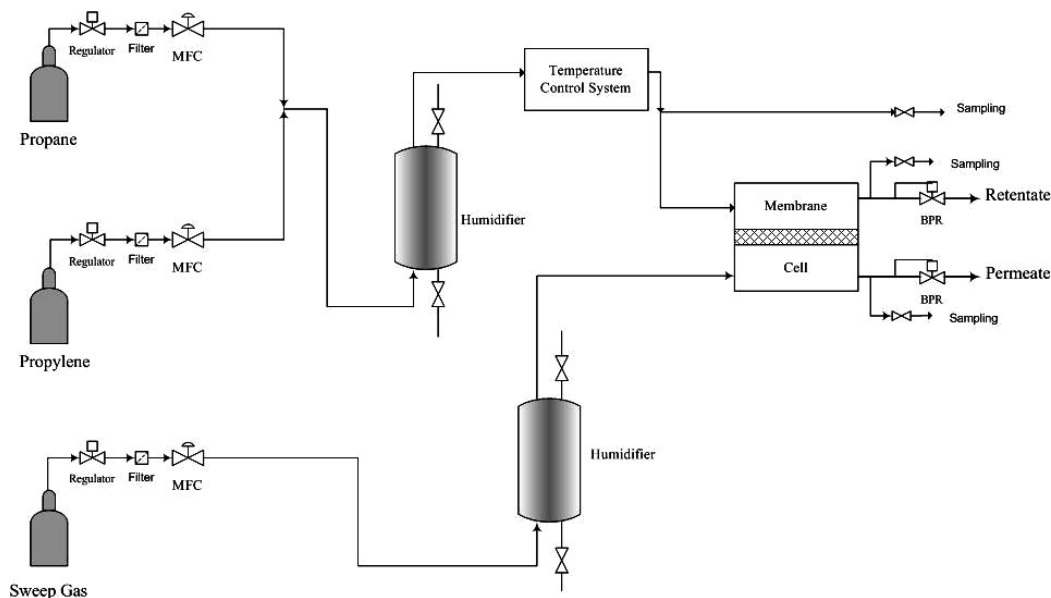

Figure 2. Schematic diagram of the supported liquid membrane system

4. Modeling

The most common generalized and overall reaction scheme for the transport of a gaseous component across a liquid film reported in the literature was [25, 26]:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P \tag{1}$$

The general equation of mass balance was written as:

$$\frac{\partial C_i}{\partial t} + V_i \nabla C_i = D_i \nabla^2 C_i + R_i \tag{2}$$

As the membrane pores are narrow and the viscosity and surface tension of the liquid phase is so high, the transport of permeants in the radial direction can be neglected. Thus, with the assumption of one-dimensional steady-state transport in a rectangular geometry and neglecting convective terms, equation (2) was simplified as shown below:

$$D_i \nabla^2 C_i + R_i = 0 \tag{3}$$

Using equation (1) for reaction rate of component i and expanding equation (3) for each component, the correlations below were obtained:

$$D_A \frac{d^2 C_A}{dx^2} = k_1 C_A C_B - k_2 C_P \tag{4}$$

$$D_B \frac{d^2 C_B}{dx^2} = k_1 C_A C_B - k_2 C_P \tag{5}$$

$$D_P \frac{d^2 C_P}{dx^2} = -k_1 C_A C_B + k_2 C_P \tag{6}$$

with boundary conditions:

$$@\, x = 0, \; C_A = C_{A0}, \; \frac{dC_B}{dx} = \frac{dC_P}{dx} = 0 \tag{7}$$

$$@\, x = L, \; C_A = C_{AL}, \; \frac{dC_B}{dx} = \frac{dC_P}{dx} = 0 \tag{8}$$

The conservation of the carrier in the membrane was expressed as:

$$\int_0^L \left(C_B + C_P \right) dx = C_{BT} L \tag{9}$$

In order to find the concentration profile of the components, equations (4) to (6) must be solved. For simplification, the above equations and boundary conditions were transformed into dimensionless form (dimensionless parameters are introduced in section "Notations"):

$$\frac{d^2 a}{dy^2} = \delta^2 ab - \frac{\delta^2}{K} p \tag{10}$$

$$\frac{d^2 b}{dy^2} = \frac{\delta^2}{q} ab - \frac{\delta^2}{qK} p \tag{11}$$

$$\frac{d^2 p}{dy^2} = -\frac{\delta^2}{rq} ab + \frac{\delta^2}{rqK} p \tag{12}$$

