

A review on olefin/paraffin separation using reversible chemical complexation technology

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Received 7 December 2007; accepted 9 April 2008

Abstract

In the present work, the facilitated transport membrane (FTMS) technology used in separation of olefins from paraffins is reviewed. Primary attentions are given to basic fundamentals, advantages and methods of facilitated transport membrane technology. The general mechanisms by which the facilitated transport proceeds under various conditions are described. The effects of different parameters on the degree of facilitated factor, permeance, and selectivity in the FTMS are thoroughly discussed. The performance of the membranes and its current application related with the polymer, solvent, and carrier structure developing during membrane preparation are also considered. A number of potential applications of the FTMS in a variety of modules can be added and optimized in a process design to achieve the desired separation are highlighted in this review. Finally, some reviews have been conducted for the modeling as well as the numerical solution to the governing system of equations.

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Keywords: Olefin/paraffin separation; Facilitated transport membrane; Modeling

1. Introduction

1.1. Importance of olefin and paraffin in industries

Separation of olefin and paraffin gases is important to the petrochemical industry. Low molecular weight olefins, such as ethylene and propylene, are important feed stocks used for the production of polymers such as polyethylene, polypropylene, styrene, etc. in the petrochemical industry. Therefore, they are too valuable to be burned as secondary components. The necessary low temperatures and high pressures make it an energy intensive separation process in the petrochemical industries. Since the boiling points of paraffin/olefin counterparts lie within very narrow temperature ranges, conventional distillation is difficult and expensive [1]. In that, the development of an alternative energy-saving separation process [2,3] has been in high demand [4]. Membranes, extraction, adsorption, advanced filtration, and hybrid systems offer the largest opportunities for energy reduction by replacing distillation and evaporation especially in separations with low relative volatilities, e.g., 1.5 or

less, or those that operate under harsh environment, e.g., high temperatures (Fig. 1).

1.2. The importance of membrane applications

Membranes have been undergoing a rapid growth during the past few decades especially in the petrochemical-related industries [6]. Environmental regulations such as the Clean Air Act will require reduction of hydrocarbon emissions from chemical processing facilities to low levels [7]. Moreover, development of novel materials for gas membrane manufacturing such as organic polymeric, hybrid organic–inorganic and inorganic will expand the use of membrane technology into new fields of applications in the petrochemical industry [8,9].

Different types of mechanisms have been largely used in hydrocarbons separation with membrane [10]:

- Mixture can be separated by means of their different rates of diffusion through the liquid membrane.
- By reacting the diffusing species in the receiving phase, the concentration of diffusing species in the receiving phase decreases. Therefore intra-membrane potential differences increases.

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Nomenclature

Abbreviations

BMIM ⁺	1-butyl-3-methyl-imidazolium
BPDA	3,3',4,4'-biphenyltetracarboxylic dianhydride
CA	cellulose acetate
DDBT	dimethyl-3,7-diaminodiphenylthiophene-5,5-dioxide
DOT	dioctyl terephthalate
DOP	dioctyl phthalate
DPP	diphenyl phthalate
EC	ethylcellulose
EO	ethylene-oxide
IPDA	4,4-(isopropylidene)dianiline
Matrimid [®]	(BTDA-DAPI) 3,3-(4,4-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4-aminophenyl)-1,3-trimethylindane
MPD	1,3-phenylenediamine
NBD	norbornadiene
ODA	4,4'-oxydianiline
PAAm	poly(acrylamide)
PA12-PTMO	nylon-12/tetramethylene oxide block copolymer
PBMA	poly(butyl methacrylate)
PDMS	poly(dimethylsiloxane)
PEO	poly(ethylene oxide)
PEPR	poly(ethyleneco-propylene)
PHMV	Poly(hexa-methylene-vinylene)
PMMA	poly(methyl methacrylate)
POZ	poly(2-ethyl-2-oxazoline)
PPSQ	poly(phenylsilsesquioxane)
PPO	poly(2,6,-dimethyl-1,4-phenylene-oxide)
PPy	polypyrrole
PS	polystyrene
PSF	polysulfone
PSM	poly(perfluorosulfonate) membrane
PTFE	poly(tetra fluoro-ethylene)
PVA	polyvinyl alcohol
PVDF	poly(vinylidene difluoride)
PVMK	poly(vinyl methyl ketone)
PVTMS	poly(vinyl tetra methylstyrene)
PVP	poly(vinyl pyrroli-done) ($M_w = 1 \times 10^6$ g/mol)
Pyralin	polyimide precursor based on 6FDA-ODA (subsequently imidized)
P4MP	poly(4-methylpentene-1-co- α -olefin)
SBS	poly(styrene-b-butadiene-b-styrene)
SR	silicone rubber
SPEEK	sulfonated poly(ether ether ketone)
TEG	tri-ethylene glycol
TeMPD	2,3,5,6-tetramethyl-1,4-phenylenediamine
THF	tetrahydrofuran
TrMPD	trimethylphenylenediamine
Torlon [®]	AI10 poly(amide-imide) precursor as supplied (subsequently imidized)

PB	polybutadiene
3,3'DMDB	3,3'-dimethyl-4,4'diaminophenyl
6FDA	4,4'(hexafluoroisopropylidene)diphthalic anhydride
6FpDA (BAAF)	4,4'(hexafluoro-isopropylidene) dianiline

