Review

Olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques

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ABSTRACT

Seeking alternative olefin/paraffin separation techniques have been attracting great interest due to the high operating and capital costs of current commercially practiced separation processes. An olefin/paraffin separation scheme using membrane based facilitated transport/chemical absorption techniques offers great advantages such as reducing the operating and capital costs, as well as eliminating the operating drawbacks occurring in absorption processes such as flooding, foam formation, etc. Consequently, the utilization of a facilitated transport/chemical absorption scheme with a suitable membrane system for olefin/paraffin separation would be an attractive option for the replacement of the current separation technologies. A comprehensive review is presented for application of membranes for light olefin/paraffin separation. This article covers all types of membrane based facilitated transport/chemical absorption techniques which include various conventional liquid membranes configurations, membrane contactors and more advanced solid membrane electrolytes. The performance evaluation, shortcomings, and advantages are discussed in details.

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Contents

1. Introduction

1.1. Significance of olefins

Light unsaturated hydrocarbons play a vital role in the chemical and petroleum industry due to their utilization as raw materials for many products. Of special importance worldwide, ethylene and propylene are produced in large quantities and used as feed stocks in the production of polyethylene and polypropylene. Furthermore, light olefins are also considered as important to the chemical synthesis industry as they are used as starting ingredients for many chemicals. Just to mention a few, propylene is the main component in the production of chemicals such as acrylonitrile, propylene oxide, iso-propanol, allyl chloride, acrolein, acrylic acid and its esters, and cumene, whereas butylene isomers is the key factor in the manufacture of high-octane fuel additive Methyl Tertiary Butyl Ether (MTBE).

1.2. Current olefin production and separation processes

Olefins are usually produced in the petrochemical industry by several processes such as steam cracking, catalytic cracking, or catalytic dehydrogenation of paraffins. Among these processes, the most widely utilized process for olefins production is the cracking of C_4-hydrocarbons fractions, followed by dehydrogenation reactions. The yield conversion occurring in the second step is around 50–60%. On the other hand, processes such as catalytic dehydrogenation produces an equimolar mixture of olefins and paraffins and therefore, olefins must be separated from the gas mixture first before further utilization. However, the obtained olefin/paraffin gas mixture is difficult to separate due to their similar physical and chemical properties such as molecular sizes and boiling point.

The most promising methods for olefin/paraffin separation in the industry are reviewed in great details by Bryan (2004). These methods include the current commercially practiced approaches such as distillation and catalytic hydrogenation as well as other techniques which are near commercialization such as absorption/stripping based on aqueous silver nitrate solution and pressure-swing adsorption based on zeolite molecular sieves (Bryan, 2004). However, the most common method for olefin/paraffin separation in the industry is the energy-intensive low-temperature distillation process, commonly known as cryogenic distillation. The process usually contains two huge splitter columns to separate the complex saturated and unsaturated hydrocarbon vapor mixtures. A typical column of 120 trays is needed to separate C_2-hydrocarbon mixtures, whereas a bigger column of 180 trays is used for C_3-hydrocarbon separation. The high capital and operating costs associated with cryogenic distillation have created enough incentives for research to be carried on olefin/paraffin separation using alternative techniques.

Several processes have been proposed and investigated as cost-effective technologies for olefin/paraffin separation. The review article presented by Eldridge (1993) discussed in great details in the cryogenic distillation process as well as other alternatives such as extractive distillation, physical, and chemical adsorption/absorption. The advantages and disadvantages of these systems were well presented and summarized. In addition, Eldridge (1993) concluded that these processes are still ineffective to replace cryogenic distillation due to their inherit problems associated with these systems. However, chemical absorption of olefins is of a great interest and is discussed in great details below.

1.3. Olefin complexation theory

Olefin complexation with transition metal ions have been known for quite over a century. The idea of electron donor/acceptor complexes between olefins and metal ions was first recognized in 1827 with the discovery of a platinum(II)–ethylene complex (Safarik and Eldridge, 1998). In 1951, Dewar (1951) explained the chemical bonding between ethylene and silver ions was due to the interactions between the metal's atomic orbitals and the olefin's hybrid molecular orbitals, known as the molecular orbital theory. A few years later, Chatt and Duncanson (1953) redefined the proposed model by Dewar for platinum(II) and palladium(II)–olefin complexes. In general, the model proposed first by Dewar (1951) and later by Chatt and Duncanson (1953) is commonly known as the π-bond complexation. The model implies that the metal ion is located symmetrically above the olefin plane where two chemical bondings occur between the olefin and the metal ion as shown in Fig. 1. The first bond is called a σ-bond which occurs by the overlap of the vacant outermost s atomic orbital of the metal with the full π molecular orbital of the olefin. This new molecular orbital contains high electron density due to the donation of electrons from the olefin to the metal. Usually for Cu(I) and Ag(I) ions, the outermost s orbitals are
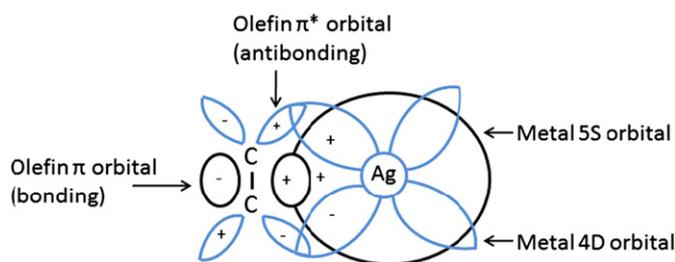
Fig. 1. π-Complexation between olefins and silver metal ions.

Table 1
Transition metals electronegativity.

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

Table 2
Lattice energy of common metal salts (kJ/mol).

	Li^+	Na^+	K^+	Ag^+	Cu^+	Co^{2+}	Mo^{2+}	Pd^{2+}	Ni^{2+}	Ru^{3+}
F^-	1036	923	823	697	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					
$CFSO_3^-$	779	685	600	719	793					
$CFCO_2^-$	822	726	658	782	848					

empty due to the absence of electrons which are lost upon ionization. On the other hand, for nonionizing facilitators, the metals are often bound to electronegative atoms where these atoms withdraw electron density from the metals, resulting in a partial positive charge and a substantially vacant outermost s orbital. In both cases, the metals' outermost s orbitals are empty and applicable for olefin complexation; however, the strength of the bond depends on the magnitude of the positive charge that the metals possess. The second bond is a π-bond which results from the back-donation of electrons from the full outer 4d atomic orbital shell of the metal to the vacant π^* (antibonding) molecular orbital of the olefin. This new molecular orbital has a nodal plane of electron density between the members of the bond.

The ability of a transition metal ion to act as a carrier for olefins is largely dependent on the intensity of the π-complexation between the metals and olefins. The intensity and the strength of the π-complexation are determined primarily by the electronegativity of the ion, which is a chemical property that describes the ability of an atom (or more rarely a functional group) to attract electrons (or electron density) towards itself in a covalent bond. An atom's electronegativity is affected by both its atomic weight and the distance that its valence electrons reside from the charged nucleus. The higher the associated electronegativity number, the more an element or compound attracts electrons towards itself. The electronegativity values of transition metals possible for olefin complexation are presented in Table 1. With greater electronegativity, the metal atom draws bonding electrons more strongly. However, if the electronegativity of the metal is excessively high, the metal is not suitable for the facilitated carrier because it is difficult for the reverse reaction to occur; otherwise if the electronegativity is too low, the metal is also impractical as a carrier due to its weak interaction with olefins. For reversible reactions to occur between the transition metal ion and olefins, the electronegativity of the metal is preferable to be in the range of 1.6–2.3 (Kang et al., 2001).

To increase the reversible reactivity of the transition metal ion with olefins, the anion of the transition metal plays an important role in determining the intensity and the rate of the interaction between the carrier and olefins. With lower lattice energy of the transition metal salt, the anion forms a weak ionic bond or ion pair with the cation and the salt is easily dissolved in solutions. It is therefore, preferable to select a transition metal's anion that possesses low lattice energy with respect to the metal's cation.

The lattice energies of the representative transition metals are presented in Table 2 (Kang et al., 2001). For facilitated transport to occur, the transition metal salt's lattice energy is preferably less than 1000 kJ/mol, reducing the tendency of the anion of the transition metal salt to form a strong ion pair with the cation.

1.4. Olefin/paraffin separation using chemical absorption

Chemical absorption can be certainly utilized to enhance olefin/paraffin separation due to the chemical characteristic of transition metal ions to bind specifically and reversibly with olefins (Herberhold 1972, 1974). Chemical complexation offers a great advantage that the bonds formed between the transition metal ions and olefins are stronger than those formed by Van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bounded. At the same time, the bonds are still weak enough to be broken by using simple engineering operations such as increasing the temperature or decreasing the pressure (King, 1987). An olefin/paraffin separation process based upon reactive absorption has several major advantages. Firstly, a chemical absorption scheme utilizes a mass transfer separating process based on the gas solubility into the liquid phase followed by the reversible reactions, rather than the transformation of mass from the liquid to the gas phase based on energy input as obtained in distillation processes. This advantage should reduce the energy requirement for the process significantly and thus, operating cost should also be lessened. Secondly, a suitable absorption medium with high olefin capacity as well as rapid reversible reaction rates would allow for the usage of a smaller absorption column or packed tower compared with the huge distillation towers. This benefit would surely decrease the capital and equipment cost as well.

Due to the potential benefits that chemical absorption can offer over current distillation techniques, many industrial firms have looked into the utilization of different transition metals as the absorbent solvents for olefin/paraffin separation. After the absorption step, the olefins would be easily released from the absorption medium due to ability of the transition metal–olefin complex to undergo reversible reactions under favorable operating conditions such as increasing the temperature or decreasing the pressure. Aqueous silver nitrate solution is considered to be the most characterized absorbent solvent for olefin/paraffin separation up to date. A complete review of olefin recovery by aqueous silver nitrate solutions is given by Keller et al. (1992). The published review included vapor–liquid equilibrium data, process engineering and design considerations, and economic and risk analysis. Keller et al. (1992) also discussed the industrial olefin separation process developed by Union Carbide using aqueous silver nitrate as the absorbent solvent. The gas stream containing ethylene is fed to the bottom of a countercurrent flow packed absorption column. A packed rather than tray column was

preferred to minimize the solution supply into the column. The column operating conditions were 240 psia and 30–40 °C. However, the presence of the impurities in the feed stream were a potential problem to the process efficiency due to silver deactivation when interacted with other compounds other than olefins. Perhaps, the major contaminants among others were hydrogen sulfide and acetylene. Keller et al. (1992) suggested the only solution to this problem was pretreatment to reduce the concentration of these compounds to low levels, possibly below 1 ppm. On the other hand, other impurities such as CO, CO_2, and saturated hydrocarbons were not a threat to silver ions because these components were only physically absorbed into the solution and can be easily desorbed in a venting tower. On the other hand, the presence of hydrogen gas can result in a gradual reduction of silver ions which results in the subsequent precipitation of metallic silver. A possible solution to this problem is the addition of small quantities of an oxidizing agent to the solvent just prior to the entrance of the absorption column, commonly hydrogen peroxide or nitric acid.

Copper(I) ion also posses similar chemical and physical properties as silver(I) ion and thus, can also be utilized for olefin/paraffin separation. However, unlike aqueous silver nitrate, the chemistry of aqueous copper solutions complexing with olefins remains partially unknown. This is because copper has been studied less extensively than the corresponding silver systems for olefin absorption and as a consequence, it is difficult in today's literature to find any particular details about gas solubility, reaction mechanisms, and/or complexation/decomplexation kinetic rates concerning aqueous copper solutions with olefin. As mentioned by Safarik and Eldridge (1998), the most fundamental study and detailed source of copper complexation with unsaturated hydrocarbons still remains the one developed by Long (1972) who published about four decades ago on the usage of solid copper salts for olefins recovery from their respective paraffin gas mixtures. However, the lack of details and theories about copper complexation with olefins have not prevented industrial firms and/or research institutions from attempting copper as a facilitation factor for olefin recovery. As pointed out by Miller (1969) and then later on by Safarik and Eldridge (1998), the first attempt on using copper solutions for olefin recovery was performed in the 1930s when Synthetic Ammonia and Nitrate Ltd. carried on experimental and pilot-plant work on copper solutions called "Copper Liquor" for the selective olefin recovery from gas streams. However, copper acetylide formation presented a safety hazard and destroyed the facilitation agent. This effort was abandoned, as no practical means of reducing the acetylene concentration below 1 ppm was available at the time. A few decades later in 1958, Imperial Chemical Industries (I.C.I.) employed aqueous ethanolamine cuprous nitrate for ethylene recovery from cracked gases (Miller, 1969; Safarik and Eldridge, 1998). The process also included an amine scrubber column to reduce the concentration of CO_2 in the gas stream from 14% to 0.4% volume. In addition, selective dehydrogenation was also implemented to reduce the acetylene concentration from 7% volume to 1 ppm to avoid copper acetylide formation and therefore, maximizing the availability of copper ions for olefin complexation.

Usually, in copper aqueous systems, the cupric state of copper is more stable than that of the cuprous state (Blytas, 1992). And since many side reactions may occur between copper ions and olefin/paraffin streams in solutions, the presence of Cu(II) rather than Cu(I) is usually more favorable. This behavior results in the depletion of Cu(I) ions which possibly would coordinate with olefins through chemical complexation and thus, less olefin absorption is obtained. As a consequence, nonaqueous copper-based solutions have also been proposed for selective separation of olefins rather than using aqueous copper aqueous solutions.

A commercial process which utilizes a bimetallic salt is detailed by Gutierrez (1978). The process licensed by Tenneco is based on a cuprous aluminum tetrachloride salt dissolved in an aromatic solvent such as toluene. The ethylene recovery in the process was approximately 96% at 99.5% purity from a refinery gas containing 12% ethylene. A combination of pressure reduction and thermal swing was used to regenerate the complexing agent. Significant feed pretreatment was also required to remove feed contaminants such as H_2S and CO_2 which can interfere with complex formations and destroy the complexing agent. Other absorption and equilibrium kinetics for copper complexation with ethylene is given by Reine and Eldridge (2005) for a novel solvent consisting of CuCl/aniline/n-methyl pyrrolidone.

For more details about chemical absorption technologies which utilize silver and copper ions for olefin/paraffin separation, the article by Safarik and Eldridge (1998) is highly recommended. The authors discussed in details the reversible chemical complexation of silver and copper ions with olefins as a potential alternative technology to distillation. Use of such a facilitated transport process could substantially reduce the capital costs and energy requirements of olefin/paraffin separations. Several pilot plants and industrial processes using chemical complexations were discussed and a comparison between such processes was carried on. However, technologies such as chemical absorption processes are prone to deactivation by feed contaminants such as CO_2 and H_2S commonly found in refinery streams. Although chemical absorption may be promising for pure olefin/paraffin mixtures, the utilized conventional columns and pack tray towers suffer from many operating drawbacks such as flooding, foaming, entraining, and channeling which consequently increases the high capital and operating costs (deMontigny, 2005).

1.5. Olefin/paraffin separation using membranes

The use of membranes for olefin/paraffin separation as a potential replacement of the current cryogenic distillation have been ranked at the high level of importance by many research institutions and industrial firms due to the low operating cost of membranes. And therefore, it is not surprising that an enormous amount of data on the separation and permeation properties of various polymeric membrane materials for olefin/paraffin separation have been published. However, it is rarely found in the literature any reports that gather, assess, and evaluate the use of membranes for olefin/paraffin separation. As a result, the authors felt that it is necessary to perform an intensive evaluation regarding this topic in order to reveal the setbacks, shortcomings, and advantages associated with these systems.