$$@\, y = 0, \; a = 1, \frac{db}{dy} = \frac{dp}{dy} = 0 \tag{13}$$

$$@\, y = 1, \; a = a_L, \frac{db}{dy} = \frac{dp}{dy} = 0 \tag{14}$$

$$\int_0^1 \left(b + p \right) dy = 1 \tag{15}$$

Solving equations (10) to (12) using conditions given in equations (13) to (15), concentration profiles along the membrane were obtained. As it is obvious, the governing differential equations for this system were nonlinear. These sets of equations were solved by orthogonal collocation method.

Facilitated transport process was characterized by facilitation factor (F) which was defined as the ratio of the solute flux in the presence of the carrier to the solute diffusion flux without carrier. Therefore, it was expressed as:

$$F = \frac{-D_A \left(dC_A/dx\right)_{x=0}}{\left(D_A/L\right)C_{A0}} = -\left(\frac{da}{dy}\right)_{y=0} \qquad (16)$$

Permeation rate was calculated as shown below:

$$J_A = -\frac{D_{eA}}{L} F \left(C_{AL} - C_{A0}\right) \qquad (17)$$

in which F was calculated from equation (16).

In the absence of a carrier in the membrane, there was no facilitation transport and solute diffused across the membrane thickness according to Fick's law [27]. Thus:

$$J_A = -\frac{D_{eA}}{L}\left(C_{AL} - C_{A0}\right) \qquad (18)$$

As solute permeation occurred in porous media, an effective diffusion coefficient must be used and is defined as [28]:

$$D_{eA} = D_A \frac{\varepsilon}{\tau} \qquad (19)$$

5. Results and Discussion
5.1. Experiments
A series of experiments were conducted at room temperature (298±5K) and the effect of trans-membrane pressure and carrier concentration on membrane separation performance was investigated, the results of which were shown in Table 3.

As it can be seen, increasing the trans-membrane pressure supports the separation factor and propylene permeation rate. Facilitated transport is a combination of two processes: absorption (on the feed side) and stripping (on the permeate side). Increasing the pressure supports absorption while decreasing the pressure supports stripping. Thus, increasing the feed pressure increases the absorbed propylene on the feed side. Due to the pressure difference between the feed side and permeate side, the complexed propylene is decomplexed on the permeate side. Therefore, the higher the trans-membrane pressure, the greater the driving force for separation. Hence, more propylene was transported across the membrane.

Propane cannot have interaction with the carrier molecule, therefore, its permeation is only via Fickian diffusion. The greater the trans-membrane pressure, the greater the driving force for its permeation. Hence, increasing the trans-membrane pressure supports propane permeation. This concept is in agreement with the experimental results of Table 3.

Addition of carrier to the membrane has a positive influence on the separation factor and propylene permeation rate. This confirms that silver ion is a suitable carrier for facilitated transport of propylene.

Table 3- Membrane performance for the separation of 50:50 (vol. %) propylene-propane mixture

Trans-membrane Pressure (kPa)	Separation Factor	Permeation Rate (10^9 mol/s)	
		Propylene	Propane
0 wt. % AgNO$_3$ Solution			
50	4.08	1.9	1.750
70	4.88	2.0	1.960
100	6.04	2.2	2.483
120	6.83	2.4	2.920
5 wt. % AgNO$_3$ Solution			
50	44.45	57.2	1.080
70	55.50	84.2	1.533
100	64.79	101.2	1.810
120	70.43	110.3	2.250
10 wt. % AgNO$_3$ Solution			
50	59.97	86.5	0.630
70	82.33	126.0	0.828
100	111.36	190.0	1.305
120	130.58	223.3	1.440
20 wt. % AgNO$_3$ Solution			
50	187.68	290.0	0.160
70	221.22	440.0	0.250
100	249.00	631.7	0.330
120	269.27	733.3	0.600

In facilitated transport membranes, propylene permeation occurs via two mechanisms: Fickian diffusion and facilitation transport. In the absence of carrier (Ag^+) in the membrane, propylene was permeated only via Fickian diffusion. The greater the trans-membrane pressure, the greater the driving force for propylene permeation. Hence, permeation rate increases with an increase in trans-membrane pressure. When the carrier was added to the membrane system, propylene was permeated via Fickian diffusion and facilitated transport. Based upon facilitated transport mechanism, when more carriers are available in the membrane, more propylene can be transported along the membrane thickness by facilitation mechanism and the separation performance of the membrane was improved.