Symbols

$C_{M,0}$	concentration of permeant at the feed interface of the liquid membrane (cm^{-3} mol)
$C_{M,\delta}$	concentration of permeant at the receiving interface of the liquid membrane (cm^{-3} mol)
$C_{L,T}$	total concentration of carrier (cm^{-3} mol)
D_M	solute diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
D_{ML}	diffusion coefficient of solute-carrier complex ($\text{cm}^2 \text{s}^{-1}$)
F	facilitation factor
FTM	facilitated transport membranes
ILM	immobilized liquid membrane
J	molar rate of gas flow through a membrane with a cross-sectional area of 1 cm^2 ($\text{mol cm}^2 \text{s}^{-1}$)
k_f	the forward-rate constant
k_r	the reversed-rate constant
K	chemical equilibrium constant ($\text{cm}^3 \text{mol}^{-1}$); $k_f C_{M,0} / k_r = K_{eq} C_{M,0}$
L	carrier
M	permeant
ML	complex
p	permeability ($1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \text{ (STP) cm} / \text{cm}^2 \text{ s cmHg}$)
P	gas permeance ($1 \text{ GPU} = 10^{-6} \text{ cm}^3 \text{ (STP) / cm}^2 \text{ s cmHg}$)
$Q = k_f C_{m,0} / k_r$	dimensionless reaction constant
$R = D_L / D_{ML}$	the ratio of carrier to complex diffusivities
T	$C_{L,T} / C_{M,0}$
SLM	supported liquid membranes
Sh	Sherwood number for permeant mass transfer

Greek symbols

α	separation factor
α_{ML}	P_M / P_L
δ	membrane thickness (cm)
ΔE_C (kcal/mol), (ΔG_C) (kcal/mol)	complexation energy
ΔE_{BD} (kcal/mol), (ΔG_{BD}) (kcal/mol)	bond dissociation energy
$\varepsilon = D_{ML} / k_r L^2$	reversed characteristic Damkohler number

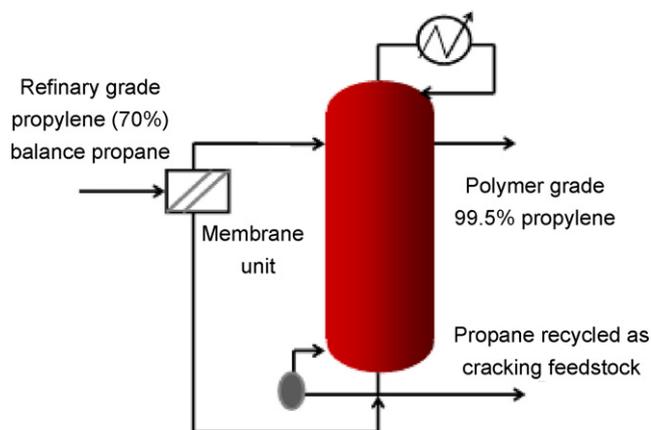


Fig. 1. Illustration of a membrane-distillation hybrid unit [5].

- Diffusing species are carried across the liquid membrane by carrier or chelating compounds in the liquid membrane.

2. Facilitated transport membrane technology

2.1. Theoretical aspects

Facilitated transport membranes (FTMs) are more selective than other membrane processes. Since the bonds formed by the chemical complexation are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound, weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure [11]. Thus, the carrier agent acts as a shuttle to selectively transport one component from the feed to the product side of the membrane. This process is sometimes called ‘coupled transport’ or ‘chemisorption’. There are many articles in practical and theoretical aspects of this separation method [10,12–14].

These are some of the benefits in FTM application:

- Since separation process in FTMs takes place without phase transitions, they require less energy than energy separating systems.

- A selective facilitator with a large permeant (olefin) capacity and fast reaction rates would permit use of smaller contactors than are currently employed in distillation [15]. Compared with conventional techniques, this process can offer a simple, easy-to-operate, low-maintenance process option industry.
- Using and producing relatively simple and non-harmful materials makes it a better process for the environment.

2.2. Different types of mechanisms which have been largely used in FTMs

For facilitated transport, three mechanisms of transportation have been mentioned which give the qualitative trends in the concentration profiles of the three kinds of species permeant (M), carrier (L), and complex (ML).

- First, the solid curves in Fig. 2a, note that M moves across the membrane in forms of free as well as complexed species. The dashed lines indicate the homogeneous chemical reactions occurring throughout the membrane, and the arrows on these lines signify a net rate of formation of ML at $x = 0$ and a net rate of dissociation of the complex at the right where some M leaves the membrane phase. At any rate it appears that this model is applicable to several experimental observations on microscopic artificial carrier mediated membranes thicker than about $2 \mu\text{m}$ [16–19].
- The other panel of the figure shows that the permeant(s) M does not enter the membrane in the free form but only through the mobile ML complex(es) formed by a heterogeneous reaction at the interfaces. Here, no net reaction is occurring within the membrane. Therefore, transport equations tend to be primarily algebraic in nature (Fig. 2b) [20].
- The last panel of the figure shows that the permeant is not soluble in the membrane itself but reacts at the interfaces with the membrane component(s). The L species may be restricted in their movement to remain on one or the other surfaces of the membrane. The individual compartments, no concentration gradients are presumed to exist (Fig. 2c) [21,22].

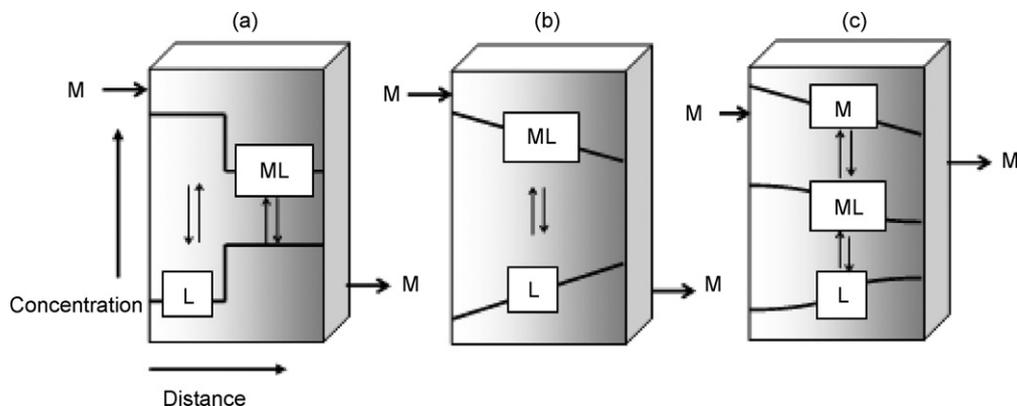


Fig. 2. Conceptual models for the mechanism of transport in membranes: (a) Homogeneous chemo-diffusion model; (b) heterogeneous surface reaction model; (c) two-compartment heterogeneous model.