Recently, a comprehensive review on light olefin/paraffin separation using polymeric membranes has been published (Faiz and Li, 2012). The authors concluded that although a number of polymeric materials have been tested for the separation of olefin/paraffin mixtures, it was not surprising that some rather low permeabilities and selectivities were obtained as olefins and paraffins usually have similar molecular sizes and solubilities and hence, resulting in poor separation performances. On the other hand, polyimides based membranes showed improved selectivities for olefins; however, the selectivity decreases dramatically for the vapor mixtures due to the strong plasticization effect. Polyimides also showed excellent ideal selectivities for olefins but it was in the cost of permeabilities, which makes it less attractive to encourage their use in large-scale applications. Therefore, many researchers have turned their attention to use facilitated transport mechanisms while utilizing a carrier within the membrane to enhance the transport of olefins while simultaneously minimizing the permeation of paraffins, which in return offers great selectivities.

In this study, a comprehensive evaluation of light olefin/paraffin separation using membrane based facilitated transport/chemical absorption techniques is presented. This article follows a historical trend starting with the first conventional liquid membranes used for olefin/paraffin separation, followed by more developed membrane techniques in both the liquid and solid states. The data for every specific membrane class is gathered, summarized, and tabulated. The advantages and shortcomings of each membrane category are also discussed in details. Finally, the efforts attempted on these membranes to enhance the separation properties as well as long term stabilities are highlighted.

2. Liquid membranes

There are a variety of types of membrane configurations which imposes a solvent for facilitated transport of a certain component from a gas mixture. Review articles about the recent development of liquid membranes and the application of liquid membranes for gas/vapor separation can be found by Kocherginsky et al. (2007) and Krull et al. (2008), respectively. Figoli (2010) also demonstrated the stabilization of liquid membranes for novel configurations and discussed their application for various gas separation applications. These membrane systems all fall within the central name of liquid membranes. Numerous researchers have made an effort to come up with special designations or titles for these membrane systems depending on their configuration and design. However, often in the literature, it can be found that majority of authors used different titles for the same membrane system. To avoid confusion and uncertainty with the reported literature, all types of liquid membranes used in this review article are classified based on their preparation method and operating mechanisms as discussed in the next few sections.

2.1. Immobilized liquid membranes (ILMs)

2.1.1. Supported liquid membranes (SLMs)

This is the simplest type of liquid membranes as it is prepared by simply impregnating the membrane in the facilitation solution where it is held within the pores of the membrane by capillary forces as shown below in Fig. 2.

Teramoto et al. (1986) were the first to investigate the facilitated transport of ethylene from ethylene/ethane vapor mixture through a microporous membrane impregnated in silver nitrate solution. It was found that the selectivity increases with increasing the concentration of silver nitrate, reaching about 1000 when the concentration of $AgNO_3$ was 4 M. However, after continuous experiments, the selectivity of ethylene was completely lost which was attributed to the evaporation of the solvent from the pores of the membrane. Although both feed and sweep gases were passed through water vapor saturators before being introduced into the permeation cell, it seemed that the vapors were not completely saturated with water vapor and thus, evaporation of the solvent occurred.

Kawakami et al. (1987) studied the solubilities and permeabilities of ethylene and propylene for a SLM prepared by impregnation a glass microfiber filter in a poly(ethylene golycol) (PEG) solution containing a series of transition metal salts. It was found that the olefin uptake by the metal ion occurred reversibly, and the selectivity of ethylene was also improved with the Rh_3 salt more than others. Addition of KNO_3 to the Rh_3^+–PEG system resulted in further enhancement of the selectivity. A conceivable reason for such enhancement would be due to the salting-out effect induced by the added salt which lowered ethane permeation proceeding by a simple dissolution–diffusion mechanism, resulted in more predominance of the carrier mediated transport.

Recently, Ravanchi et al. (2010a, 2010b) used a poly(vinylidene fluoride) (PVDF) membrane filter impregnated in different $AgNO_3$ solutions as a facilitated transport membrane for propylene/propane separation. In order to avoid membrane drying, the feed and sweep gases were passed through humidifiers before entering the permeation cell. The results showed that the selectivity of propylene increased with increasing the concentration of $AgNO_3$ and/or the trans-membrane pressure. However, their work in this matter is similar to that of Teramoto et al. (1986) who suggested the long term stability of the membrane was a major concern and the addition of water vapor to the feed and permeate streams and the required subsequent removal of water vapor from the olefin-rich permeate stream make the use of these membranes impractical for industrial applications.

In order to improve the stability of SLMs, Duan et al. (2003) developed a double layer liquid membrane for propylene/propane separation. The double layer membrane consisted of a hydrophilic treated poly(tetrafluoro ethylene) (PTFE) membrane containing a non volatile facilitation solvent consisted of triethylene glycol (TEG) and different silver salts. This hydrophilic membrane was placed on another hydrophobic poly(vinylidene fluoride) (PVDF) membrane. This scheme of the double layer membrane was effective in holding a trans-membrane pressure over 200 kPa. It was also noted that the hydrophobicity of the PVDF membrane insured that the facilitation solvent did not penetrate through the second membrane under the operating trans-membrane pressure. Duan et al. (2003) studied the effect of salt concentration, operating temperatures, and the presence of water vapor in the feed on the propylene/propane separation performance. The reported selectivities were 2.4, 40, and 100 for TEG, TEG/$AgNO_3$, and TEG/$AgBF_4$, respectively, in the presence of water vapor in the feed. However, the absence of the water vapor in the feed resulted in a selectivity decline from 100 to 50 for the TEG/$AgBF_4$ system. Increasing the operating temperature has led to a decrease in the permeation rate of propylene and therefore the selectivity was also reduced. This behavior was attributed to the decrease in propylene solubility and the instability of the formed Ag-complex at higher temperatures. The results presented by Teramoto et al. (1986); Ravanchi et al. (2010a, 2010b), and Duan et al. (2003) for propylene/propane separation using SLMs are summarized in Table 3.
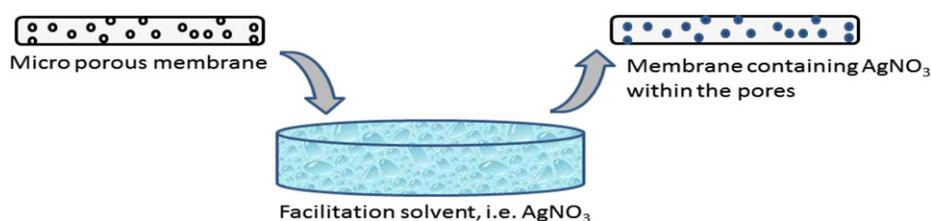

Fig. 2. Supported liquid membranes.

Table 3
Permeation and separation characteristics through liquid membranes.

Class	Membrane type	Carrier	Permeance (mol m^{-2} s^{-} kPa^{-})	Selectivity α	Reference
SLM	Cellulose filter	4.0 M AgNO$_3$		1000[a]	(Teramoto et al., 1986)
	PVDF*	1.0 M AgNO$_3$		270[a]	(Ravanchi et al.,2010a;2010b)
	PTFE?PVDF*	TEG		2.4[a]	(Duan et al., 2003)
		TEG/AgNO$_3$		40[a]	(Duan et al., 2003)
		TEG/AgBF$_4$		110[a]	(Duan et al., 2003)
		TEG/AgBF$_4$		50[b]	(Duan et al., 2003)
IEM	SPPO	AgNO$_3$	1.01×10^{-5}	287[a]	(LeBlanc Jr. et al., 1980)
	Nafion	2.0 M AgBF$_4$	1.94×10^{-6}	470[a]	(Eriksen et al., 1993a)
	Nafion	2.0 M AgBF$_4$	1.57×10^{-6}	460[a,d]	(Eriksen et al., 1993b)
	Nafion	2.0 M AgBF$_4$	1.01×10^{-5}	500[a,c]	(Eriksen et al., 1993b)
	Nafion	2.0 M AgBF$_4$	1.24×10^{-5}	541[a,c]	(Eriksen et al., 1993b)
	Nafion	6.0 M AgBF$_4$	2.73×10^{-5}	1934[a,c]	(Eriksen et al., 1993b)
FLM	PP	4.0 M AgNO$_3$	1.97×10^{-6}	500	(Teramoto et al., 1989)
	PDMS/PPSQ	1.0 M AgNO$_3$	1.55×10^{-4}	51[e]	(Bessarabov et al., 1995)
	PDMS/PPSQ	1.6 M AgNO$_3$	9.57×10^{-5}	56[f]	(Bessarabov et al., 1995)
	PDMS/PPSQ	1.6 M AgNO$_3$	1.39×10^{-4}	562[e]	(Bessarabov et al., 1995)
BFLM	PESF	4.0 M AgNO$_3$	3.94×10^{-5}	1100[g]	(Teramoto et al., 2002)
HFMC	PSF	1.0 M AgNO$_3$	3.33×10^{-6}	140[i]	(Tsou et al., 1994)
	PSF	1.0 M AgNO$_3$	1.96×10^{-6}	105[j]	(Tsou et al., 1994)
	PSF	5.0 M AgNO$_3$	6.04×10^{-6}	491[i]	(Tsou et al., 1994)
	PSF	5.0 M AgNO$_3$	3.89×10^{-6}	350[j]	(Tsou et al., 1994)
	EPDEM	3.5 M AgNO$_3$	2.01×10^{-6}	14.7[m]	(Nymeijer et al., 2004a)
	EPDEM	3.5 M AgNO$_3$	6.93×10^{-7}	72.5[k]	(Nymeijer et al., 2004a)
	SPEEK/SPEEK	3.5 M AgNO$_3$	3.30×10^{-7}	>2700[l]	(Nymeijer et al., 2004b)
	EPDEM/SPEEK	3.5 M AgNO$_3$	4.95×10^{-7}	300[l]	(Nymeijer et al., 2004b)
	SPEEK/EPDEM	3.5 M AgNO$_3$	3.30×10^{-7}	75[l]	(Nymeijer et al., 2004b)
	EPDEM/EPDEM	3.5 M AgNO$_3$	6.60×10^{-7}	20[l]	(Nymeijer et al., 2004b)
BFHFMC	PESF	4.0 M AgNO$_3$	1.10×10^{-4}	375[h]	(Teramoto et al., 2005)

All data are presented for ethylene/ethane separation except in * are for propylene/propane separation.
[a,b]Humidified and dry feed, respectively.
[c,d]Swollen and unswollen membranes, respectively.
[e,f]Absorber $T=20°C$, desorber $T=45°C$; absorber $T=25°C$, and desorber $T=25°C$, respectively.
[g,h,i,j]Feed partial pressure of 9, 164, 202.45, 713 kPa, respectively.
[k,l,m]Liquid flow rate of 35, 50, and 350 ml min^{-1}, respectively.

Supported Liquid Membranes (SLMs) have been attracting attention for olefin/paraffin separation since very high selectivities were obtained compared with the conventional polymeric membranes. However, SLMs have several critical problems such as the loss of liquid solution from the membrane support. This could possibly occur due to the evaporation of the liquid into the feed and sweep streams (Teramoto et al., 1986) or due to chemical degradation of carrier by irreversible reactions with some components in the feed gas mixture (Hughes et al., 1986). These membranes also suffer from low permeation rate due to the difficulty of preparing very thin membranes with high stability. Finally, humidifying the feed and sweep streams with water vapor to stabilize the membrane is considered as a non-practical solution because of the significant rise in the operating cost when it comes to the addition and subsequent removal of water vapor of the gas streams.

2.1.2. Ion exchange membranes (IEMs)

IEMs are often prepared by obtaining a proton-form membrane and then impregnating it in aqueous solutions. It is also commonly found that pretreatments were carried out on the proton-form membranes to swell the membrane and thus, absorb higher amount of solution after impregnating it in the solvent as shown in Fig. 3. IEMs are considered to be more stable than their SLM counterparts, since the facilitation solution is not only physically trapped within the pores of the membrane, but is also retained by electrostatic interactions with the ion exchange sites within the membrane.

LeBlanc Jr. et al. (1980) were the first to demonstrate the facilitated transport of ethylene in IEMs. A cation-exchange membrane of sulfonated polyphenyleneoxide (SPPO) was converted to Ag$^+$ form by soaking it in aqueous AgNO$_3$. The ethylene permeability was 2300 Barrer while using water vapor saturated feed at 25 °C. However, the permeability of ethane under the same conditions was only 8 Barrer. These findings strongly suggested that ion exchange membranes should readily separate ethylene from ethane. This work of LeBlanc Jr. et al. (1980) has established a great research interest in the facilitated transport of olefins using silver salt solutions in ion exchange membranes. Eriksen et al. (1993a) worked with Nafion membranes which were ion-exchanged in 2 M AgBF$_4$ and demonstrated that the Ag-IEM offered a very efficient and stable system. When a humid 1:1 mixture of ethane and ethylene was used at atmospheric pressure, the permeability of ethylene was about 1000 Barrer with a separation factor of 470. This is a very high permeability for ethylene and almost comparable to the ethylene permeability of 2300 Barrer reported by LeBlanc Jr. et al. (1980), especially taken into account the lower ion-exchange capacity of the Nafion membranes compared with the SPPO membranes. The ion-exchange capacity of Nafion (Eriksen et al., 1993b) and SPPO (LeBlanc Jr. et al., 1980) membranes were 0.91 and 2 meq/g, respectively.

The swelling of Nafion membranes in polar solvents has been well documented in the literature. Pellegrino et al. (1988) showed that heat treatments of sodium exchanged Nafion membranes in glycerin increases the water content from 15 to 55 wt.%. This increase in water content within the membrane was demonstrated to be very effective in increasing the flux of CO$_2$ through the membrane. The use of Ag-exchanged swollen Nafion membranes for the separation of ethylene from ethane was described in a patent by Kraus (1986).
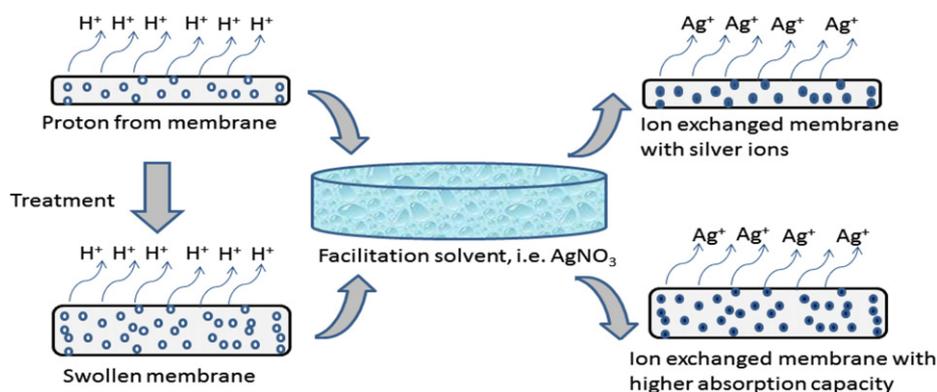
Fig. 3. Ion-exchanged liquid membranes.