Carrier concentration has an inverse influence on propane permeation rate. In liquid solutions, diffusion coefficient is inversely proportional to viscosity. Therefore, when the carrier concentration was increased, diffusion coefficient of propane was decreased. As propane permeation is based upon Fickian diffusion, with a decrease in diffusion coefficient, propane permeation rate is decreased as well. This is the same as what is observed in Table 3.

From the results of Table 3, it can be concluded that when a specified concentration of carrier is incorporated in the membrane and at a specific trans-membrane pressure, the propylene permeation rate is higher than propane permeation rate. This confirms that this facilitated transport membrane is more selective to propylene.

5.2. Modeling

In order to investigate the influence of operating parameters on permeation rates, equation (17) (in case of the presence of carrier in the membrane) and equation (18) (in case of the absence of carrier in the membrane) were used.

The physico-chemical properties of the present membrane system were summarized in Table 4.

Table 4. Physico-chemical properties of the membrane system [29, 30]

Property	Value
Diffusion coefficient (10^9 m²/s)	
propylene-water	1.26
propylene- 5wt.% AgNO₃	1.11
propylene-10wt.% AgNO₃	1.09
propylene-20wt.% AgNO₃	1.02
propane-water	1.18
propane - 5wt.% AgNO₃	1.04
propane -10wt.% AgNO₃	1.02
propane -20wt.% AgNO₃	0.95
carrier	1
complex	1
Henry's constant (mol/kPa.m³)	
propylene	0.047
propane	0.014
K_{eq} (m³/mol)	0.116
k_1 (m³/mol.s)	20

In equation (19), D_A is the diffusion coefficient in the carrier solution. Wilke-Chang equation [27] was used for calculating diffusion coefficients.

Cho and co-workers [31] developed an empirical expression for the propylene-Ag⁺ system involving the solubility of propylene as a function of AgNO₃ concentration, pressure and temperature:

$$\ln C_A = 0.6004 \ln P_A + \frac{6750}{T + 210.4} + 0.8425 \ln C_B - 13.41 \tag{20}$$

in which

C_A: propylene concentration in silver nitrate solution (mol/L)

P_A: absolute partial pressure of propylene (MPa)

C_B: carrier concentration (mol/L)

In the case of the solubility of propylene and propane in water, Henry's law was used.

$$C_A = H_A P_A \tag{21}$$

The effect of trans-membrane pressure and carrier concentration on propylene and propane permeation rates were depicted in Figs. 3 and 4. In these figures, solid lines were the modeling results and the symbols were the experimental results.

As it is obvious, increasing the trans-membrane pressure and carrier concentration is in favor of the propylene permeation rate (Fig. 3). On the other hand, increasing the trans-membrane pressure and decreasing the carrier concentration is in favor of the propane permeation rate (Fig. 4). These results are in agreement with what is observed experimentally and there is a good agreement between the experimental and modeling results.
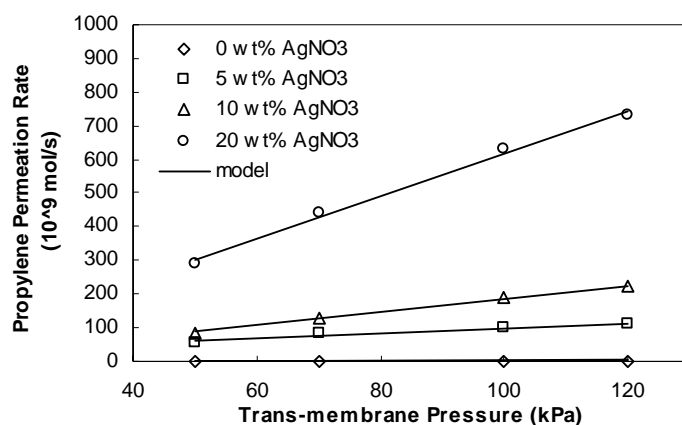
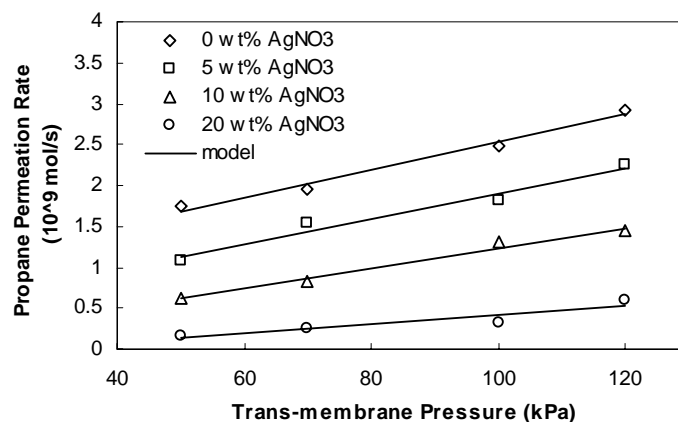**Figure 3.** The effect of trans-membrane pressure on propylene permeation rate