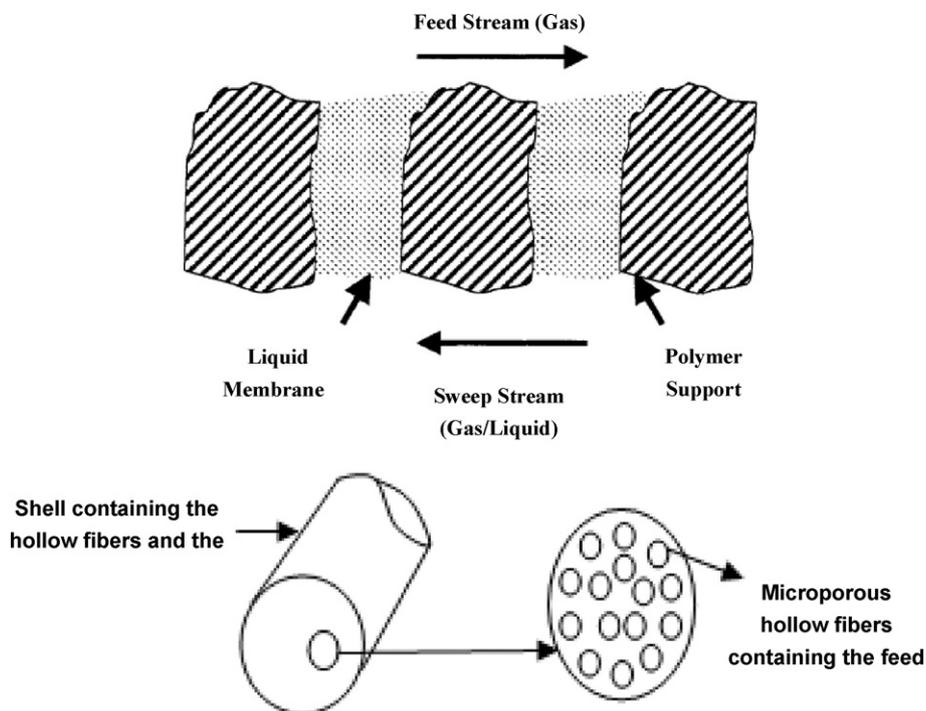


Fig. 3. Schematic of Supported Liquid Membrane (SLM).

2.3. Existing facilitated transport membrane types

2.3.1. Immobilized liquid membranes (ILMs)

In this membrane, the liquid film is immobilized within the pores of a microporous support membrane. In this case, a mobile carrier is dissolved in the liquid membrane. By complexing with a specific solute, the carrier increased the flux of that solute. The carrier–solute complex diffuses across the membrane [23]. Therefore, the porous membrane serves only as a framework or supporting layer for the liquid film. This type of membrane is called an immobilized liquid membrane (ILM) or supported liquid membrane (SLM). An ILM is applicable to the separation of gases and vapors using the flat-sheet or hollow-fiber geometry of the host membrane. Hollow-fiber [24] geometry has an outer nonporous shell, through which the materials inside cannot leak out (Fig. 3) [25]. This kind of membrane only works in presence of humidity thus, drying up of the membrane can deteriorate the separation properties of the membrane rapidly [26–32].

2.3.2. Polymer/metal salt blends

ILMs suffered serious stability problems which limited the membrane lifetime. One approach to overcome these limitations was the use of polymer/metal membranes as supports. In which, the carrier can be bound chemically or physically to

a solid polymer, thus the carrier washing out of the membrane material is prevented [15]. Functional polymers with transition metal compounds have been studied for use under mechanically harsh conditions and high temperatures [33].

2.4. Complexation and bond dissociation theories and energies

In facilitation transport the transport mechanism becomes more complicated [29,34]. It was calculated that the complexation reactions with bond energies less than 10 kJ/mol are similar to van der Waals forces. The gas-phase complexation energies of three samples of complexed membranes are given in Table 1.

The most popular model to explain the structure of bonding of platinum(II) and palladium(II)–olefin complexes was proposed by Dewar [36] and Chatt and Duncanson [37]. In which both metal and alkene act as an electron donor and acceptor in the complexation interaction [38,39]. The metal–olefin bonding described by the Dewar–Chatt model is commonly known as π -bond complexation. These findings are also consistent with the Pearson's concept of hard and soft acid–base theory [40]. Kim et al. also investigated role of anions of silver solutions on the structures of complexes of PVP [41]. It is known that if the olefin

Table 1
The gas-phase complexation energies at 298 K [35].

	Complexation energy		Bond dissociation energy	
	ΔE_C (kcal/mol)	(ΔG_C) (kcal/mol)	ΔE_{BD} (kcal/mol)	(ΔG_{BD}) (kcal/mol)
PVP/AgBF ₄	–28.2	–19.5	100.1	91.5
PVP/AgCF ₃ SO ₃	–27.7	–17.5	104.9	95.4
PVP/AgNO ₃	–26.0	–15.3	117.0	107.4

bond of ethylene is the rotational axis, rotation will rupture both the σ - and π -coordination bonds [42].

2.5. Membrane materials

Suitable membrane materials, not only can enhance the permeability and selectivity, but also improve the mechanical properties of the membrane [43–45].