Nafion membranes were immersed in aqueous 6 M AgNO₃ solution overnight, dried and swollen in glycerin at room temperature for two days. Testing these Nafion membranes for a dry 1:1 feed mixture of ethylene and ethane at atmospheric pressure resulted in ethylene permeability of 7 Barrer with a separation factor of 10. Other tests of Nafion membranes were demonstrated by Eriksen et al. (1993b) who conducted preliminary tests on the separation of a dry 1:1 ethylene/ethane mixture through Nafion membranes which was ion-exchanged in aqueous 2 M AgBF₄ solution for two days and then swollen in glycerin at room temperature. A permeability of 2–3 Barrers for ethylene was obtained; however, when the feed and purge gases were humidified before entering the permeation cell, the ethylene permeability through this membrane increased to 100–150 Barrer with a corresponding separation factor of 40–50. Furthermore, Eriksen et al. (1993b) studied the effect of heat pretreatment of the IEMs on the increase of water content in the membrane and further investigated the separation performance. Two schemes of heat pretreatments were studied, first, preswollen in glycerin by heating at 225 °C, and secondly by dry heating in oven to 340 °C and then quenched and preswollen in glycerin at 225 °C. Afterwards these membranes were immersed in 2 M AgBF₄ for four days. The results revealed that the separation factors of ethylene for a humidified 1:1 mixture of ethylene and ethane were 462, 500, and 541 for untreated membranes, pretreatment under scheme 1, and scheme 2, respectively. Additionally, soaking the ion exchanged membranes of scheme 2 in 6 M AgBF₄ resulted in a separation factor of nearly 2000. The complete results of several authors who used IEMs for olefin/paraffin separation are summarized in Table 3.

Although high olefins selectivities and fluxes were possible using IEMs, it was only observed when swollen or hydrated membranes were used which enhanced the transport of the Ag–olefin complex through the membrane (Eriksen et al., 1993a, 1993b; Kraus, 1986). Unfortunately, these cation-exchange membranes do not retain water sufficiently for prolonged periods resulting in a decrease in olefin fluxes and olefin/paraffin selectivity. This could only be prevented if water vapor is continuously added to the feed mixture to substitute the loss from the membrane. However, in many olefin/paraffin separation applications, water-free processing is a must. It is also worth mentioning that the majority of IEMs in the literature were used for liquid phase olefin/paraffin separation (Bryant et al., 1997; Goering et al., 1998; Koval et al., 1989, 1992; Thoen et al. 1994) which is beyond the scope of this review.

2.2. Flowing liquid membranes (FLMs)

2.2.1. Flat sheet liquid membranes

In order to overcome these inherent problems of the previous types of immobilized liquid membranes, flowing liquid membranes for olefin/paraffin separation were proposed. Teramoto et al. (1989)
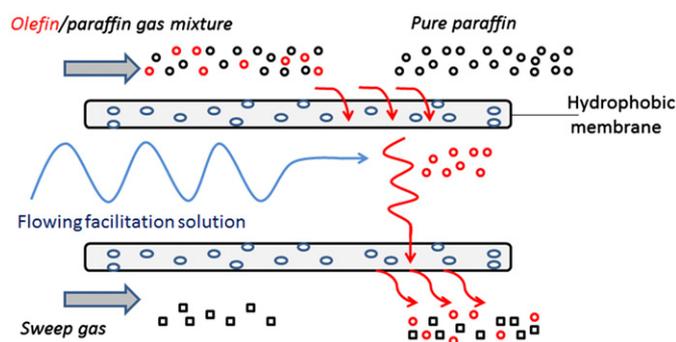

Fig. 4. Scheme of flowing liquid membranes proposed by Teramoto et al. (1989).

used a membrane system where a solution of aqueous silver nitrate is circulated through a thin channel between two flat hydrophobic microporous membranes separating the feed and sweep streams as shown in Fig. 4. The mass transfer rate through the liquid membrane was enhanced by the turbulence of the flowing membrane solution through the channel. Moreover, the permeation resistances through the two microporous membranes were minimized due to the hydrophobic nature of these membranes which prevents membrane wetting from the solution. As a result, the membrane pores were available for gas-phase diffusion only and thus, the permeation rate was much faster than filled pores with aqueous solution. Observed maximum ethylene permeance and selectively were 0.2×10^{-5} mol m^{-2} s^{-1} kPa^{-1} and 500, respectively. However, after repeated use of FLM for about one hundred hours, a decrease in the permeation rate was observed as brown spots were observed on the surface of the hydrophobic microporous membrane in the degraded module. The analysis of the brown spots suggested the formation of Ag and Ag₂O. Teramoto et al. (1989) anticipated that the degraded module could be regenerated by passing an aqueous nitric acid solution, which can dissolve Ag and Ag₂O on the membrane surface. Therefore, this type of FLMs is expected to have higher permeation and stability compared with conventional ILMs because the regeneration of the solvent could be achieved without any discontinuity of the process.

Bessarabov et al. (1995) developed a membrane permabsorber system for the separation of ethylene from ethylene/ethane mixture while using silver nitrate solution as the facilitation solvent. The membrane permabsorber consisted of at least one membrane absorption module (absorber) and one membrane desorption module (stripper) as shown in Fig. 5. The absorber and stripper sections contained non-porous polymeric membranes prepared from a polydimethylsiloxane (PDMS)/poly(phenylsilsesquixane) (PPSQ) copolymer. This system had one inlet for the feed and two outlets for the products (retentate and desorbate). The first component of the feed (ethane) was insoluble in

the solvent and exits the system as a retentate. However, ethylene diffuses through the non-porous polymeric membrane and is absorbed into the liquid and pumped away to be degassed in the stripper section. Bessarabov et al. (1995) studied the effect of silver nitrate concentration, liquid flow rates, liquid temperature, and membrane surface area on the permeance and selectivity of ethylene. The results revealed that ethylene permeances and selectivities were dependent on the liquid flow rate for all conducted experiments. At low liquid flow rates, the obtained selectivity was high and the permeation rate was controlled by the chemical absorption in the absorber as well as the degassing step in the stripping module. On the other hand, when the liquid flow rate was high, gas permeation through the composite membrane limited the permeation rate and the selectivity became low. The permeation rate and selectivity of ethylene were in the range of $0.76–0.96 \times 10^{-4}$ mol m^{-2} s^{-1} kPa^{-1} and 56–9.6, respectively, when the operating temperature was 25°C for both the absorption and desorption modules.

2.2.2. Bulk flowing liquid membranes (BFLMs)

Teramoto et al. (2002) later developed a novel facilitated transport membrane system in which a carrier solution permeates through the membrane, and referred to as "Bulk Flowing Liquid Membrane" (BFLM) as shown below in Fig. 6. An aqueous silver nitrate solution is continuously supplied to the feed side (high pressure side) of the membrane and absorbs ethylene to form a complex. The carrier solution is allowed to permeate though the membrane to the receiving side (low pressure side) where the complex decomposes to release ethylene and the carrier Ag$^+$. An important observation to note is that ethylene is transported mainly as its complex with Ag$^+$ ion by molecular diffusion as well as convection of the carrier solution. This is a sharp contrast to the case of FLMs discussed previously, where only the gas/vapor diffused through the pores of the membrane, i.e. no transport of the solvent through the membrane. The transferred carrier solution in this scheme is always recycled back to the feed side by a pump. This prevents the drying-up of the membrane and thus, the membrane would be stabilized. Furthermore, gas permeation accompanied by the convective transport of the carrier solution can contribute remarkably to the enhancement of the gas permeation as compared with FLMs whereas only molecular diffusion contributes to the gas permeation. The ethylene permeance of 3.94×10^{-5} mol m^{-2} s^{-1} kPa^{-1} and selectivity of ethylene over ethane of 1100 were achieved when the partial pressure of ethylene was 9 kPa.

The membrane properties, operating conditions, carrier types, and the separation characteristics of FLMs for olefin/paraffin separation are summarized in Table 3. These parameters are included together to allow for a simple comparison between different systems and conditions.

2.2.3. Hollow fiber membrane contactors (HFMC)

Although FLMs showed more stability than ILMs, the obtained gas permeance per module volume was not so high due to the
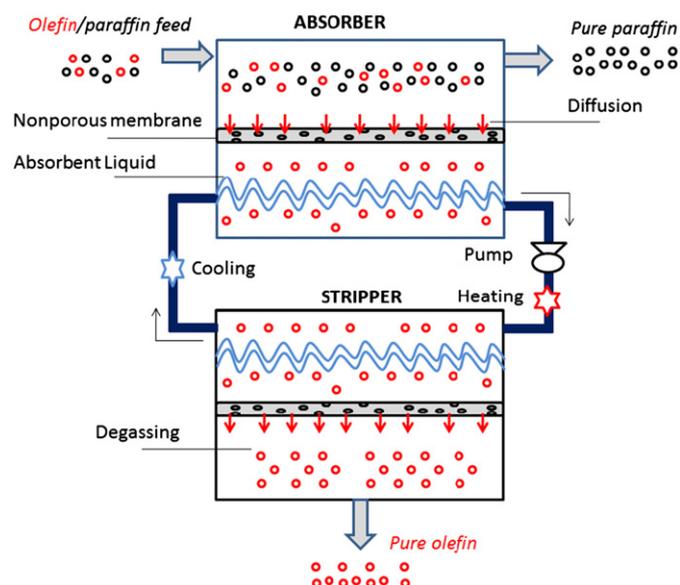

Fig. 5. Scheme of absorber–desorber system proposed by Bessarabov et al. (1995).
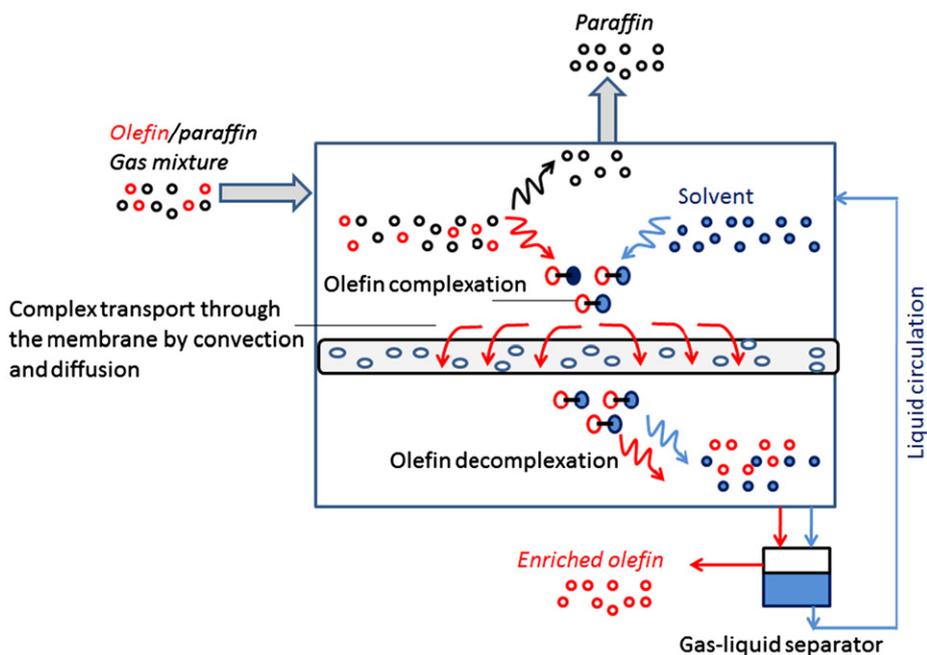

Fig. 6. Demonstration of bulk flowing liquid membrane proposed by Teramoto et al. (2002).

inefficient gas–liquid contact as well as small membrane surface area. To overcome these drawbacks, hollow fiber membrane contactors are proposed as a continuous gas–liquid contact with large surface area for mass transfer. In a membrane contactor configuration, the gas mixture of olefins and paraffins is flowing on one side of the membrane module, i.e. lumen side, whereas the facilitation solution is continuously flowing on the other side of the membrane module, i.e. shell side. At the membrane–shell interface, only olefins are soluble in the solvent due to the chemical complexation. However, paraffins have negligible solubility in the solvent and therefore, do not penetrate to the liquid side but rather continues to flow in the lumen side and exits as a purer form as shown in Fig. 7. One of the most important advantages of this scheme is that HFMCs offer a large surface area (interfacial area) for transport which was not available in other membrane configurations. Owing to their high surface area, HFMCs promise higher surface area per volume compared to the conventional scrubbers, i.e. typically in the range of 500–5000 m^2/m^3 for membrane contactors as compared to 20–500 m^2/m^3 in conventional scrubbers (Iversen et al., 1997).

Tsou et al. (1994) proposed polymeric hollow fiber membrane contactors using silver nitrate solution as the absorbent solvent for ethylene/ethane separation. In their system, the carrier solution which absorbs ethylene selectively is circulated between the permeate side and a flash pot where the dissolved gas is stripped and recovered. The lean solution is then recycled back to the membrane module for continuous absorption of ethylene. The absorption process is considered stable since the membrane is always wetted by the carrier solution which offers a steady gas–liquid interface. Tsou et al. (1994) studied the effect of varying the recycling liquid flow rate, liquid and gas pressures, and the concentration of silver nitrate solution. The highest observed ethylene permeance and selectivity were 6.04×10^{-6} mol m^{-2} s^{-1} kPa^{-1} and 491, respectively, when the operating gas and liquid flow rate were 50 and 8 ml/min, respectively. These were obtained at an ethylene partial pressure of 202.45 kPa and solvent concentration of 5 M AgNO$_3$. This ethylene permeance is considered rather low when compared with Teramoto et al. (2002) for FLMs, given that the concentration of the solvent used by Tsou et al. (1994) was 5 M. This can be explained due to the membrane wetting which increases the resistance for mass transfer significantly.

Therefore, a major disadvantage of HFMCs compared to conventional gas–liquid absorption processes which impose direct contact between gas and liquid phases, is the introduction of the additional mass transfer resistance due to the presence of the membrane. This membrane resistance becomes significant when the absorption liquid penetrates into the pores. In order to increase the stability of the process and avoid membrane wetting, composite membranes with dense polymeric layers on top of a microporous support are recommended.

A patent of Creusen et al. (1995) described in general the application of composite membranes consisting of a semi-selective gas separation membrane with a non-porous active layer in a membrane contactor for olefin/paraffin separation. Nymeijer et al. (2004a) used ethylene propylene diene terpolymer (EPDM) as a top layer material for composite hollow fiber membranes prepared by dip coating. Hollow fiber membrane modules containing 10 composite membranes (8 μm in thickness) with an effective surface area of 101.8 cm^2 were used with silver nitrate solutions for ethylene/ethane separation. A feed stream containing pure ethylene or a gas mixture of ethane (20%) and ethylene (80%) was fed to the inner side of the fibers of the absorption module under a total pressure of 1–3 bars. The absorption and desorption modules operated continuously in a membrane contactor system for more than twenty weeks without any changes in the membrane performance. In the absorber module, the transport of ethylene was highly enhanced by the chemical reaction and the desorption step was the limiting factor in this separation process. The results revealed that ethylene and ethane permeances and separation factors depend greatly on the liquid flow rate and the concentration of the absorbent solvent. The permeance of ethylene increased with increasing liquid flow rates reaching an absolute maximum at a flow rate of 150 ml min^{-1} and then decreased for higher liquid flow rates, while the selectivity continuously decreased with increasing liquid flow rate. This behavior was attributed to the diffusion limitations in ethylene mass transfer as well as the complexation–decomplexation reaction occurring in the desorption module. At low liquid flow rates, the permeance was limited by the liquid phase layer resistance which inhibited the supply of silver ions. On the other hand, for higher liquid flow rates, the permeance was limited by the reduced time for decomplexation which in return slowed down the diffusion of ethylene to the membrane surface.
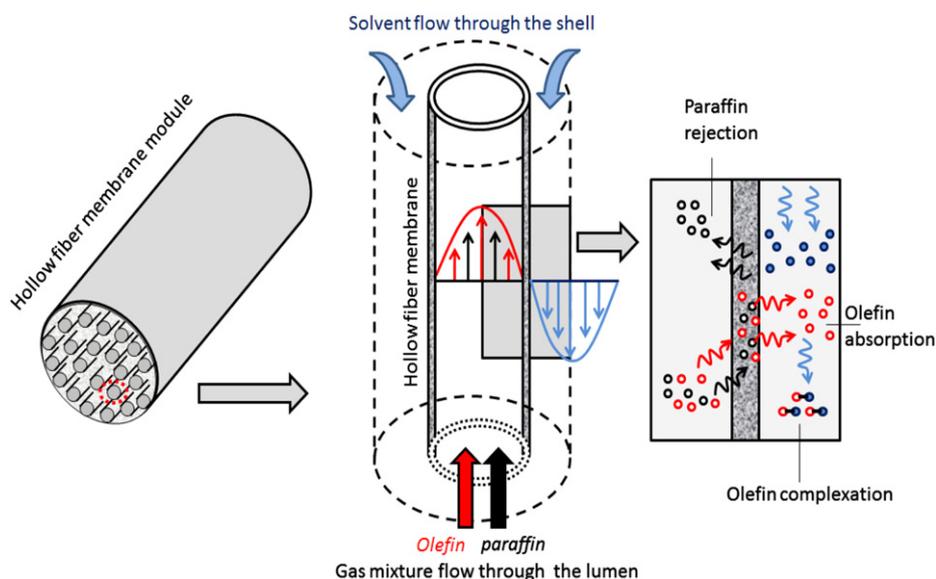

Fig. 7. Demonstration of hollow fiber membrane contactors for olefin/paraffin separation.