Figure 4. The effect of trans-membrane pressure on propane permeation rate

6. Comparison between Various Membrane Systems for Propylene-Propane Separation

Different membrane systems used for propylene-propane separation were listed in Table 5. As it is obvious, polymeric membranes have weak performance for propylene-propane separation. The highest separation factor obtained is 9, which is very low for industrial purposes. Solid polymer electrolyte membranes presented a better separation performance for the propylene-propane mixture. As can be seen in Table 5, with the use of a solid polymer electrolyte membrane which was PAAm-AgBF$_4$ containing 67mol. % Ag$^+$, a separation factor of 170 was obtained which is significantly higher than that of polymeric membranes.

Duan and co-workers [32] reported a double-layer membrane in which triethylene glycol (TEG) and its mixture with AgBF$_4$ and AgNO$_3$ were used as immobilized liquid

membrane. The highest separation factor obtained was 110 for TEG/AgBF$_4$ liquid membrane.

By means of a gas/liquid membrane contactor containing AgBF$_4$ as the absorption liquid, for propylene-propane separation, Chilkuri and co-workers [33] reported a separation factor of 250.

In the present work, with the use of an immobilized liquid membrane containing 20wt.% Ag$^+$ for propylene-propane separation, a separation factor of 270 was obtained which is higher than the previous results obtained in solid polymer electrolyte membranes and immobilized liquid membrane. Thus the current immobilized liquid membrane system performs the best in comparison with other available membrane configurations in terms of the separation factor for propylene-propane separation.

7. Conclusions

The separation of a 50:50 (vol. %) propylene-propane mixture using facilitated transport mechanism was investigated. The effect of two operating parameters, trans-membrane pressure and carrier concentration, on the separation performance of the membrane was studied experimentally and mathematically. It was found that with increase in trans-membrane pressure and carrier concentration, the separation factor and propylene permeation rate were increased, while the propane permeation rate was decreased. Hence, a more purified product can be obtained. It is worth mentioning that in order to determine the optimum values of operating parameters at industrial scale, some separation experiments should be performed at a pilot scale and feasibility studies should be done.

Table 5- Separation performance of different membrane systems for propylene-propane separation

Membrane system[1]	Separation Factor	Reference
PDMS	1.1	16
PSF	1.4	22
CA	2.6	22
PPO	9.1	16
PAAm-50 mol.% AgBF$_4$ [2]	40	17
PVMK-50 mol.% AgBF$_4$ [2]	54	18
PVP- AgBF$_4$ [2]	68	20
PAAm-67 mol.% AgBF$_4$ [3]	170	21
TEG [3]	2.4	32
TEG-AgNO$_3$ (50 wt. %)[3]	40	32
TEG-AgBF$_4$ (43 wt. %)[3]	110	32
Gas-liquid membrane contactor containing AgBF$_4$	250	33
20 wt.% AgNO$_3$ aqueous solution (3)	270	Present work

1- A detailed chemical description of the abbreviations used for polymer materials was given in [2]