Obstacles which limit the use of facilitated transport membranes for industrial applications:

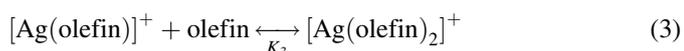
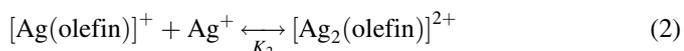
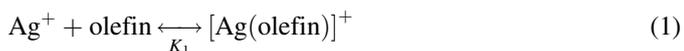
- The difficulty in preparing thin, high-flux composite membranes.
- Deterioration of the selectivity and flux over a period of a few weeks due to loss of water from the fibers. Periodic regeneration by pumping fresh silver nitrate solution through the fibers partially restored their properties [31].
- Poor chemical stability due to carrier poisoning.
- Concentration polarization or fouling problems.
- Reducing silver ions to form silver metal nano-particles and thus lose their olefin carrier activity [46–50].

2.5.1. Support

The support is a porous membrane, which may be made of glass, ceramic materials, composed, as well as polymers and copolymers, such as polyesters, polyamides, polyimides, polyacrylonitrile, polysulfones and polycarbonates, in the form of flat film or hollow fiber [51,52]. Consequently, materials contain more ion-exchange sites and absorb greater quantities of water exhibit slightly greater fluxes and separation factors for most alkene separations [53]. Zeolites were also selected as the substrates because of their high Henry's law region adsorption for hydrocarbons [54].

2.5.2. Carrier

In this section we are going to review different types of carriers in FTMs. Many researchers have made use of silver salts as the carrier in FTMs [55–58]. In which the facilitation happens toward the following reversible reactions.



As the silver ion concentration increases, $\text{Ag}_2(\text{olefin})^{2+}$ becomes more common, although it can often be ignored since K_2 is typically small. Experiment has shown that the $\text{Ag}(\text{olefin})_2^+$ complex does not form in dilute aqueous AgNO_3 [59–62].

- *Silver nitrate*: Silver nitrate solutions are mainly used because of the low cost and relatively good stability compared to other silver salts [31].
- *Silver tetrafluoroborate*: A comparison of facilitated transport membranes performance for absolute ethylene absorption capacity at the respective operating conditions reveals

that AgBF_4 is over 8 times costlier than AgNO_3 and the Ideal Separation Factor increases as the following trend: $\text{TEG} > \text{TEG}/\text{AgNO}_3 > \text{TEG}/\text{AgBF}_4$ [63].

The ionic liquids such as $\text{BMIM}^+\text{NO}_3^-$, 1-butyl-3-methylimidazolium) and $\text{BMIM}^+\text{BF}_4^-$ reduce the interactions between Ag^+ and NO_3^- produced by the interaction between BMIM^+ and NO_3^- . Thus, the silver ions activity enhances. This effect does not occur in the presence of common salts such as NaNO_3 [64].

- *Silver tetrafluoroborate (AgBF_4) and tetrafluoroboric acid (HBF_4)*: Addition of HBF_4 or AgBF_4 also increases the activity coefficient of $\text{Ag}(\text{I})$ by reducing the solvation of silver ions [65,66]. Thus, the presence of tetrafluoroborate effectively frees more Ag^+ ions to complex with olefins [6].
- *Silver perchlorate (AgClO_4) and silver trifluoroacetate (AgCF_2CO_2)*: These salt solutions exhibit ethylene absorptivity greater than that of AgNO_3 but less than that of AgBF_4 [65,67].
- *Other metal ions*: The copper(I) ion is chemically similar to the silver(I) ion. A thorough examination of the use of solid CuCl and CuBr salts for separation of unsaturates from a hydrocarbon mixture has been published [65]. However, the chemistry of aqueous copper complexing solutions has been studied less intensively than the corresponding silver systems [68].

2.6. Technological status

Although the separation of olefin/paraffin mixtures through various polymeric membranes without carriers has been studied such as: Silicone rubber [69], polysulfone, cellulose acetate [70], PDMS, 1,2-polybutadiene, polyethylene, PPO, 6FDA-mPD, 6FDA-IPDA, 6FDA-6FpDA [71], 6FDA-1,5-NDA/Durene copolyimides [72] and PVA [73] polymeric membranes seems not to be as effective as facilitated transport membranes. Therefore, many researchers have concentrated their attention to this field of studies. Steigelmann and Hughes at Standard Oil concentrated most of their efforts on propylene/propane and ethylene/ethane separation, using concentrated silver salt solutions as carriers. Propylene/propane selectivities of several hundreds were obtained, and the process was developed to the pilot plant stage [6]. Flat-sheet membranes are easy to produce and are used in laboratory experiments. While, on an industrial scale the hollow fiber module has been taken to the pilot-plant stage, due to their high surface area and compactness [74].

2.7. Important definitions

Facilitation factor (F): The ratio of the flux of a component across a membrane with carrier divided by the trans-membrane flux of the same component across an identical membrane without carrier.

Permeability (p): Gas flow rate through a membrane of 1 cm thickness with a cross-sectional area of 1 cm² and a trans-membrane differential pressure of 1 cmHg (1 Barrer = 10⁻¹⁰ cm³ (STP cm)/cm² s cmHg).

Gas permeance (P): Transport flux per unit trans-membrane driving force with a cross-sectional area of 1 cm² for carrier-mediated transport (1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg).

Separation factor (α): Parameter defined as the ratio of the permeability coefficient of component M to that of component L; $\alpha_{ML} = P_M/P_L$.

Permeation rate (J): Molar rate of gas flow through a membrane with a cross-sectional area of 1 m^2 ($\text{mol m}^{-2} \text{ s}^{-1}$).

Sweep (S): Nonpermeating stream directed past the downstream membrane face to reduce downstream permeant concentration.

2.7.1. Effective parameters

The effects of different parameters on the degree of facilitation factor, permeance, and selectivity in the FTMS are thoroughly discussed in this section.