Ethylene permeances were found to be in the range of 0.35–1.0×10^{-6} mol m^{-2} s^{-1} kPa^{-1} and gas mixture selectivities in the range of 72.5–14.7.

Wessling and coworkers (Nymeijer et al., 2004a, b) continued to investigate composite hollow fiber membranes for olefin/paraffin separation in a membrane contactor system. Nymeijer et al. (2004b) used sulfonated poly(ether ether ketone) (SPEEK) instead of EPDM as a top layer for composite HFMCs while using AgNO$_3$ as the absorbent solvent. The SPEEK layer was considered to be a selective stabilizing material due to its interactions with silver ions. Membrane surface interactions take place via electrostatic forces between the negatively charged SO$_3^-$ groups and the positively charged Ag$^+$ ions. Unlike SPEEK, the previous composite layer of EPDM used by Nymeijer et al. (2004a) did not interact with silver ions and was not considered to be selective. The utilization of such a super-selective membrane resulted in a very low permeability of ethane that could not even be detected by gas chromatography analysis. High ethylene selectivities (> 2700) with reasonable good permeances of 0.3×10^{-6} mol m^{-2} s^{-1} kPa^{-1} were observed when SPEEK composite hollow fibers were used in both the absorption and desorption modules. To increase the productivity of ethylene while obtaining high selectivity, Nymeijer et al. (2004b) further investigated the combination of SPEEK and EPDM hollow fibers in the absorption and desorption modules. The results showed that using SPEEK in both the absorber and desorber modules resulted in the highest separation factor, while using EPDM for both the absorber and desorber resulted in the highest ethylene productivity. The remarkably high selectivities obtained for SPEEK coated composite membranes were either caused by a reduction in ethane permeation, an increase in ethylene permeation, or a combination of both.

2.2.4. Bulk flowing hollow fiber membrane contactors (BFHFMCs)

Unlike the previous conventional HFMCs where the gas and liquid phases are flowing in separate compartments, i.e. gas in the lumen side and liquid in the shell side, Teramoto et al. (2003, 2004, 2005) developed a novel hollow fiber facilitated transport membrane module for gas separation where both the gas mixture and the carrier solution being continuously supplied together to the feed side (lumen side, high-pressure) where the solution absorbs selectively the desired component to be separated from the gas mixture. The solution is forced to permeate through the membrane to the permeate side (shell side, low pressure), where the solution releases the gas component and then is recycled back to the lumen side by a pump as shown above in Fig. 8 for olefin/paraffin separation. It should also be noted that in this present membrane system, although the membrane is for gas separation, it is the carrier solution and not the gas that permeates through the membrane. This type of hollow fiber membrane contactor was classified by Teramoto et al. (2005) as "Bulk Flow Liquid Membrane" (BFLM). However, to avoid confusion with the previous BFLM proposed by the same author (Teramoto et al., 2002), this membrane system is classified within as "Bulk Flowing Hollow Fiber Membrane Contactors" (BFHFMCs). Since the membrane is always wetted with the carrier solution, the membrane is very stable even at relatively high temperatures without the formation of open pores or unfilled liquid pores where the gas flows to the low pressure side unselectively. Furthermore, since the gas and carrier solution permeation occurs simultaneously by a convective transport mechanism; very high gas permeances are obtained compared to the conventional FLMs in which the gas permeates the membrane by molecular diffusion mechanism only as discussed previously. Another advantage of the BFHFMCs is that not only special membranes can be used but also conventional hydrophilic ultrafiltration membranes can be utilized.
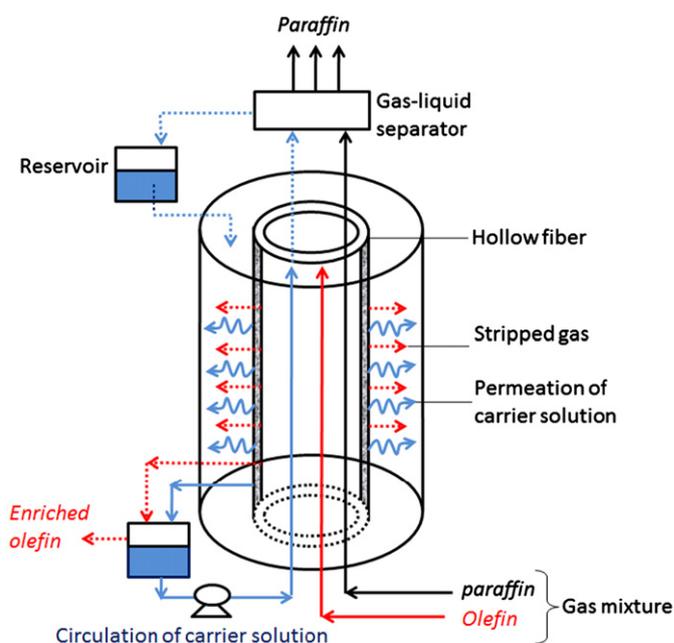

Fig. 8. Demonstration of bulk flowing hollow fiber membrane contactors proposed by Teramoto et al. (2005).

In the experiments carried out by Teramoto et al. (2005) for olefin/paraffin separation, the mixture consisted of 80 mol% ethylene and 20 mol% ethane, while the concentration of aqueous silver nitrate was 4 M. The feed side pressure was ranging from 200 to 500 kPa and the permeate side pressure was atmospheric. Three modules with different liquid permeabilities and design were used in the experiments. Long-term stability tests of these modules were not performed. However, it was confirmed that the modules were stable over a three-week testing period without any decline in permeance or selectivity, as well as there was no gas or liquid leakages observed. Although the testing period was not so long, the module was considered to be stable similarly to the modules which had been previously used for CO$_2$/N$_2$ separation (Teramoto et al., 2003, 2004). It was also confirmed that the color of silver nitrate solution did not change with time, which suggested that silver nitrate was chemically stable during the experiments. The maximum ethylene permeance was 1.1×10^{-4} mol m^{-2} s^{-1} kPa^{-1} and the selectivity of ethylene over ethane was about 375 at an ethylene partial pressure of 164 kPa. The results for olefin/paraffin separation using HFMCs are summarized in Table 3 for various configurations and properties.

Regarding industrial applications of hollow fiber membrane contactors, BP Amoco (Kwasniewski et al., 1999) studied the membrane-based contactors for olefin separation extensively using polypropylene (PP) hollow fiber membranes and silver nitrate as a carrier up to a pilot plant stage. It was found that although the process was technically sound, the operating cost of process was too expensive mainly due to short life span of the membranes which lasted roughly three months before replacement caused by limited thermal and chemical stability when extensively used with silver nitrate, even though the possibility of other carriers such as molybdenum sulfides were also explored (Koval et al., 1995).

HFMCs seem to be the most effective and efficient method for olefin/paraffin separation using a facilitation solvent because it provides high membrane surface area for mass transfer as well as a continuous gas–liquid contact for facilitated transport without any operating drawbacks such as flooding and foam formation. However, it still suffers from critical drawbacks such as

membrane wetting with the solvent and limited membrane thermal and chemical stability due to permanent exposure of the solvent with the polymer which in return destroys the long term application of the separation process. Other negative aspects of HFMCs could also arise from the presence of any impurities in the gas mixture which could possibly destroy the membrane material and thus, demands the frequent replacement of the membranes.

3. Membrane electrolytes

Membrane electrolytes are another novel class of facilitated transport membranes which do not impose the utilization of liquids as facilitation carriers. Instead, membrane electrolytes are composed of metal salts dissolved in the polymeric matrix where both anions and cations are sufficiently mobile without the need of a solvent or plasticizer to promote ionic motion and conductivity (Allcock, 1992; Gray, 1991). Consequently, the dissolving behavior and ionic constituents of metal salts in polymer matrices are very important in determining the ionic conduction and mass transport properties occurring within. Unlike ILMs where the complexing agent is physically trapped into the pores of the membrane, dense complex membrane electrolytes have the advantage to sustain higher pressure difference across the membranes without the physical loss of the complexing agent. In solid membrane electrolytes, the salt dissolves into the polymer matrix in the solid state and dissociates into anions and cations. Accordingly, interactions between the metal cation of the dissolved salt and electron donor pairs of heteroatoms present in the polymer matrix are possible. Such interactions favor ion-pair separation of the dissolved salt and result in a new ion-pair between the salt's cation and polymer's heteratoms. This new ion-pair interaction produces a conductive solid for various applications depending on the cation's properties. The majority of the published work on polymer electrolytes has focused on rubbery poly(ethylene oxide) (PEO)-based conductors of lithium(I) ions for applications in high-energy batteries (Allcock, 1992; Gray, 1991; Yang and Farrington, 1993; Zhang and Wan, 1993). However, in the past decade, mass transport properties through silver-based polymeric membrane electrolytes have been paid much attention for olefin/paraffin separation. The idea of using silver-based membrane electrolytes for olefin/paraffin separation was first introduced by Pinnau and Toy (1994) and developed through the next few years where the work was patented in 1997 (Pinnau et al., 1997a). Pinnau and colleagues continued to work in this topic through the years (Merkel et al., 2003; Pinnau and Toy, 2001; Pinnau et al., 1997b; Sunderrajan et al., 2001); however, in today's literature it can be found that the majority of the published work on olefin/paraffin separation using silver-based membrane electrolytes is dominated by Kang and coworkers from South Korea (Hong et al., 2000; Kim et al., 2002b, 2002c, 2003c; Yoon et al., 2000). Both efforts by the authors as well as additional relevant research by others are discussed in great details within this section for olefin/paraffin separation using membrane electrolytes.

3.1. Transport mechanism

In solid membrane electrolytes, the ionic species transport occurring within the membrane relies greatly on the local polymer relaxation process of the flexible polymer's chains (Gray, 1991). In other words, in order for the polymeric matrix to be an effective membrane electrolyte, the polymer should have two important characteristics (Pinnau and Toy, 2001): (I) atoms with sufficient electron donor capacity to form coordinate bonds with metal cations and (II) low bond rotation barriers to provide
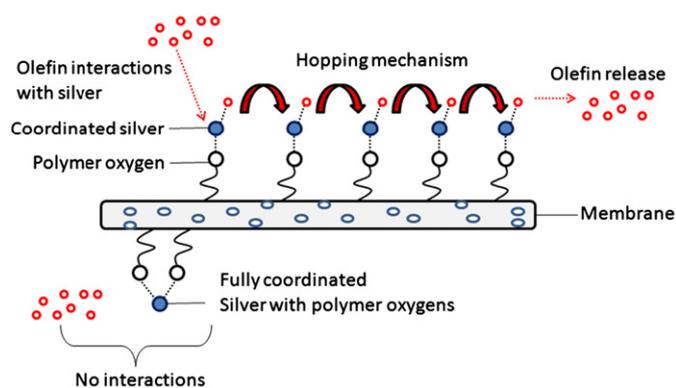

Fig. 9. Demonstration of facilitated transport mechanism occurring in solid membrane electrolytes.

sufficient segmental motion of the polymer chains. Previously, the facilitated transport mechanism in solid membrane electrolytes was not clear until Cussler et al. (1989) and Noble (1990) suggested that transport occurs via the hopping mechanism from one site to the next as shown below in Fig. 9.

Once the metal salt such as silver nitrate dissolves in the membrane material, i.e. poly(ethylene oxide) (PEO) polymer, the salt dissociates into Ag^+ and NO_3^- ions. The Ag^+ ions tend to form new bonds with any atoms present in the polymer matrix that can donate its electrons to stabilize Ag^+. In the case of the PEO polymer, coordination between Ag^+ and oxygen electron donor groups occurs. Once this membrane electrolyte is exposed to olefins, complexation takes place between olefins and Ag^+ ions which are partially coordinated with oxygen atoms in the membrane. The olefin–Ag complex then transports from one site to the next by the hopping mechanism until it reaches the other side of the membrane where the silver releases the olefin. In 1996, Kang et al. (1996) proposed a concentration fluctuation model for interpreting facilitated transport through solid-state membranes as shown below in Eq. (1)

$$\frac{P_f}{P} = 1 + \left(\frac{p_d}{p_0}\right)\sqrt{n^2 + \left\{\frac{2\pi k_2 L^2 C_B^0}{P}\frac{\ln(1+Kp_0)}{p_0}\right\}^2} \qquad (1)$$

where P_f and P are the permeabilities of the facilitated transport membrane and the membrane matrix, respectively. p_0 and p_d are the applied pressure and pressure fluctuation due to the reversible reaction, respectively, n is the parameter defined as $n = N_A C_B^0 (\pi r_s^2 L)$, where L is the membrane thickness, r_s is the permeant radius, C_B^0 is the carrier concentration, and k_2 and K are the backward reaction rate constant and the equilibrium constant of the carrier–solute reaction, respectively. This theory predicts a linear relationship between the solute permeance and the facilitation solvent concentration. Another important observation is that the permeance increases with increasing the membrane thickness. Although this is a major contrast with previous models where high gas flux is obtained for very thin membranes, the fact that there are more silver sites for higher membrane areas justify the increase in permeability with increasing the membrane thickness due to facilitated transport.

3.2. Dense membrane electrolytes

Bai et al. (1998, 2000) studied the separation of propane/propylene mixtures using dense complex polymer membranes prepared from poly(phenylene oxide) (PPO) (Bai et al., 1998) and ethyl cellulose (EC) (Bai et al., 2000) using different metal salts. It was found that the selectivity enhances with the incorporation of metal salts in the PPO membrane, especially for Rd and Pd metals.

The improved selectivity values of the metal incorporated polymers have been explained by a decrease in the effective distance, d_{eff}, between the adjacent intersegment chains due to formation of metal/ion complex with the polymer matrix and hence, a decrease in the free volume of the polymer was achieved as well upon metal incorporation. However, the significant improvements in propylene permeability have been realized mainly due to the selective transport of propylene molecules mediated by the incorporation of selected metal ions.