2- Solid polymer electrolyte membrane

3- Immobilized liquid membrane

Notations

a	$\dfrac{C_A}{C_{A0}}$, (dimensionless)
A	Component being transported across the membrane
b	$\dfrac{C_B}{C_{BT}}$, (dimensionless)
B	Active chemical carrier
C_i	Concentration of component i, (mol/m^3)
D_i	Diffusion coefficient of component i, (m^2/s)
D_{ei}	Effective diffusion coefficient of component i, (m^2/s)
F	Facilitation factor, (dimensionless)
H_i	Henry's constant of component i, (mol/kPa.m^3)
J_i	Permeation rate of component i, (mol/m^2.s)
k_1	Forward reaction rate constant, (m^3/mol.s)
k_2	Reverse reaction rate constant, (s^{-1})
K	$K_{eq}C_{A0}$, (dimensionless)
K_{eq}	Reaction equilibrium constant, $\dfrac{k_1}{k_2}$, (m^3/mol)
L	Membrane thickness, (m)
p	$\dfrac{C_P}{C_{BT}}$, (dimensionless)
P	Active carrier complex
q	$\dfrac{D_B C_{BT}}{D_A C_{A0}}$, (dimensionless)
r	$\dfrac{D_C}{D_B}$, (dimensionless)
R_i	Reaction rate of component i
V_i	Velocity of component i, (m/s)
y	$\dfrac{x}{L}$, (dimensionless)

Subscript:

A	Permeant species
B	Carrier species
BT	Total carrier species
P	Complex species
0	Value at x=0 or y=0
L	Value at x=L or y=1

Greek Symbols:

δ	$\sqrt{L^2 \dfrac{k_1 C_{BT}}{D_A}}$, (dimensionless)
ε	Porosity
τ	Turtuosity

References

[1] Eldridge, R. B., "Olefin/paraffin separation technology: A review", *Ind. Eng. Chem. Res.,* **32**, 2208 (1993).

[2] Takht Ravanchi, M., Kaghazchi, T., and Kargari, A., "Application of membrane separation processes in petrochemical industry: A Review", *Desalination* **235**, 199 (2009).

[3] Takht Ravanchi, M., Kaghazchi, T., and Kargari, A., "Immobilized liquid membrane for propylene-propane separation", proceedings of *World Academy of Science, Engineering and Technology,* Paris, France, **30**, pp. 696-698 (2008).

[4] Kargari, A., Kaghazchi, T., and Soleimani, M., "Extraction of gold (III) ions from aqueous solutions using polyamine type surfactant liquid membrane", *Can. J. Chem. Eng.*, **82,** 1301 (2004).

[5] Kaghazchi, T., Kargari, A., Yegani, R., and Zare, A., "Emulsion liquid membrane pertraction of L-lysine from dilute aqueous solutions by D2EHPA mobile carrier", *Desalination*, **190**, 161 (2006).

[6] Nabieyan, B., Kaghazchi, T., Kargari, A., Mahmoudian, A., and Soleimani, M., "Bench-scale simultaneous extraction and stripping of iodine using bulk liquid membrane system", *Desalination*, **214**, 167 (2007).

[7] Kargari, A., Kaghazchi, T., Sohrabi, M., and Soleimani, M., "Batch extraction of gold (III) ions from aqueous solutions using emulsion liquid membrane via facilitated carrier transport", *J. Memb. Sci.*, **233**, 1 (2004).

[8] Mohammadi, S., Kaghazchi, T., and Kargari, A., "A model for metal ion pertraction through supported liquid membrane", *Desalination* **219**, 324 (2008).

[9] Kim, J. H., Park, S. M., Won, J., and Kang, Y. S., "Dependence of facilitated olefin transport on the thickness of silver polymer electrolyte membranes", *J. Membr. Sci.,* **236**, 209 (2004).

[10] Semenova, S. I., "Polymer membranes for hydrocarbon separation and removal", *J. Membr. Sci.,* **231**, 189 (2004).

[11] Krol, J. J., Boerrigter, M., and Koops, G. H., "Polymeric hollow fiber gas separation membranes: preparation and the suppression of plasticization in propane/ propylene environments", *J. Membr. Sci.,* **184**, 275 (2001).

[12] Bai, S., Sridhar, S., and Khan, A. A., "Metal-ion mediated separation of propylene from propane using PPO membranes", *J. Membr. Sci.,* **147**, 131 (1998).

[13] Sridhar, S., and Khan, A. A., "Simulation studies for the separation of propylene and propane by ethylcellulose membrane", *J. Membr. Sci.,* **159**, 209 (1999).

[14] Staudt-Bickel, C., and Koros, W. J., "Olefin/paraffin gas separations with 6FDA based polyimide membranes", *J. Membr. Sci.*, **170**, 205 (2000).