2.7.1.1. Effects of temperature.

- In the silver(I)-composite membranes with a given liquid flow rates, as temperature decreases ethylene/ethane separation factors increases, while the permeation of gases decreases. As the permeation of organic vapors depends on its solubility, the flux increases. Generally a trade-off can be observed, i.e., high flux or high permeability is related to low selectivity and vice versa [42,60,75].
- The equilibrium constant between metal ions and olefin of the reaction is strongly dependent on temperatures. Increased temperature discourages the exothermic π -complexation reaction [76].
- High temperatures which cause the water to evaporate through the nonporous membranes limit the purity of the products [77].

2.7.1.2. Effects of pressure.

- The flux of the organic vapor is highly dependent on the vapor pressure difference of feed and receiving phases of membrane.

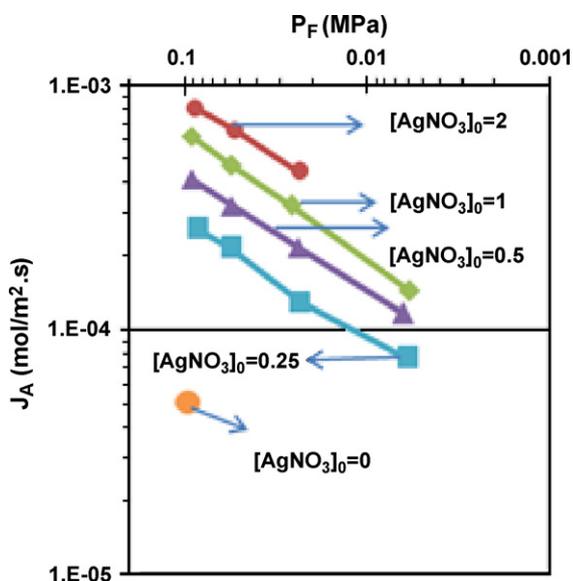


Fig. 4. Effect of ethylene partial pressure on olefin flux (single permeation) [60].

Table 2

The electronegativity of transient metals.

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

At higher partial pressure difference is known as “carrier saturation” the molar and absolute absorptivity and the olefin flux increases [77], while the permeance and the observed separation factor decreases remarkably due to the saturation of carrier [78–80]. While, increases in pressure of receiving side resulted in a slight initial drop in ethylene flux that quickly leveled off to a constant (Fig. 4) [60].

- Increasing feed gas pressure shifts the chemical equilibrium on ethylene transport. It should be noted that the liquid pressure should never be higher than the feed gas pressure in order not to blow the liquid out of the pores of the membrane [66].

2.7.1.3. Effects of cation.

- The incorporation of selected metal ions has a close relation with the significant improvements in permeabilities. Salt solubility in a polymer electrolyte depends upon the competition between the cation such as Ru(III), Pd(II), Ag(I), Ir(III) salvation energy [81–83]. The intensity of the π -complexation with alkenes is determined primarily by the electronegativity. Metal atoms with greater electronegativity draw bonding electrons more strongly. For reversible reaction between the transition metal ion and the alkene, the electronegativity of the metal is preferably in the range of 1.6–2.3. Therefore, Mn, Fe, Co, Ni, Cu, Mo, Tc, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt are good choices to be facilitating agents [84]. Due to reversibility of their complexes and relatively low cost, silver(I) and copper(I) are the most suitable transition metals for olefin/paraffin separations [85,86]. Other transition metals such as Pd(II), Hg(II), and Pt(II) which complex with olefins, are impractical due to safety concerns or expense. These agents also form comparatively stable complexes that are difficult to reverse [87]. The electronegativity of transient metals has been shown [84] in Table 2.

2.7.1.4. Effects of anions.

- The facilitation transport through polymer/silver complex membranes is sensitive to the type of the counter-anion of salt [40,75]. Large anions with relatively low lattice energies have little tendency to form tight ion pairs, and are favorable for the formation of solid polymer electrolyte complexes [88]. Therefore it is preferable to select the anion of the transition metal salt that has low lattice energy. Because in this case the anion form a weak ionic bond with the cation is easily dissolved in a polymer. The effect of anion properties on silver–olefin complex strength has been shown in Table 3.

Table 3
Anion properties.

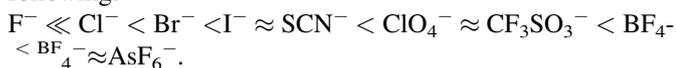
Property	Predicted silver–olefin complex strength
Anion size	$\text{CF}_3\text{SO}_3^- > \text{BF}_4^- > \text{NO}_3^- > \text{CF}_3\text{CO}_2^-$
Ag-anion separation	$\text{CF}_3\text{SO}_3^- > \text{BF}_4^- > \text{NO}_3^- > \text{CF}_3\text{CO}_2^-$
Electron density at the donor atom	$\text{CF}_3\text{CO}_2^- > \text{CF}_3\text{CO}_2^- > \text{BF}_4^- > \text{NO}_3^-$
Softness parameter	$\text{NO}_3^- > \text{BF}_4^-$

Table 4
The lattice energy.

	Li ⁺	Na ⁺	K ⁺	Ag ⁺	Cu ⁺	Co ²⁺	Mo ²⁺	Pd ³⁺	Ni ³⁺	Ru ³⁺
F ⁻	1036	923	823	967	1060	3018			3066	
Cl ⁻	853	786	715	915	996	2691	2733	2778	2772	5245
Br ⁻	807	747	682	904	979	2629	2742	2741	2709	5223
I ⁻	757	704	649	889	966	2545	2630	2748	2623	5222
CN ⁻	849	739	669	914	1035	–	–	–	–	–
NO ₃ ⁻	848	756	687	822	854	2626	–	–	2709	–
BF ₄ ⁻	705	619	631	658	695	2127	–	–	2136	–
ClO ₄ ⁻	723	648	602	667	712	–	–	–	–	–
CF ₃ SO ₃ ⁻	779	685	600	719	793	–	–	–	–	–
CF ₃ CO ₃ ⁻	822	726	658	782	848	–	–	–	–	–

Kim et al. showed that the reduction rate of silver ions to silver nanoparticles, strongly depends on the counter anions of silver salt [89]. Soft ions are large, highly polarizable, easily oxidized, and have low electronegativity, while hard ions are small, difficult to polarize, not easily oxidized, and highly electro-negative i.e. ether oxygens. A strong bond is formed between a hard cation and a hard anion, and a weak bond is formed between a soft cation and a hard anion [63]. The lattice energy of different metals has been shown [84] in Table 4.