EC membrane electrolytes also appeared to have a good potential for the commercial recovery of propylene from a hydrocarbon rich off-gas mixture containing the olefin as a major constituent (Bai et al., 2000). A reasonably selectivity of 3.9 accompanied by high transport rates was obtained for propylene with respect to propane in the multi-component mixture. The wide-angle X-ray diffraction (WAXD) analysis of these membrane electrolytes carried out by Bai et al. (2000) provided enough evidence of reduced crystalline structures implying an increase in the amorphousness of the polymer. However, the d_{eff} was indeterminable as the diffraction pattern became too broad upon metal incorporation at 5% concentration (Bai et al., 2000). Reduced crystallinity offered a high degree of disorder to the EC polymer leading to an increase in diffusivity of the permeating gas molecules. Moreover, since Ag is acting as a selective carrier for propylene gas molecules through the formation of reversible complexes, the propylene to propane permselectivity was also improved. Among the metal-incorporated membranes, the best results were obtained with silver (5 wt.%) in EC membrane which yielded a permeate stream of around 65 mol% propylene. The results of permeability and selectivity of PPO and EC incorporated metals are summarized in Table 4 for dense membrane electrolytes.

Ryu et al. (2001) used dense Cellulose Acetate (CA) membranes to investigate the effect of incorporation silver salts on olefin/paraffin separation. It was found that selectivity for propylene and ethylene over their respective paraffins increases with increasing the molar ratio of $AgBF_4/CA$ up to 3:1 and then gradually decreases with further increase in the molar ratio. The maximum selectivity at the molar ratio of $AgBF_4/CA$ up to 3:1 implies that the coordination environment of silver ions in the CA membrane has a significant effect on the facilitated transport of olefins. The monomer unit of CA (acetyl content: 39.8 wt.%) has approximately 4.9 carbonyl groups and thus, in principle, each silver ion in the $AgBF_4/CA$ membrane with a ratio of 3:1 is coordinated by 1.6 carbonyl groups roughly (Ryu et al., 2001). It is likely that the silver ions in the $AgBF_4/CA$ membrane should be approximately twofold coordinated by carbonyl groups for the membrane to be highly selective in the facilitated transport of ethylene and propylene. Considering the maximum coordination number of four for a silver ion, it is interesting to note that the membrane with the molar ratio of $AgBF_4/CA$ of 1:1 also exhibited some selectivity for propylene over propane and for ethylene over ethane since silver was already fully coordinated with the carbonyl groups. These results imply that propylene and/or ethylene can coordinate to the fully coordinated silver ion by replacing other coordinated carbonyl group(s). The higher selectivity of ethylene/ethane over that of propylene/propane can be ascribed to the difference in diffusion rates and/or to the difference in affinities of olefins for silver ions in the membrane. The separation performances for membrane electrolytes by Bai et al. (1998, 2000) and Ryu et al. (2001) are summarized in Table 4.

3.3. Functional membrane electrolytes

It has been mentioned that silver–olefin complexes are extremely unstable and lose olefin easily upon exposure to air (Quinn et al., 1965). Therefore, in order to characterize reversible olefin coordination to silver ions in a solid membrane electrolyte, the polymer matrix should contain some functional group(s) to stabilize the silver–olefin complexes to a certain extent. Antonio and Tsou (1993) suggested that the stability of silver–olefin complexes could be enhanced by weak interactions between silver ions and oxygen atoms present in the polymer. Among various oxygen-containing polymers on which silver ions can interact with are poly(vinyl methyl ketone) (PVMK), poly(vinyl

Table 4
Permeation and separation characteristics through dense electrolyte membranes.

Polymer	Metal mole fraction	Permeability (barrer)		Selectivity		Reference
		C_3H_8	C_3H_6	$\alpha_{C_3H_6/C_3H_8}$	$\alpha_{C_2H_4/C_2H_6}$	
EC	–	2 (1.7)	7(5.2)	3.5(3.05)		(Bai et al., 2000)
EC-Ag	1[a]	3.3	(5.7)	(2)		(Bai et al., 2000)
	5[a]	2.1 (1.9)	8.2 (6)	3.9 (3.3)		(Bai et al., 2000)
EC-Pd	1[a]	(1.7)	(4.7)	(2.76)		(Bai et al., 2000)
EC-Ru	1[a]	1.8 (1.6)	5.9 (4.2)	3.3 (2.63)		(Bai et al., 2000)
EC-Ir	1.25[a]	1.7 (1.4)	6.3 (2.5)	3.7 (3.11)		(Bai et al., 2000)
PPO	–	2.1 (1.7)	9 (6)	4.25 (3.5)		(Bai et al., 1998)
PPO-Ru	0.05[a]	2 (1.6)	14 (8)	7 (5)		(Bai et al., 1998)
PPO-Pd	0.63[a]	2.9 (2.4)	18.4 (12.5)	6.35 (5.2)		(Bai et al., 1998)
PPO-Ag	1[a]	1.4 (0.9)	8 (4)	5.7 (4.5)		(Bai et al., 1998)
PPO-Ir	0.7[a]	2	10	5		(Bai et al., 1998)
CA/AgBF₄	0.50			10	10	(Ryu et al., 2001)
	0.60			40	50	(Ryu et al., 2001)
	0.66			80	100	(Ryu et al., 2001)
	0.75			200	280	(Ryu et al., 2001)
	0.80			125	200	(Ryu et al., 2001)
	0.86			20	110	(Ryu et al., 2001)

All data are presented for pure gases, except in parenthesis are for gas mixtures containing 55% C_3H_6 and 45% C_3H_8.
1 Barrer $= 10^{-10}$ cm^3 cm cm^{-2} s$^-$ cmHg$^-$.

[a] Values are presented for wt.%.

pyrrolidone) (PVP), poly(2-ethyl-2-oxazoline) (POZ), poly(methyl methacrylate) (PMMA), and poly(butyl methacrylate) (PBMA). Other functional groups that silver can interact with in the polymer material are hydroxyl oxygens and amide nitrogens. In this section, membrane electrolytes for olefin/paraffin separation are discussed based on their functional groups rather than the type of salt used. In this manner, a direct comparison between different membrane materials can be easily obtained. Additionally, the effect of using different silver salts on olefin/paraffin separation with the same membrane material is demonstrated when applicable.

3.3.1. Silver coordination with polymer carbonyl oxygens

The majority of the work that has been carried out on facilitated olefin transport through silver membrane electrolytes was mainly due to the coordination between silver ions and the non-bonding electrons of oxygen atoms present in the polymer. This interaction between silver ions and the polymer matrix has to be weak enough to enable the olefin to form a complex with the coordinated silver ions. If the interaction between silver ions and the polymer matrix is strong, olefins will not be able to form a complex with silver ions because all the coordination sites on silver ions are occupied by the polymer matrix as shown in Fig. 9.

3.3.1.1. Role of carbonyl oxygen type on olefin transport. The separation of propylene/propane gas mixtures using polymer/silver salt complex membranes was evaluated for three kinds of electron-donating carbonyl oxygen ligands as shown in Fig. 10, i.e. ester, ketone, and amide groups (Kim et al., 2003b). The separation performance was found to strongly depend on the characteristics of the ligand as well as on the nature of the anion of the silver salt. Table 5 shows the selectivity of propylene as a function of silver salt concentration for several polymeric/silver salt membranes. The PMMA and PBMA membranes (i.e. those with ester groups) showed a low silver content for facilitated olefin transport to occur (silver mole fraction of 0.09), whereas the POZ and PVP membranes (i.e. those with amide groups)
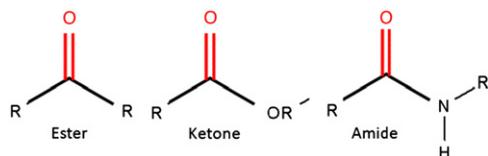
exhibited a higher content of silver concentration for facilitated transport to take place (mole fraction of 0.25). on the other hand, PVMK membranes (with ketone groups) exhibited an intermediate silver content (mole fraction of 0.14). In summary, the minimum silver concentration needed in polymeric membrane electrolytes for facilitated propylene transport to occur is relatively low for ester ligands, medium for ketone ligands, and high for amide ligands. It was also found that the effect of using different polymer matrices on propylene transport properties is negligible if these polymers have the same ligands. In other words, PBMA had nearly the same onset concentration as PMMA, and POZ had nearly the same onset concentration as PVP. Furthermore, the separation performance of a membrane containing $AgBF_4$ was always found to be higher than a membrane containing $AgCF_3SO_3$ for a given polymeric matrix. The differences between the threshold concentrations for facilitated olefin transport can be attributed to the relative strengths of the two interactions occurring; these are interaction of silver ions with different polymeric ligands, and interactions between silver ions and olefin molecules. The threshold concentration was high when the former interaction was stronger than the latter, and was low when the latter is stronger than the former. In other words, if silver ions have strong interactions with the membrane's ligands, silver interactions with olefins will be minimal and thus, higher concentration of silver is needed for facilitated olefin transport to occur. The extent of silver coordination with the polymer's oxygens and its effect on olefin transport is demonstrated in Fig. 11.

Another investigation was performed by Kim et al. (2000) with PVMK membrane electrolyte to study the permeation and separation properties of ethylene/ethane and propylene/propane gas mixtures. Table 6 shows the effect of the molar ratio of PVMK/

Fig. 10. Chemical structure of several oxygen electron-pair donor groups in solid membrane electrolytes.
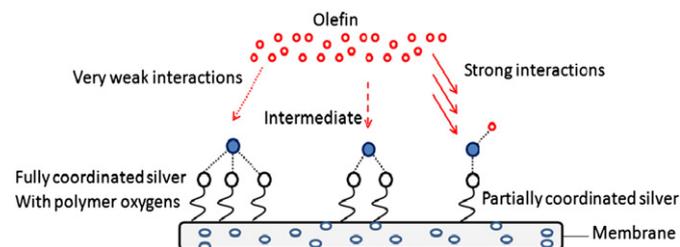
Fig. 11. Demonstration of Ag–olefin interactions occurring in solid membrane electrolytes.

Table 5
Effect of Ag content on propylene selectivity for different electron-donating carbonyl oxygen ligands.

Polymer	Selectivity $\alpha_{C_3H_6/C_3H_8}$								Reference
	Ag mole fraction								
	0	0.05	0.09	0.14	0.2	0.25	0.33	0.5	
PMMA/AgBF$_4$[a]	1	1.5	14	15	19	20	22	38	(Kim et al., 2003b)
PMMA/AgCF$_3$SO$_3$[a]	1	1.5	11	12	13	14	14.5	16	(Kim et al., 2003b)
PBMA/AgBF$_4$[a]	2	2.5	3	5	7	9	9.5	36	(Kim et al., 2003b)
PBMA/AgCF$_3$SO$_3$[a]	2	2.5	3	5	6	6	8	7	(Kim et al., 2003b)
PVMK/AgBF$_4$[b]	1	1	1	2	9	19	27	52	(Kim et al., 2003b)
PVMK/AgCF$_3$SO$_3$[b]	1	1	1	1	1.5	3	5	12	(Kim et al., 2003b)
PVP/AgBF$_4$[c]	1	1	1	1	1	2	14	50	(Kim et al., 2003b)
PVP/AgCF$_3$SO$_3$[c]	1	1	1	1	1	2	12	48	(Kim et al., 2003b)
POZ/AgBF$_4$[c]	1	1	1	1	1	1.5	2	18	(Kim et al., 2003b)
POZ/AgCF$_3$SO$_3$[c]	1	1	1	1	1	1.5	3	19	(Kim et al., 2003b)

[a] Ester ligand.
[b] Ketone ligand.
[c] Amide ligand.

Table 6
Effect of different silver–polymer coordination ligands on the permeation and separation characteristics of propylene and ethylene.

Polymer	Ag mole fraction	Permeance (GPU)		Selectivity		Reference
		C_3H_8	C_3H_6	$\alpha_{C_3H_6/C_3H_8}$	$\alpha_{C_2H_4/C_2H_6}$	
PVMK/AgBF$_4$	0.2			(20)	(40)	(Kim et al., 2000)
	0.33			(50)	(120)	(Kim et al., 2000)
	0.5			(100)	(250)	(Kim et al., 2000)
	0.6			(60)	(150)	(Kim et al., 2000)
	0.66			(30)	(80)	(Kim et al., 2000)
PVP/AgCF$_3$SO$_3$	0	0.0324	0.0324	1		(Kim et al., 2002e)
	0.25	0.0125	1	80		(Kim et al., 2002e)
	0.33	0.0053	7.5	2000		(Kim et al., 2002e)
	0.50	0.0044	32	7200		(Kim et al., 2002e)
	0.667	0.53	44	83		(Kim et al., 2002e)
	0.75	4.8	53	11		(Kim et al., 2002e)
POZ/AgCF$_3$SO$_3$	0	0.051	0.051	1		(Kim et al., 2002d)
	0.25	0.004	1	250		(Kim et al., 2002d)
	0.33	0.003	7.5	2500		(Kim et al., 2002d)
	0.5	0.003	30	10,000		(Kim et al., 2002d)
PHMV	0	45.5	54.1	1.2		(Kim et al., 2004a)
PHMV/AgBF$_4$	0.33	< 0.1	33.6	> 336(16)		(Kim et al., 2004a)
PHMV/AgClO$_3$	0.33	< 0.1	16.8	> 168		(Kim et al., 2004a)
PHMV/AgCF$_3$SO$_3$	0.33	< 0.1	12.8	> 128		(Kim et al., 2004a)
PVA/AgSbF$_6$	0	0.05	0.05	1		(Kim et al., 2002a)
	0.05	0.05	0.05	1		(Kim et al., 2002a)
	0.09	0.04	0.2	3		(Kim et al., 2002a)
	0.14	0.0375	1.5	40		(Kim et al., 2002a)
	0.2	0.0328	4.1	125		(Kim et al., 2002a)
PAAm/AgBF$_4$	0	< 0.1	< 0.1	–		(Park et al., 2001)
	0.33	< 0.1	< 0.1	–(80)		(Park et al., 2001)
	0.5	< 0.1	10.4	> 104(125)		(Park et al., 2001)
	0.66	–	–	(175)		(Park et al., 2001)
PAAm-g/AgBF$_4$	–	2200	2200	1		(Park et al., 2001)
PAAm-g/AgBF$_4$[b]	–	200[b]	840[b]	4.2[b]		(Park et al., 2001)
PDMS/AgBF$_4$	0	24	24	(1)		(Kim et al., 2004b)
	0.1[a]	5	13	(2.6)		(Kim et al., 2004b)
	0.21[a]	0.55	11	(20)		(Kim et al., 2004b)
	0.31[a]	0.2	10	(50)		(Kim et al., 2004b)
	0.47[a]	0.156	12.5	(80)		(Kim et al., 2004b)
	0.57[a]	0.086	13	(150)		(Kim et al., 2004b)
	0.73[a]	0.075	15	(200)		(Kim et al., 2004b)

All data are presented for pure gases, except in parenthesis are for mixed gases (50/50 mol%).
1 GPU $= 10^{-6}$ cm^3 cm^{-2} s$^-$ cmHg$^-$.

[a] Values are presented for weight fraction.
[b] Plasma treated PAAm/AgBF$_4$ membranes were immersed in aqueous silver solution.

AgBF$_4$ on the selectivity of olefins over paraffins. The selectivity of propylene and ethylene increases with increasing molar ratio of PVMK/AgBF$_4$ up to a silver mole fraction of 0.5 and then decreases with further increase in the silver mole fraction. As discussed previously by Ryu et al. (2001), such a selectivity dependence on the molar ratio of PVMK/AgBF$_4$ implies that the coordination environment of silver ions in PVMK has a significant effect on the facilitated transport of olefins. Although the silver mole fraction in the membrane where maximum selectivity occurs is different for PVMK and CA, i.e. 0.5 and 0.75 silver mole fraction, respectively, the same principal of silver coordination with membrane's ligands is still applicable. Higher ethylene selectivities than propylene were also observed which once again can be attributed to the higher silver affinity for ethylene than propylene.