[15] Burns, R. L., and Koros, W. J., "Defining the challenges for C_3H_6/C_3H_8 separation using polymeric membranes", *J. Membr. Sci.,* **211**, 299 (2003).

[16] Tanaka, K., Taguchi, A., Hao, J. Q., Kita, H., and Okamoto, K., "Permeation and separation properties of polyimide membranes to olefin and paraffins", *J. Membr. Sci.,* **121**, 197 (1996).

[17] Kim, J. H., Min, B. R., Won, J., Joo, S. H., Kim, H. S., and Kang, Y. S., "Role of polymer matrix in polymer-silver complexes for structure, interaction, and facilitated olefin transport", *Macromolecules,* **36**, 6183 (2003).

[18] Kim, H. S., Ryu, J. H., Kim, H., Ahn, B. S., and Kang, Y. S., "Reversible olefin complexation by silver ions in dry poly (vinyl methyl ketone) membrane and its application to olefin/paraffin separations", *Chem. Commun.,* **14**, 1261 (2000).

[19] Kim, J. H., Min, B. R., Lee, K. B., Won, J., and Kang, Y. S., "Coordination structure of various ligands in crosslinked PVA to silver ions for facilitated olefin transport", *Chem. Commun.,* **22**, 2732 (2002).

[20] Yoon, Y., Won, J., and Kang, Y. S., "Polymer electrolyte membranes containing silver ion for facilitated olefin transport", *Macromolecules,* **33**, 3185 (2000).

[21] Park, Y. S., Won, J., and Kang, Y. S., "Facilitated transport of olefin through solid PAAm and PAAm-graft composite membranes with silver ions", *J. Membr. Sci.,* **183**, 163 (2001).

[22] Kang, Y. S., Park, H. Ch., Won, J. O., Hong, S. U., and Kwon, T. M., US Pat. 2001/0015334, Korea Institute of Science and Technology, (2001).

[23] Baker, R. W., Membrane technology and

applications, 2nd ed., John Wiley & Sons Ltd, England, p. 425 (2004).

[24] Takht Ravanchi, M., Kaghazchi, T., and Kargari, A., "A new approach in separation of olefin-paraffin gas mixtures by a membrane system", *Amirkabir Journal of Science and Research,* **19** (68), 47 (2008) (in Persian).

[25] Way, J. D., and Noble, R. D., Facilitated transport, in Winston Ho, W. S., and Sirkar, K. K. (Eds.), Membrane Handbook, Van Nostrand Publishing Company, New York, USA, p. 833 (1992).

[26] Noble, R. D., and Koval, C. A., Review of facilitated transport membranes, in Yampolskii, Y., Pinnau, I., and Freeman, B., (Eds.), Materials science of membranes for gas and vapor separation, 1st ed., John Wiley and Sons Ltd., England, p. 411, (2006)

[27] Treybal, R. E., Mass transfer operation, 3rd ed., Mc-Graw Hill, London, p. 21 (1990).

[28] Bird, R. B., Stewart, W. E., and Lightfoot, E. N., Transport Phenomena, 2nd ed., John Wiley, New York, USA, p. 793 (2002).

[29] Nymeijer, K., Visser, T., Brilman, W., and Wessling, M., "Analysis of the complexation reaction between Ag^{+} and ethylene", *Ind. Eng. Chem. Res.,* **43**, 2627 (2004).

[30] Craig, N. C., Goldberg, R. N., and Koetzle, T. F., (Eds.), CRC Handbook of chemistry and physics, 79th ed., New York, USA (1998).

[31] Cho, I. H., Cho, D. L., Yasuda, H. K., and Marrero, T. R., "Solubility of propylene in aqueous silver nitrate", *J. Chem. Eng. Data,* **40**, 102 (1995).

[32] Duan, Sh., Ito, A., and Ohkawa, A., "Separation of propylene/propane mixture by a supported liquid membrane containing triethylene glycol and a silver salt", *J. Membr. Sci.* **215**, 53 (2003).

[33] Chilukuri, P., Rademakers, K., Nymeijer, K., Ham, L. van der, and Berg, H. van den, "Propylene/propane separation with a gas/liquid membrane contactor using a silver salt solution", *Ind. Eng. Chem. Res.,* **46**, 8701 (2007).