The lattice energy less than 1000 kJ/mol is suitable for a transition metal salt to be used as a carrier in the facilitated transport membrane. Thus, according to the table the tendency of the anion to form a strong ion pair with the cation decreases in the order of decrease in the lattice energy [90,91] as the following:



2.7.1.5. *Effects of thickness on the diffusivity, permeability and flux.* The thicker membrane showed higher olefin permeability and olefin/paraffin permeability ratio compared to the results obtained from the thinner membranes [42,92].

Table 5
Effect of AgNO₃ concentration and feed pressure on permeability and separation factor [32].

[AgNO ₃] (M)	Feed gas pressure (Pa)	Permeability (Barrer)		Separation factor
		Ethylene	Ethane	
1.0	5 × 10 ⁴	6.427 × 10 ⁻¹¹	5.775 × 10 ⁻¹³	110
1.0	12.7 × 10 ⁶	4.47 × 10 ⁻¹¹	4.26 × 10 ⁻¹³	105
3.5	5 × 10 ⁴	1.162 × 10 ⁻¹⁰	3.3975 × 10 ⁻¹³	341
3.5	12.7 × 10 ⁶	9.975 × 10 ⁻¹¹	3.4875 × 10 ⁻¹³	285
5.0	5 × 10 ⁴	1.177 × 10 ⁻¹⁰	2.67 × 10 ⁻¹³	443
5.0	12.7 × 10 ⁶	8.85 × 10 ⁻¹¹	2.5275 × 10 ⁻¹³	350

Although thinner membranes have higher permeation rates, in order to be mechanically stable, they must be supported by another material [93].

2.7.1.6. *Effects of flow rate.* At low liquid flow rate, ethylene flux increases suddenly with increasing liquid flow rate. At high liquid flow rates the ethylene flux is at a maximum and leveled off rapidly. At the plateau region which is limited by diffusion through the membrane wall further increase in liquid flow rate will have little or no effect on ethylene flux [60]. In addition, the mass transfer rate through the liquid membrane is enhanced by the turbulence of the membrane solution flowing through the channel [32].

2.7.1.7. *Effects of concentrations.*

- Increasing olefin concentration in the feed gas mixture [32] causes the effective permeance and the amount of ethylene absorbed per mole of silver nitrate to decrease considerably [61,94–96]. On the other hand, increasing carrier concentration leads the effective permeance and olefin selectivity to increase (Table 5) [32].

Table 6

Ethane and ethylene permeabilities as a function of ethane partial pressures at various temperatures.

C ₂ H ₆ partial pressure (Pa)	C ₂ H ₄ permeability (Barrer)	C ₂ H ₆ partial pressure (Pa)	C ₂ H ₄ permeability (Barrer)	C ₂ H ₆ partial pressure (Pa)	C ₂ H ₄ /C ₂ H ₆ permeability ratio
313 K					
86,659	0.02	106,658	0.35	119,990	12.1
133,322	0.015	119,990	0.34	133,322	12.2
323 K					
86,659	0.035	66,661	0.4	53,329	11.2
133,322	0.04	119,990	0.45	119,990	11.5
343 K					
39,997	0.088	66,661	0.9	53,329	9
106,658	0.10	93,326	0.93	119,990	8.8

- The equilibrium constant increases at higher concentrations of silver nitrate [32,97] In which leads to the lowering of free olefin concentration and to shift the complexation equilibrium toward the left (to dissociate complex interaction). Similar studies were also reported by Featherstone and Sorrie [94].

3. Current applied membrane for olefin/paraffin separation

The choice of a suitable membrane and membrane module and material becomes very important. We tried to categories these publications in olefin/paraffin separation application, in groups such as, ethylene/ethane, propylene/propane, and other olefin/paraffin separation.

3.1. Ethylene–ethane separation

Many experiments have been conducted to separate ethylene/ethane with facilitated transport membranes [31,98–102].

3.1.1. Flat facilitated transport

In 1995, Bessarabov et al. [77] used a large-scale composite liquid membrane with a nonporous layer made of PDMS/PPSQ

block copolymer consisting of absorbing and desorbing parts (both had the same area. The process efficiency closely relates to the varying of the liquid carrier-flow rate along turbulence-promoter spacers between the membranes. For the separation of ethylene/ethane mixtures using a silver nitrate solution as the carrier phase, at low carrier loadings, little or no facilitation is observed until, at a certain critical loading, facilitation occurs, and thereafter increases rapidly [61,62]. Sungpet et al. [103] used a composite membrane of silver(I) (2 wt%)–Nafion–poly(pyrrrole) in the absence of solvent to separate a gaseous feed stream of C₂H₄/C₂H₆. Their experiments clarified the relation between ethane/ethylene permeabilities and partial pressures at various temperatures (Table 6).

In 2002, Teramoto et al. [15] used a cell of poly(methacrylic acid) resin with the flowing AgNO₃ (4 M) as the carrier. Kang et al. [86] used a polymer (POZ) with AgNO₃, AgBF₄ (1:1) improved with amino acid (NH₃⁺) to separate a feed gas of C₂H₄/C₂H₆ at 343 K. Amino acids by reacting with counter anions of silver ions of substances, can loosen the silver ions interaction [104,105]. Table 7 shows the Effects of amino acid on POZ/AgNO₃ and POZ/AgBF₄ performance [86].