3.3.1.2. Role of ionic constituents on olefin transport. When metal salts are dispersed in a polymer matrix, they may exist as free ions, contact ion pairs, or ionic aggregates depending on both the concentration of the metal salt and the intensity of the interactions between the metal ions and polymer matrix. Furthermore, the interactions between olefins and silver ions

occurring in membrane electrolytes depend greatly on the kind of ionic constituents present within the polymeric matrix and thus, have a great impact on the facilitation transport of olefins.

Kim et al. (2002e) examined the facilitated transport mechanism of propylene/propane separation occurring in solid membrane electrolytes of AgCF$_3$SO$_3$ dissolved in PVP. As done previously by Jin et al. (2000), FT-Raman Spectra analysis was conducted to investigate the ionic species present at different concentrations of dissolved silver salt in the polymer matrix. It was found that only free ions, ion pairs, and higher-order ionic aggregates were present up to 0.33, 0.5, and 0.66 Ag mole fractions, respectively. The permeance of propylene did not vary significantly up to 0.25 mol fraction of silver ions. However, it increased sharply at silver mole fraction above 0.25, nearly in linear proportion to the silver concentration, demonstrating the facilitated propylene transport. The linear increase in the permeance of propylene with total silver concentration regardless of the presence of different ionic constituents is very characteristic, because the role of each ionic constituent for the facilitated transport is expected to be different at different silver concentrations. On the other hand, propane permeance decreased from

0.0324 to 0.0044 GPU with increasing silver mole fractions up to 0.5, then it started to increase slightly afterwards for higher mole fractions of silver in the polymer matrix. This may be due to the fact that the structural defects of PVP/AgCF$_3$SO$_3$ electrolytes were significant at higher mole fractions of the silver salt. These defects were caused by the incompatibility between the polymer matrix and higher order ionic aggregates. Consequently, the permeances of both propylene and propane increased simultaneously resulting in a lower selectivity. Although the increase in the permeance of propylene with increasing Ag concentration in the polymer matrix is due to the facilitated transport as well as the structural defects of membrane, it can be concluded that the effect of the facilitated transport was dominated because the propane permeance did not increase until high concentration of Ag (0.66 mol fraction), whereas the permeance of propylene started to increase significantly with 0.25 mol fraction of silver. The permeation and separation characteristics of the PVP/AgCF$_3$SO$_3$ membranes are shown in Table 6.

3.3.1.3. Role of polymer structure on paraffin transport. In membrane electrolytes, paraffins such as ethane and propane do not have any specific interaction with silver ions and thus, permeate only via Fickian transport. Therefore, the permeation behavior of ethane and propane in membrane electrolytes is strongly associated with the structure of the polymer matrix which it passes through assuming a defect-free membrane surface.

Kim et al. (2002d) studied the effect of structure formation of silver membrane electrolytes upon the increase of silver salt in the polymer matrix upon propylene/propane separation. The membrane electrolytes were prepared from polymers such as POZ and PVP with different silver salts such as AgCF$_3$SO$_3$, AgBF$_4$, and AgClO$_4$. Previously as shown by several authors (Choi et al., 2001; Mitchell and Windle, 1984; Vega and Paul, 1993), Wide-Angle X-ray Scattering (WAXS) spectra were broadly used for polymer's structures inspection. Kim et al. (2002d) used the same principal to determine the inter-chain distance, d_1, and the distance between the POZ's pendant groups, d_2, of pure POZ and POZ/silver membranes. The analysis showed that the d spacing corresponding to both distances decreased with increasing silver concentration in the polymer up to 0.25 mol fraction. The decrease in the d spacing was a direct cause from the formation of transient cross-links between polymer chains due to coordinative interactions between the silver cations and the carbonyl oxygens of POZ. However, when the silver mole fraction was raised higher than 0.25, the inter-chain distance (d_1) increased, whereas the distance between the POZ's pendant groups spacing (d_2) decreased gradually. This increase of the inter-chain distance at high silver concentrations may have resulted from the electrostatic repulsion between the large free anions pushing apart the polymer chains (Schantz, 1991). These results show that silver polymer electrolytes undergo a significant structural change at around 0.25 mol fraction of silver salt in POZ membranes. This

phenomenon of the change in the d spacing is demonstrated in Fig. 12.

The permeation results obtained by Kim et al. (2002d) through POZ and their complexes with AgCF$_3$SO$_3$ at 25 °C are shown in Table 6. The propane permeance of the POZ system decreased rapidly up to silver mole fraction of 0.25, and decreased very slowly for higher mole fractions of silver afterwards before reaching a constant value 0 f 0.03 GPU. The coordination of silver ions to the carbonyl oxygens of POZ causes the polymer chains to become more rigid due to transient cross-links between the chains. This in return results in increasing the packing density of the polymer and a consequent reduction in the propane permeance. This effect dominates up to the silver mole fraction of 0.25. However, at silver concentrations higher than silver mole fraction of 0.25, the "pushing-apart" effect due to the free anions compensates for the effect of silver ion coordination, leading to a gradual decrease in the propane permeance. Thus, it was concluded that the structure of the polymer electrolytes largely depends on the combination of the interaction of the silver ions with the carbonyl oxygens of POZ and the repulsion of the anions, which in turn affects the gas transport behavior of paraffins. As far as for propylene behavior is concerned, the permeance was extremely low up to a mole fraction of silver ions of approximately 0.25. However, at higher mole fractions the propylene permeances increased almost linearly with silver concentration, which is in agreement with the concentration fluctuation theory developed by Kang et al. (1996). Therefore, the facilitated propylene transport only above silver mole fraction of 0.25 may be strongly associated with the coordination behavior of the silver ion as an olefin carrier.

3.3.2. Silver coordination with polymer C = C ligands

Kim et al. (2004a) proposed poly(hexamethylene vinylene) (PHMV) as a membrane electrolyte containing different silver salts for facilitated transport of propylene. PHMV is an attractive polymer material because it contains $C = C$ bonds but no heteroatoms such as carbonyl oxygens or amide groups. Therefore, it is expected that that silver salts are dissolved in the polymer due to the π-complexation between silver ions and the $C = C$ bonds present in the polymer to form solid polymer electrolytes, which in return facilitates the transport of olefins through π-complexation with coordinated silver ions in the polymer. The decline in the separation performance with time was also not expected due to the absence of heteroatoms in the polymer matrix. The presence of heteroatoms are known to enhance the reduction of silver ions to silver metal nanoparticles, which was frequently observed in silver polymer electrolyte membranes containing amide groups such as POZ and PVP (Jose et al., 2001). Gas permeation through the polymer membranes consisting of PHMV and silver salts were performed using pure propylene and propane while the Ag mole fraction in the polymer matrix was fixed at 0.33. As shown in Table 6, pure PHMV membranes
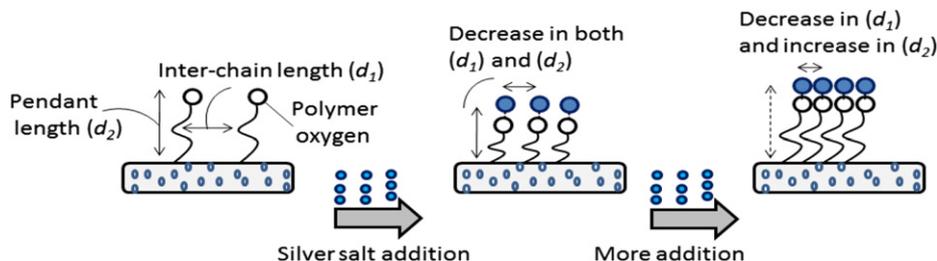

Fig. 12. Effect of silver salt addition on the polymer structure in solid membrane electrolytes.

exhibited very poor selectivity of propylene/propane separation. However, upon the incorporation of silver salts in PHMV, the separation performance was remarkably improved. The propylene selectivity through the silver–polymer matrix was found to be strongly depending on the type of anion of the silver salt. An ideal selectivity of 336 was observed when AgBF$_4$ was used, whereas a selectivity of 168 was obtained when AgClO$_4$ was used instead. As demonstrated by the Fourier Transform Infrared (FT-IR) spectroscopy analysis by Kim et al. (2004a), this was attributed to the different carrier activities caused by different strengths of the π-complexation between the silver ions and the $C=C$ bonds of the PHMV polymer. Long term mixed gas permeation tests were also performed to investigate the stability of the PHMV membranes. The selectivity of the membrane was slightly fluctuated during the first day of the experiment but remained almost constant afterwards for six days demonstrating that the membrane was stable in the solid state. However, the mixed gas selectivity, α_{mix}, was only 16 which was much lower than that for pure gas ($\alpha_{ideal} = 336$) when AgBF$_4$ was used in the PHMV polymer matrix at 0.33 mol fraction.

3.3.3. Silver coordination with polymer hydroxyl oxygens and amide nitrogens

Poly(vinyl alcohol) (PVA) is an interesting membrane material for silver polymer electrolytes where silver cations are coordinated by hydroxyl oxygens of the PVA polymer. There are several functional groups present in the PVA membrane such as OH, O, and CHO groups which can coordinate to silver ions. Several authors used crosslinked PVA membranes containing AgNO$_3$ salts for gas (Ho and Dalrymple, 1994) and liquid phase (Bryant et al., 1997) olefin/paraffin separations. However, facilitated olefin transport was only observed when the feed stream was saturated with water, and not in the dry state. Certainly, the addition of water and the subsequent removal from the feed gas streams causes critical problems for industrial applications as well as increasing operation costs and therefore, dry facilitated transport membrane electrolytes is a must. In the previous work by Ho and Dalrymple (1994) and Bryant et al. (1997), PVA was crosslinked by crosslinking agents such as formaldehyde, vinyl sulfone, or toluene diisocyanate at high temperatures (70 °C) up to three days. The heating step was necessary to ensure the crosslinking reaction of all the hydroxyl groups in the PVA membrane. However, it was found that heat treatments of polymer membranes containing silver salts enhanced the reduction of Ag$^+$ to metal Ag$^\circ$ and consequently, the performance of the facilitated olefin transport was deteriorated (Jose et al., 2001).

To avoid possible reductions of silver ions in PVA membranes, Kim et al. (2002a) used other crosslinking agents such as glutaraldehyde while crosslinking was achievable at room temperature. AgSbF$_6$ was also chosen as an olefin carrier since it possesses a low enough lattice energy and can be easily dissolved in the PVA matrix (Kim et al., 2001a, b, c). Table 6 shows the gas permeances and the selectivity of propylene/propane separation through crosslinked PVA membranes as a function of silver concentration at 25 °C. The separation performance was very poor until the concentration of silver salt was increased up to 0.09 mol fraction. Further increase in the salt concentration, resulted in additional incline in the propylene selectivity values in proportion to the silver concentration in the PVA matrix. At silver mole fraction of 0.2, the observed propylene permeance and selectivity were 4.1 GPU and 125, respectively. The FT-IR spectra analysis conducted by Kim et al. (2002a) suggested that the observed facilitated olefin transport was due to the formed complexes of silver cations that were coordinated by oxygens from the CHO groups among the others.

Another polymer worth mentioning is poly(acrylamide) (PAAm), where silver ions are coordinated to the nitrogen atoms from the N–H bond rather than coordinating with the carbonyl oxygen (Pinnau et al., 1997b). This is very interesting since the presence of amide ligands in the polymer, silver ions usually tend to coordinate with carbonyl oxygen of the amide groups as mentioned before for PVP and POZ polymers (Kim et al., 2000; Kim et al., 2003b). Park et al. (2001) prepared PAAm composite membranes by casting the polymer–silver electrolyte solution onto asymmetric microporous supports of PSF membranes. The permeation and separation characteristics of propylene/propane as a function of silver salt content through the PAAm/AgBF$_4$ composite membranes are summarized in Table 6. Both gas permeances of propane and propylene through the composite membrane of pure PAAm were lower than 0.1 GPU. However, with increasing the silver ion content up to 0.5 mol fraction, the propylene permeance increased while the propane permeance was held constant below 0.1 GPU, which in return led to an increase in selectivity values. It is also worth mentioning that the reported mixed gas selectivities were greater than that of pure gases. A reasonable explanation that led to this behavior was not discussed by the authors as it is widely known that lower selectivities are obtained for mixed gases rather than pure gas permeations as demonstrated by the recent review by Faiz and Li (2012) for olefin/paraffin separation using polymeric membranes. Park et al. (2001) also prepared ultra-thin layers of PAAm/AgBF$_4$ composite membranes by plasma treatments. The surface oxidation occurring during plasma irradiation results in the formation of several functional groups such as carboxyl, hydroxyls, ketone, and peroxide groups on the membrane surface (Yasuda, 1976). Among these functional groups, peroxide can act as an initiator for surface graft polymerization. The gas permeance was improved significantly through PAAm-graft/AgBF$_4$ membranes compared with that through the PAAm/AgBF$_4$ membranes; however, no selectivity was observed. This phenomenon indicated the plasma-treated membranes coated with silver salt cannot induce the facilitation transport and requires a medium or a solvent. Once the grafted composite membranes were impregnated in aqueous solution of 0.1 M AgBF$_4$, a selectivity of 4.2 was obtained accompanied by propane and propylene permeances of 200 and 480, respectively. It was concluded that using PAAm-graft/AgBF$_4$ membranes improved the gas permeance significantly compared with PAAm/AgBF$_4$ composites membranes, although there was a sacrifice in selectivity values.

3.3.4. Silver dissolution in inert polymers

Usually, silver salts are dissolved in the polymer matrix due to the coordination between silver ions and carbonyl oxygens (Kim et al., 2000; Kim et al., 2002d, 2002e, 2003b), hydroxyl oxygens (Kim et al., 2002a), polymer double bonds (Kim et al., 2004a), or nitrogens present in amide groups (Park et al., 2001). The facilitate transport of olefins through these polymeric membranes depends greatly on the degree of silver coordination within the polymer. However, the presence of heteratoms such as oxygens or nitrogens usually assists in the degradation of the facilitated transport due to the reduction of silver ions (Jose et al., 2001). Kim et al. (2004b) proposed poly(dimethyl siloxane) (PDMS) as a polymer material for membrane electrolyte where silver salts are physically dispersed in the membrane. PDMS is considered to be an inert polymer because it does not have any functional groups to coordinate with silver ions. PDMS is also known to have high permeability to most gases. In these membranes, the silver salts are not dissolved molecularly in the polymer matrix, but instead they are physically dispersed. When silver salts are physically dispersed in PDMS, they are present in

the form of higher order ionic aggregates. However, upon the exposure of propylene, these aggregates start to dissolve into free ions and as a consequence, results in facilitated olefin transport.

Kim et al. (2004b) investigated the permeation properties of a propylene/propane mixture using PDMS/AgBF$_4$. In the initial permeation experiments, the observed propylene selectivity was very low because the silver salt was rather physically dispersed as ionic aggregates in the inert PDMS matrix and thus, was inactive as an olefin carrier. However, the ionic aggregates gradually dissolved with permeation time due to the coordination of propylene molecules with silver ions and eventually were converted to free ions, resulting in facilitated propylene transport. This observation of facilitated transport dependence on time was the first to be reported on solid membrane electrolytes. Additionally, unlike previous work on facilitated transport membrane electrolytes (Kim et al., 2000; Kim et al., 2002e, 2003b), where those membranes typically exhibited a threshold carrier concentration for facilitated transport to occur, these PDMS/silver salt membranes were functional at any silver loading and hence, a threshold carrier concentration did not exist. In fact, PDMS/AgBF$_4$ membrane with 0.73 silver salt weight fraction showed a very high performance for propylene/propane mixture separation as the reported mixed vapor selectivity and propylene permeance were 200 and 15 GPU, respectively. This mixed vapor selectivity of 200 for propylene/propane separation is considered the highest to be ever reported in the literature for solid membrane electrolytes. The permeation and separation characteristics of the PDMS/AgBF$_4$ membrane electrolyte for propylene/propane separation are shown in Table 6.

3.4. Enhanced membrane electrolytes

It is well known that one of the major shortcomings of silver membrane electrolytes is the reduction of silver ions to silver nanoparticles (Jose et al., 2001) and thus, the performance of the membrane for olefin/paraffin separation is significantly reduced. Although silver reduction may occur for various reasons, it is believed that the counter ions of silver salts play an important role on silver stabilization. Complex formation of silver ions and olefin molecules is known to be quite sensitive to the type of silver salt, i.e. to the counter anion (Kang et al., 2001). Large and low electronegativity anions such as BF$_4^-$, CF$_3$SO$_3^-$, and ClO$_4^-$ form silver salts with lower lattice energy and act as effective olefin carriers when dissolved in polymer matrices. In contrast, small and highly electronegative anions such as F$^-$, Cl$^-$, Br$^-$, and NO$_3^-$ form salts with higher lattice energy and hinder the complexation of silver ions with olefin molecules due to the strong interaction between the salts' cations and anions. Furthermore, as previously confirmed by Kim et al. (2003b), silver membrane electrolytes which possess strong silver interaction with the polymer matrix than with salt's counter anion exhibit more favorable silver ion complexation with olefins, resulting in higher olefin solubility and improved permeation. As a consequence, the addition of additives to membrane electrolytes have attracted the attention of many researchers as a new means to reduce the interaction between silver ions and counter anions and therefore, causes the silver ions to be more active for olefin coordination, as well as reducing the tendency of silver ions to be reduced. In this section, the efforts by several authors to enhance the method of membrane electrolytes for olefin/paraffin separation is highlighted.

3.4.1. Addition of amino acids

The idea of using amino acids was proposed by the fact that they were quite reactive with chemical substances involving metal ions such as silver ions (Garipcan et al., 2001). In particular, asparagines containing NH$_3^+$, CNO, and COOH in acidic conditions are expected to interact with silver ions as well as counter anions of the salt. Kang et al. (2003) introduced asparagines into two systems of POZ/AgBF$_4$ and POZ/AgNO$_3$ membrane electrolytes and investigated their effect on propylene/propane separation. In addition to the interactions of the positive charge of NH$_3^+$ with the counter anion of the silver salt, asparagines possess carbonyl groups which can also coordinate to silver ions. Before the addition of asparagines, the POZ/AgBF$_4$ membrane exhibited very high separation performance for olefin/paraffin mixtures, whereas the POZ/AgNO$_3$ membrane showed almost no separation. Table 7 shows the effect of asparagines' presence on the facilitated propylene transport through the POZ membranes. The selectivity increases significantly with the introduction of small amounts of asparagines to the polymer matrix for both POZ/AgBF$_4$ and POZ/AgNO$_3$ membrane electrolyte. The remarkable improvement in the membrane separation performance confirms the enhanced facilitated transport of propylene which can be attributed to two factors, the weaker interactions between Ag$^+$ ions and BF$_4^-$ and NO$_3^-$ anions, and/or the additional coordinative interactions between Ag$^+$ and the carbonyl oxygens of the asparagines. However, if only the electrostatic interaction was effective (first factor), then the separation performance of the POZ/AgBF4 membranes would not be significantly enhanced because the interaction between Ag$^+$ and BF$_4^-$ is originally weak (Kang et al., 2001). A few years later, Kang et al. (2005) studied the effect of several amino acids types on the facilitated propylene transport in POZ/AgBF$_4$ and POZ/AgNO$_3$ membranes. The chemical structures of these amino acids are shown in Fig. 13. Similar to the previous results (Kang et al., 2003), the addition of small amino acids to the polymer matrix was very effective in enhancing propylene/propane separation. However, this enhancement in selectivity and gas permeance was strongly sensitive to the kind of amino acid used. The separation performance of membrane was arranged in the order: asparagines > valine ≈ glutamic acid > lysine. These findings suggest that other functional groups in amino acids besides NH$_3^+$ and COOH are also of pivotal importance in determining the activity of silver ions. It was demonstrated that amide groups (CON) in asparagine was the most effective in improving the separation performance, whereas amine groups (NH$_2$) in lysine was the least effective among them. The groups of CH(CH$_3$)$_2$ in valine and COOH in glutamic acid were intermediate.

3.4.2. Addition of plasticizers

Incorporation of plasticizers was also suggested to increase the stability of silver-membrane electrolytes significantly (Jose et al. 2001, 2002). This stabilization of silver ions in the polymer matrix can be explained due to the strong interactions of silver ions with the two carbonyl groups of the phthalate. Jose et al. (2001) studied the effect of different plasticizers such as dibutyl phthalate (DBP), dioctyl phthalate (DOP), and diphenyl phthalate (DPP) in a PVP/AgBF$_4$ polymer matrix on propylene/propane separation. The selectivity of propylene for the PVP/AgBF$_4$ membrane without a phthalate decreased with time. On the other hand, the incorporation of a plasticizer significantly improved the performance of the PVP/AgBF$_4$ membranes. The selectivity and permeance of the membranes containing phthalates nearly remained constant throughout the experiments for up to one hundred hours. Furthermore, the selectivity and permeance measured at one hundred hours were much higher for the membranes containing phthalates in comparison with those without phthalates. From these results, it is likely that phthalates in PVP/AgBF$_4$ membranes are playing an important role in preventing the reduction of silver ions as well as in increasing the mobility of the silver ions, thereby facilitating the propylene transport. To compare the effect of phthalates and non-phthalate plasticizers, Jose et al. (2001) used 2 wt.% of glycerol, which is a weak coordinating plasticizer to silver ions. As shown in Table 7, PVP/AgBF$_4$ membrane containing 2 wt.% glycerol showed an initial propylene selectivity of 103; however, the selectivity decreased

Table 7
Effect of adding a third component to silver–polymer matrix on the long term stability of the membrane.

Polymer	Type of enhancement	Amount	Time	Selectivity		Reference
				$\alpha_{C_3H_6/C_3H_8}$	$\alpha_{C_2H_4/C_2H_6}$	
	Amino acids	Ag/NH$_3$				
POZ/AgNO$_3$	Asparagines	1/0		0.95		(Kang et al., 2003)
		1/0.01		34		(Kang et al., 2003)
POZ/AgBF$_4$	Asparagines	1/0		45.2		(Kang et al., 2003)
		1/0.01		65.5		(Kang et al., 2003)
	Plasticizer	Weight %	(Hours)			
PVP/AgBF$_4$		0	0	65		(Jose et al., 2001)
			50	40		(Jose et al., 2001)
			100	30		(Jose et al., 2001)
	DBP	2%	0	50		(Jose et al., 2001)
			50	85		(Jose et al., 2001)
			100	85		(Jose et al., 2001)
	DOP	2%	0	105		(Jose et al., 2001)
			50	160		(Jose et al., 2001)
			100	160		(Jose et al., 2001)
	DPP	2%	0	130		(Jose et al., 2001)
			50	135		(Jose et al., 2001)
			100	135		(Jose et al., 2001)
	Glycerol	2%	0	103		(Jose et al., 2001)
			50	50		(Jose et al., 2001)
			100	20		(Jose et al., 2001)
	Acid (HBF$_4$)	AgBF$_4$/HBF$_4$	UV time(min)			
POZ/AgBF$_4$		1/0	0		95	(Kim et al., 2003a)
			60		100	(Kim et al., 2003a)
			120		30	(Kim et al., 2003a)
			240		1	(Kim et al., 2003a)
		1/0.2	0		95	(Kim et al., 2003a)
			60		100	(Kim et al., 2003a)
			120		100	(Kim et al., 2003a)
			240		100	(Kim et al., 2003a)
		1/0.4	0		95	(Kim et al., 2003a)
			60		95	(Kim et al., 2003a)
			120		95	(Kim et al., 2003a)
			240		95	(Kim et al., 2003a)
	Surfactant(8G1)	AgBF$_4$/8G1	(Days)			
PVP/AgBF$_4$		1/0	2	50		(Park et al., 2003)
			15	25		(Park et al., 2003)
			30	15		(Park et al., 2003)
		300/1	2	60		(Park et al., 2003)
			15	60		(Park et al., 2003)
			30	60		(Park et al., 2003)
		100/1	2	60		(Park et al., 2003)
			15	60		(Park et al., 2003)
			30	50		(Park et al., 2003)

All data are presented for mixed gases (50/50 mol%).

rapidly reaching a value of 20 after hundred hours of operation. Furthermore, the color of the membrane containing glycerol became dark brown within a day, indicating the rapid formation of silver particles. On the other hand, no color change was observed after one week for the membrane containing phthalates. These results suggest that enhanced performance of the membranes can be achieved only in the presence of a plasticizer which can strongly interact with silver ions such as phthalates.

3.4.3. Addition of acids

POZ and PVP are well known materials to be used as reducing agents for silver ions as well as protecting agents for silver colloids from ionization (Henglein, 1998; Huang et al., 1996; Silvert et al., 1997; Zhang et al., 1996). Therefore, it would be of pivotal importance to prohibit the reduction of silver salt and stabilize the

silver ions when POZ or PVP are used as polymeric materials in membrane electrolytes for olefin/paraffin separations. Pastoriza-Santos and Liz-Marzán (1999) proposed that the reduction of silver ions to silver nanoparticles was possible by the presence of a polymeric material, N,N-dimethylformamide (DMF) in water. The addition of acid containing H$^+$ ions was suggested to possibly prevent the forward reduction reaction of silver ions occurring and thereby, prohibiting the formation of silver nanopaticles. Kim et al. (2003a) used HBF$_4$ acid as a source of H$^+$ ions to prohibit the photo reduction of silver ions enhanced by UV irradiation in POZ/AgbF$_4$ membranes. The structure of POZ used was very similar to that of DMF, in the aspect of containing amide groups and thus, similar reduction process was expected to proceed in the POZ/AgBF$_4$ membrane. The effect of HBF$_4$ on silver reduction on the ethylene/ethane mixture separation was monitored with time. Table 7 shows the mixed gas selectivity of ethylene/ethane as a function of UV
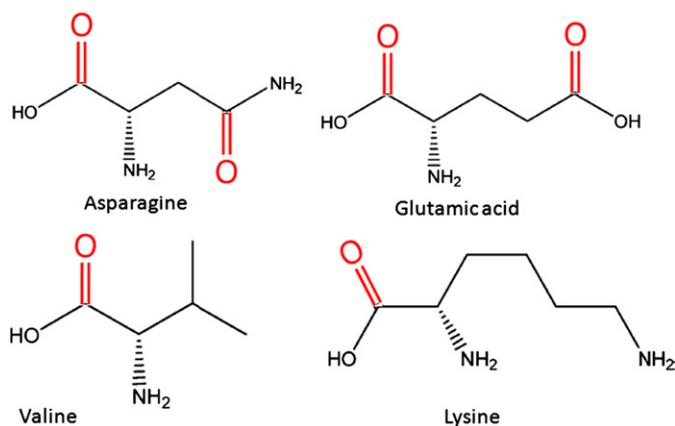
Fig. 13. Chemical structure of several types of amino acids used to enhance solid membrane electrolytes' performances.

irradiation time through the POZ/AgBF$_4$ membranes containing different amounts of HBF$_4$. The mole ratio of POZ to silver salt was fixed at 1:1 for all investigated membranes. The mixed gas selectivity through the POZ/AgBF$_4$ membranes without HBF$_4$ decreased significantly up to 30% of the initial value after two hours of exposure to UV irradiation. This confirms the formation of nanosized silver particles with UV irradiation time and thus, the concentration of silver ion was decreased. Furthermore, after four hours of exposure to UV irradiation, the selectivity dropped to 1 and hence, no further separation was obtained. This can be explained by the rapid growth and accumulation of silver nanoparticles, inducing the formation of holes or defects at the interface between metal particles and the polymer matrix, where both ethane and ethylene gas molecules can easily transport through. The defects may be originated from the incompatibility between large-sized silver particles and polymer matrix. On the other hand, the selectivity of ethylene/ethane through the membranes containing HBF$_4$ upon UV irradiation was sustained, implying prohibition or limitation of the reduction of silver ions. However, the addition of excess HBF$_4$ into the silver–polymer complex membranes appears to have a negative effect on the facilitated olefin transport as both the permeance and selectivity through the membranes decreased with increasing HBF$_4$ concentration. This may be ascribed to the fact that excess BF$_4^-$ anions interact strongly with silver ions and thereby reduce the probability for the complexation of silver ions with ethylene in the POZ matrix (Kim et al., 2003a).

3.4.4. Addition of nonionic surfactants

Nonionic surfactants are commonly employed to prevent the growth of metal particles (Rosen, 1989). It is expected that the presence of surfactants with silver membrane electrolytes provide more favorable environments for silver salts and lower the reduction of silver ions. Surfactants contain both hydrophilic and hydrophobic parts within their molecular structure and upon their addition into silver membrane electrolytes; they would adsorb onto the surface of silver atoms due to their unique molecular structure and form surfactant films, which in return prevents the growth of silver particles in the membrane. Park et al. (2003) used nonionic *n*-octyl β-d-glucopyranoside (8G1) surfactant as a protecting agent to examine the long term stability of PVP/AgBF$_4$ membranes for propylene/propane mixture separation. The 8G1 was miscible with PVP at all compositions as evident by the single glass transition temperature measured by Differential Scanning Calorimeter (DSC) (Park et al., 2003). The result showed that after continuous experiments for fifteen days with PVP/AgBF$_4$ membranes excluding 8G1, the gas permeance

and selectivity was increased and decreased, respectively. This behavior was attributed to the formation of the interfacial rifts or defects between silver metal particles and matrix due to the incompatibility between metal particles and polymer matrix. However, the separation performance was maintained almost invariable up to thirty days for the PVP/AgBF$_4$/8G1 membranes, implying that the surfactant played an important role in prolonging the life time of the membrane. The effect of surfactant addition to PVP/AgBF$_4$ membrane on propylene/propane separation is shown in Table 7.

3.4.5. Use of mixed salts

The idea of using mixed metal salts in membrane electrolytes was generally employed to increase the ionic conductivity and transport properties within these polymer systems. Several authors demonstrated that introducing mixed alkali salts into PEO based polymers have resulted in higher ionic conductivity than those of polymer electrolytes containing a respective single salt (Lascaud et al., 1998; Perrier et al., 1995; Preechatiwong and Schultz, 1996). The unusual high conductivity of mixed salts systems was ascribed to higher degrees of salt dissociation and higher configuration entropy or disorder occurring in the membrane electrolyte (Preechatiwong and Schultz, 1996), which led to a positive deviation from the average values of two ionic conductivities alone. Kim et al. (2005) investigated the effect of using mixed salts in POZ membrane electrolytes for propylene/propane separation. As shown in Table 8, the propylene and propane permeances decreased with increasing the concentration of a non-active olefin carrier salt such as AgNO$_3$ into POZ/AgBF$_4$ and POZ/AgCF$_3$SO$_3$ membranes. However, the propylene selectivity unexpectedly increased with increasing the AgNO$_3$ mole ratio with respect to the other salt in the membrane. The obtained propylene selectivity of 95 at 0.3 AgNO$_3$ mole fraction with respect to AgBF$_4$ was much higher than those obtained in pure POZ/AgBF$_4$ and POZ/AgNO$_3$ membranes alone. Similarly, a propylene selectivity of 30 obtained at a 0.7 mol fraction of AgNO$_3$ with respect to AgCF$_3$SO$_3$ was higher than those obtained in pure POZ/AgCF$_3$SO$_3$ alone. The increase in selectivity was due to the increased structural compactness resulting from transient cross-links of the polymer chains by small sized AgNO$_3$ (Kim et al.,

Table 8
Effect of mixed polymer salts on the permeation and separation characteristics of propane and propylene.