Herrick et al. used composite membranes chelated with silver or cuprous material. After some pre-processes such as sulfur-reduction, humidification, the feed passed through the membrane, they did experiments on a gaseous feed stream of C_{2–8} olefins, C_{1–8} paraffins, and less than 500 ppm of C_{2–4} acetylenes [66,84,105]. In 2001, Kim et al. provided polymer–metal complexes composed of Cu (1, 3-butadiene), and cellulose acetate (CA). Cu–CA, have been successfully applied to facilitated olefin transport membranes for the olefin/paraffin separation [104]. Using a PA12-PTMO/AgBF₄ solid polymer electrolyte composite membrane Morisatoa et al. [61] separated a dry feed gas of C₂ = C/2 (70/30 vol%). It is illustrated that by

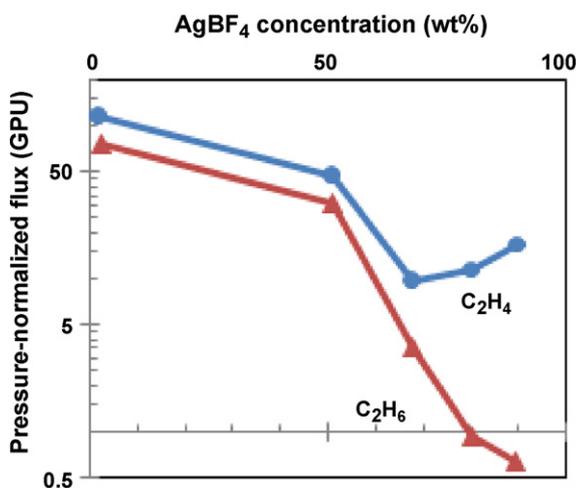


Fig. 5. Mixed-gas pressure-normalized ethylene and ethane flux as a function of AgBF₄ concentration of PA12-PTMO/AgBF₄ polymer electrolyte membranes [106].

Table 7

Effects of amino acid on POZ/AgNO₃ and POZ/AgBF₄ performance [84].

Mole ratio of NH ₃ ⁺	POZ/AgNO ₃		POZ/AgBF ₄	
	Permeance (GPU)	αC ₂ H ₄ /C ₂ H ₆	Permeance (GPU)	αC ₂ H ₄ /C ₂ H ₆
0	0.1	1	12.4	45
0.01	1.5	35	18	65
0.1	1.4	28	14.7	57

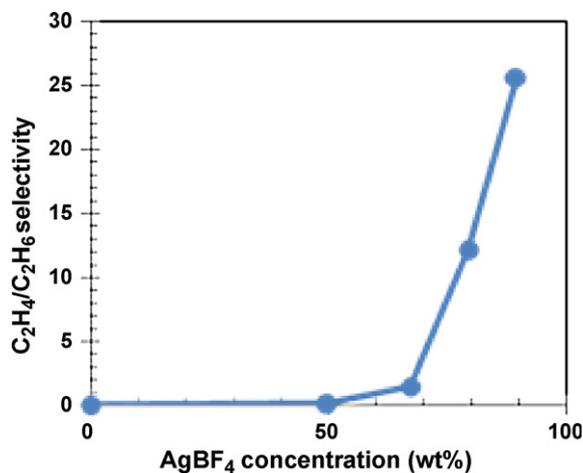


Fig. 6. Mixed-gas ethylene/ethane selectivity as a function of AgBF₄ concentration of PA12-PTMO/AgBF₄ polymer electrolyte membranes.

increasing AgBF₄ concentration the ethane flux decreases while the ethylene/ethane selectivity increases (Figs. 5 and 6).

3.1.2. Hollow fiber facilitated transport

To separate olefin/paraffin streams, many researchers have concentrated on hollow fiber facilitated transport membranes. In 1994, Tsou et al. [60] used a high-pressure polysulfone hollow fiber membrane with a flowing AgNO₃ solution as a carrier to separate a stream of ethylene/ethane. The carrier was circulated through the inner bore of the fiber. By increasing liquid recycle and flow rate, the observed ethylene flux increased suddenly and leveled off rapidly. At the plateau region which was not a rate-limiting step, further increase in liquid flow rate had little or no effect on ethylene flux. In 2004, Teramoto et al. [107] applied a hollow fiber facilitated transport membrane module using an aqueous silver nitrate 4 M solution as a carrier solution to separate a feed gas stream of C₂ = /C₂.

Table 8
Results published in literature for ethane/ethylene separations with polymer/silver ions matrix.

Reference	Author	Polymer	Separation factor (α)	Permeability (Barrer)	Remark
[42]	Sungpet et al.	Nafion–poly(pyrrole)–silver(I) ions	12	8.7	Ion-exchange membr.
[63]	Sunderrajan et al.		250	800	–
[61]	Morisato et al.	PTMO/AgBF ₄	15	1,700	–
[27]	Eriksen et al.	Nafion–6 M AgBF ₄	400	700	ILM (humid gas)
[27]	Eriksen et al.	Nafion–6 M AgBF ₄	30	400	ILM(purge gas)
[60]	Tsou et al.	Polysulfone + AgNO ₃	200	1,800	ILM
[77]	Bessarabov et al.		55	28,000	–
[107]	Teramoto et al.	PEO–4 M AgNO ₃	250	–	Hollow fiber ILM
[32]	Teramoto et al.	PEO ^a –10 M AgNO ₃	290	1,200	SLM
[29]	Teramoto et al.	pEO	53	1,100	–
[103]	Sungpet et al.	Nafion–poly(pyrrole) + silver(I)	200	1,200	–
[49]	Nymeijer et al.	SPEEK	2700	10,000	Hollow fiber
[49]	Nymeijer et al.	EPDM–SPEEK	250	230	–
[49]	Nymeijer et al.	SPEEK–SPEEK	3800	180	–
[49]	Nymeijer et al.	EPDM–EPDM	70	200	–
[49]	Nymeijer et al.	EPDM–EPDM	17	10	–
[31]	Hughes et al.	6 M AgNO ₃ aqueous solution	1000	5,130	SLM
[92]	Pinnau et al.	Thin membrane PEO–AgBF ₄	120	11.1	ILM (dry gas)
[108]	Bessarabov et al.	PVTMS with flowing AgNO ₃	–	450,000	Nonporous

^a PEO = poly(ethylene oxide).