Polymer	Mixtures fraction		Permeance (GPU)		Selectivity	Reference
			C_3H_8	C_3H_6	$\alpha_{C_3H_6/C_3H_8}$	
POZ	AgNO$_3$	AgBF$_4$				
	0	1	0.24	11	45	(Kim et al., 2005)
	0.3	0.7	0.05	4.7	95	(Kim et al., 2005)
	0.7	0.3	0.1	1	10	(Kim et al., 2005)
	1	0	0.2	0.2	1	(Kim et al., 2005)
	AgNO$_3$	AgCF$_3$SO$_3$				
	0	1	0.31	4.6	15	(Kim et al., 2005)
	0.3	0.7	0.1	2.8	28	(Kim et al., 2005)
	0.7	0.3	0.01	0.3	30	(Kim et al., 2005)
	1	0	0.3	0.3	1	(Kim et al., 2005)
	AgCF$_3$SO$_3$	AgBF$_4$				
	1	0	0.3	5	15	(Kim et al., 2005)
	0.7	0.3	0.3	7	21	(Kim et al., 2005)
	0.3	0.7	0.25	9	35	(Kim et al., 2005)
	0	1	0.23	10.5	45	(Kim et al., 2005)

All data are presented for a gas mixture containing 50% C$_3$H$_8$ and 50% C$_3$H$_6$.

2005). WAXS spectra analysis showed that the inter-segmental d spacing in $POZ/AgNO_3/AgBF_4$ membranes was much smaller than that in POZ membranes containing a single salt, supporting the higher extent of the transient cross-links in polymer electrolytes containing mixed salts. Therefore, the introduction of mixed salts was found to strongly affect the structural changes as well as the separation performances of polymeric membrane electrolytes, especially when one of the salts contains small anions such as $AgNO_3$ and the other possess large anions such as $AgBF_4$ or $AgCF_3SO_3$. However, mixing two salts together where both anions are large such as $AgBF_4$ and $AgCF_3SO_3$ exhibited simple mixing behavior as the propylene selectivity increased with increasing the molar ratio of $AgBF_4$ in the polymer matrix reaching the maximum selectivity value of 45 at pure $AgBF_4$.

4. Ionic liquids membranes

Ionic Liquids (ILs) have been attracting much attention in the past few decades due to their versatile properties and applicability for a wide range of applications. Recently, an intensive review concerning ionic liquids has been published by Olivier-Bourbigou et al. (2010). The review article tackles a wide variety of topics such as design of new generations, fundamental properties, effect on several reactions processes, applications for industrial processes, and key events of ILs in environmental catalysis. Ionic liquids have also been widely utilized in SLMs for gas separation (Bara et al., 2009; Hanioka et al., 2008; Huang et al., 2008; Myers et al., 2008; Scovazzo et al., 2004, 2009). Unlike conventional solvents used in SLMs, ILs have several advantages such as high polarity, low vapor pressure, high ionic conductivity, and thermal stability (Fortunato et al., 2004; Jiang et al., 2007; Matsumoto et al., 2005; Sheldon, 2001). In particular, the characteristic of possessing low vapor pressure prevents evaporation from the membrane and consequently, enhances the long term stability of SLMs. The report provided by Scovazzo (2009) covers the majority of the data concerning gas separations using Room Temperature Ionic Liquids (RTILs) in SLMs. The analysis carried out by Scovazzo (2009) offered major critical points and recommendations for further successful development in the field of gas separation using supported ionic liquid membranes.

In this section, the application of ionic liquids for olefin/paraffin separation using several membrane systems is presented. It is worth mentioning that the utilization of ILs can be performed both in the liquid and solid states such as the case in liquid membranes and membrane electrolytes, respectively. Therefore, instead of discussing the topic on ILs twice in the previous sections, both liquid and solid membranes are combined within where a direct comparison can be obtained on olefin/paraffin separation using ILs membrane systems.

4.1. Ionic liquids membrane electrolytes

Kang et al. (2008a) reported that the surface interactions of silver nanoparticles with anions of ILs such as BF_4^- and PF_6^- induced positive charges on the surface of the nanoparticles by forming free ions in the ILs. Consequently, ILs can also be utilized as an electron acceptor or polarizer for silver nanoparticles. Afterwards, Kang et al. (2008c) demonstrated the effect of ILs on the formation of a partial positive charge on the surface of silver nanoparticles and its subsequent effect on facilitated olefin transport. The ILs/Ag composite membranes were prepared by dispersing Ag nanopowder in ILs, followed by coating onto polyester microporous membrane supports. Three different ILs of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$), 1-butyl-3-methylimidazolium triflate ($BMIM^+Tf^-$), and 1-butyl-

3-methylimidazolium nitrate ($BMIM^+NO_3^-$) were employed to control the positive charge density of the surface of silver nanoparticles. The characterization of these partially positive silver nanoparticles revealed that $BMIM^+BF_4^-/Ag$ and $BMIM^+NO_3^-/Ag$ had the highest and lowest binding energy, respectively. This behavior was consistent with the tendency of ILs to form free ions as the best separation performance was obtained through composite membranes consisting of $BMIM^+BF_4^-$. These membranes resulted in a mixed gas selectivity of 17 and propylene permeability of 7 GPU. It was therefore, concluded that the facilitated olefin transport was a direct consequence of the surface positive charge of the silver nanoparticles induced by ILs.

The surface properties of the silver nanoparticles play the most important role in determining the interactions occurring between olefin molecules and silver nanoparticles in facilitated transport mechanisms. And since these interactions occur at the surface of the membrane, it is essential to obtain a large surface area with smaller-sized silver nanoparticles. Mun et al. (2009) employed a plasma-ion method to obtain clean and small-sized silver nanoparticles on sugar crystals. These silver crystals were subsequently dispersed in $BMIM^+BF_4^-$ and coated onto a microporous polyester membrane support. The separation characteristics of these membranes showed facilitated transport of propylene with a mixed vapor selectivity up to 14.4. Mun et al. (2009) confirmed this facilitated olefin transport was due to the partially positive charged surfaces of silver nanoparticles, which was induced by $BMIM^+BF_4^-$. The formation of this partially positive surface charge may have occurred due to the interactions of the silver nanoparticles with the free anions of $BMIM^+BF_4^-$.

4.1.1. Ionic liquids membrane stability

As brought to the attention by several researchers, one of the major short comings of membrane electrolytes is the issue of long term stability. The decline in membrane performance starts to appear with the continuous reduction of silver ions to silver nanoparticles which eventually accumulates together and forms holes and defects on the membrane's surface and thus, no further separation can be achieved. Although the investigation of ILs membrane electrolytes' stability is essential, not many reports in the literature discussed this topic, which suggests that investigations are still ongoing. However, the work of Kang and co-workers virtually covered all aspects regarding membrane electrolytes and briefly reported on the stability of ILs membrane electrolytes.

Kang et al. (2008b) studied the effect of ILs anions on the reduction behavior of silver cations and the separation performance of olefin/paraffin mixtures through $POZ/AgNO_3/ILs$ membranes. The investigated ILs were $BMIM^+BF_4^-$, $BMIM^+CF_3SO_3^-$, and $BMIM^+NO_3^-$. The $POZ/AgNO_3/ILs$ membrane electrolytes were prepared by dissolving $AgNO_3$ salt and each IL in an aqueous solution containing 20 wt.% POZ. The POZ:Ag molar ratio was held constant at 1:1 for all membranes investigated while the amount of IL was only 0.1 M ratio. The $POZ/AgNO_3$ membranes without ILs clearly had no effect on propylene/propane separation as the separation performance indicated propylene mixed vapor selectivity and permeability of 0.95 and 0.1 GPU, respectively. However, when ILs were added to the membrane electrolytes, the separation properties enhanced significantly regardless of the IL type as the average mixed vapor selectivity and permeability values were increased to 5.4 and 32.3, respectively, for all ILs investigated. The enhanced performance was due to the partial interaction between the $BMIM^+$ and NO_3^- anions which weakened the original interaction of Ag^+ with NO_3^- and eventually led to Ag^+ activation for facilitated olefin transport. As for long term stability analysis, the results indicated that ILs membranes consisted of $BMIM^+NO_3^-$ exhibited stable separation performance

throughout continuous operation for hundred and forty hours whereas the separation performance of the $BMIM^+CF_3SO_3^-$ membrane was deteriorating for the same operating period. Furthermore, the $BMIM^+BF_4^-$ membrane was the worst among the others as the separation performance rapidly decreased with time. These findings strongly suggest that there was a strong dependence of the membrane stability, i.e. silver reduction, on the nature of the ILs counter anions. The reason of such behavior was not clear as it was suggested that since the stability of silver salts were in the order of $AgNO_3 > AgCF_3SO_3 > AgBF_4$, then the stability of ILs would follow in the same order. However, Kang et al. (2008b) indicated that detailed investigation were still in progress and should be reported in the near future.

4.2. Ionic liquids membrane contactors

The application of ILs for olefin/paraffin separation can also be achieved in the liquid state with various membrane configurations. Ortiz and co-workers (Ortiz et al., 2008, 2010a, 2010b; Fallanza et al., 2011a, 2011b) examined extensively the chemical absorption properties of propylene by chemical complexation of silver ions in ILs solutions. Primarily, Ortiz et al. (2008) studied the effect of temperatures and pressures on propylene and propane absorption in a reactive medium consisting of $AgBF_4$ salt and $BMIM^+BF_4^-$ IL solution. The results revealed that propylene absorption definitely did not follow a simple Henry's law model as the absorption capacity of the $Ag/BMIM^+BF_4^-$ for propylene was much higher than that of $BMIM^+BF_4^-$ alone. On the other hand, propane absorption in $Ag/BMIM^+BF_4^-$ was basically the same as in $BMIM^+BF_4^-$ without the silver salt which suggested that salting out effects due to the presence of Ag^+ and BF_4^- ions did not take place. The absorption of propylene was also demonstrated to increase with decreasing the temperature for the range of 278–318 K. Conversely, the dependence of pressure on propylene absorption showed a different behavior as the chemical complexation reaction took place only below propylene partial pressures of 3 bar for the given operating conditions. However, increasing the pressure beyond this point showed that the equilibrium curve had the same slope as predicted by physical absorption. As a consequence, the selectivity of propylene to propane absorption was found to be higher at lower pressures creating a trade-off with capacity for the optimum absorption pressure. Furthermore, complete regeneration of the reaction media was possible by stirring at room temperature with 20 mbar vacuum for three hours.

Recently, Ortiz et al. (2010a) determined the reaction kinetics properties of propylene into $Ag^+/BMIM^+BF_4^-$. The conducted analysis established reaction rate expressions and constants, mass transfer coefficients, and diffusion coefficients of propylene absorption into the IL medium. One of the major observations was that for higher concentrations of Ag^+ above 0.25 M in $BMIM^+BF_4^-$, the reaction regimes were considered to be instantaneous and the rate of absorption was limited by the diffusion of propylene and Ag^+ in the IL $BMIM^+BF_4^-$. Furthermore, the IL absorption medium was utilized in HFMCs for olefin/paraffin separation and the results were compared with simple absorption method in a batch reactor (Ortiz et al., 2010b). The HFMCs system showed that higher absorption of propylene was achievable with the $Ag^+/BMIM^+BF_4^-$ medium rather than the $Ag^+/aqueous$ solutions when the concentrations of Ag^+ was 0.1 M. However, for higher concentrations of Ag^+, i.e. 0.25 M, the Ag^+ aqueous solution showed higher absorption of propylene than the IL medium. This phenomenon was attributed to the strong dependency of the viscosity of the $Ag^+/BMIM^+BF_4^-$ reactive medium with the increase in silver ions concentration which limited propylene diffusion in the solvent. On the other hand, the

propylene fluxes measured in the stirred tank reactor were directly a function of the initial propylene mole fraction in the feed. A comparison between both systems has been performed based on the overall volumetric mass transfer coefficients obtained from the experimental data. These values were 5.9×10^{-4} and $236 \times 10^{-4} \, s^{-1}$ for the HFMCs and the stirred tank, respectively. Therefore, from a kinetic point of view, the stirred tank reactor performed better than the membrane contactor for the considered experimental operating conditions. However, Ortiz et al. (2010b) suggested that although the use of the membrane contactor resulted in lower values of mass transfer coefficients, a considerable enhancement can be induced by acting on the design of the membrane module as well as optimizing the operating conditions.

5. Summary and conclusions

Facilitated Transport Membranes (FTMs) where transition metal ions are utilized as olefin carriers have a great potential for olefin/paraffin separation due to the large permeation rates and selectivities achieved when compared with conventional polymeric membranes. However, there are several inherit problems with each specific type of FTMs.

SLMs suffer from several critical drawbacks such as the loss of the solvent due to evaporation caused by the trans-membrane pressure. One of the proposed solutions was the addition of water vapor to the feed and sweep streams. However, this is considered as a non-practical solution because of the significant rise in operating costs due to the addition and subsequent removal of water vapor from olefin streams.

IEMs are considered to be more stable than their respective SLMs due to the electrostatic interactions occurring between the facilitation solvent and the ion exchange sites on the membrane surface. Although high olefins fluxes and selectivities were also possible with IEMs, it was only observed when swollen or hydrated membranes were used. Unfortunately, IEMs do not retain water sufficiently for long periods of time resulting in a decrease in olefin fluxes and olefin/paraffin selectivity. This could only be prevented if water vapor was continuously added to the feed mixture to substitute the loss from the membrane. Similarly to SLMs, the addition of water vapor would not encourage the usage of IEMs in the industry due to the high operating costs.

FLMs solved the stability problems occurring in ILMs such as SLMs and IEMs due to the continuous flow of the facilitation solvent. Although FLMs showed promising stability, low permeation rates were achieved due to the small membrane surface area and non-efficient gas liquid contact.

To overcome these drawbacks, HFMCs are proposed as a continuous gas–liquid contact with large surface area for mass transfer. Although HFMCs seem to be the most effective and efficient method from a practical point of view for olefin/paraffin separation using a facilitation solvent, yet it still suffers from several shortcomings such as membrane wetting with the solvent and limited membrane's thermal and chemical stability due to the incompatibility between polymeric materials and chemical solvents, which in return destroys the long term application of the separation process

Membrane electrolytes are another novel class of FTMs where olefin transport occurs in the solid state. In this manner, problems taking place in liquid FTMs do not exist. However, a practical application of membrane electrolytes for industrial use is still pending because of the stability of silver ions as an olefin carrier. Silver ions are subject to reduction to form silver nanoparticles and further aggregate each other, which leads to the damage of the membrane. Once the membrane is degraded, regeneration is

not possible and the membrane should be discarded. However, if such problems happen in liquid FTMs, regeneration of the solvent was possible. In addition, any impurities such as CO_2 and H_2S present in the gas mixture would destroy the complexing agent and deteriorate the process performance which would eventually fail.

The application of ILs for olefin/paraffin in various membrane configurations is a new concept and yet to be investigated extensively. Nevertheless, initial studies showed that ILs can be successfully implemented in both the liquid and solid states for olefin/paraffin separation. However, long term stability of ILs membranes is still a concern and more investigations are still required.

Acknowledgments

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