Table 9
Polymer/silver salt permeance and selectivity as a function of mole ratio of Ag.

	Permeance (GPU)				Selectivity			
	Mole ratio of Ag				Mole ratio of Ag			
	0	0.35	0.5	1	0	0.35	0.5	1
PVP/AgBF ₄	1	3	8	36	1	5	15	67
PVP/AgCF ₃ SO ₃	1	2	5	27	1	3	4	15
PEOx/AgBF ₄	1	2	8	34	1	4	10	58
PEOx/AgCF ₃ SO ₃	1	2	7	32	1	3	5	18

Some of the other results published in literature for ethane/ethylene separations with polymer/silver ions matrix are given in Table 8.

3.2. Propylene–propane separation

Among variety of methods reported on the separation of C₃H₆/C₃H₈ via reversible complexation [109,110], Kim et al. [111] used a complex membrane of (PVMK) and Bai et al. found that EC membrane had a good potential for commercial aspects with a feed gas comprising hydrocarbons of C₃H₆/C₃H₈ and non-hydrocarbons of CO, CO₂, H₂ and N₂. The results of permeability and ideal selectivity coefficients of EC and metal–EC membranes have been indicated in Table 10 [112].

Complexed membranes of CA/AgBF₄ [113], PVP/AgCF₃SO₃, POZ/AgCF₃SO₃ [90], PVP/AgBF₄ [47], SBS/AgBF₄, SBS/AgCF₃SO₃ [114], PVA/AgSbF₆ [115], polar complexed polymer membranes of PEO, PVP, PEPR/AgBF₄, AgCF₃SO₃ (Table 9) [116], PAAm-graft/AgBF₄ [88,117] and ceramic membrane consists of a zirconia coating on the inside surface of an α -alumina substrate are samples of membrane which have been used to separated gaseous feed stream of C₃H₆/C₃H₈, C₂H₄/C₂H₆. Table 11 [14] and Table 12 [47] show some results of their experiments.

Table 10
Permeability and ideal selectivity coefficients of EC and metal–EC membranes (values in parenthesis refer to pure gas).

Metal content in (EC–x) [x]: (wt.%)	p [$\times 10^{19}$ Barrer]		Selectivity
	C ₃ H ₆	C ₃ H ₈	
–	5.2 (7.0)	1.7 (2.0)	3.05 (3.5)
[Ag]: 1	5.7	3.3	2
[Ag]: 5	6.0 (8.2)	1.9 (2.1)	3.30 (3.9)
[Pd]: 1	4.7	1.7	2.76
[Ru]: 1	4.2 (5.9)	1.6 (1.8)	2.63 (3.3)
[Ir]: 1.25	4.5 (6.3)	1.4 (1.7)	3.11 (3.7)

Experiments on polymer complexes such as POZ/PVP with two silver salts such as AgBF₄ or AgCF₃SO₃ [118] indicated that using two silver salts, improves the selectivity of separation system (Table 13).

PDMS, PHMV, PS with silver salts were prepared to separate propylene from propane [51,119]. PDMS was chosen because: first, it does not contain any functional groups that can coordinate with silver ions and thus is inert to silver salts, and finally, they are highly permeable to most gases (Table 14).

In 2003, Duan et al. studies on a flat-type TEG/AgBF₄ liquid membrane. It is shown that the existence of water vapor in the feed stream increased the permeation to separate C₃H₆/C₃H₈ (Table 15) [120].

In 2005, Kim et al. used polymers containing PMMA, PBMA, PVMK, POZ, PVP and AgBF₄, AgCF₃SO₃ as the silver salts [118,121]. Table 16 shows the effect of different ligands type as well as the silver salt concentration on system's characteristics.

In 2006, Hess et al. used of 6FDA–4MPD/15-crown-5/DABA 4:4:1, cross-linked with the diamine 15-crown-5 or EG impregnate with AgBF₄/AgNO₃ to separate a gaseous feed of C₃H₆/C₃H₈. The main advantage of this type of facilitated transport polymers is that no carrier medium is necessary which means “dry” membranes can be applied. As a result, increasing content of crown ether units in the copolymer leads to a decrease in permeability while selectivity increases [23] (Table 17).

Furthermore, some other FTMs used in the separation of propylene/propane have been summarized in Table 18.

In order to separate a mixture of propylene/propane Yoshino et al. prepared an asymmetric hollow fiber membrane. Silver salts in the composite membranes were physically dispersed in rubbery poly(dimethyl siloxane) (PDMS). Physical dispersion of silver salts in the PDMS matrix without specific interaction leads

Table 11
Effect of AgBF₄ on pure gas permeance of PEO/AgBF₄ composite membranes [14].

AgBF ₄ wt.%	PEO:Ag mole ratio	Pressure-normalized flux (pure-gas) (GPU)			Pure-gas selectivity		
		C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₂ H ₄ /C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈
0	–	0.55	0.46	0.89	0.36	1.2	2.5
33	8	0.18	0.10	0.22	0.11	1.8	2.0
50	4	1.6	<0.01	2.6	<0.01	>160	>260
80	1	55	<0.01	48	<0.01	>5500	>4000

Table 12
Pure propylene permeance through 1:1 PVP/AgBF₄ membranes as a function of temperature [47].

1000/T (K ⁻¹)	ln (permeability (GPU))		Selectivity C ₃ H ₆ /C ₃ H ₈
	C ₃ H ₆	C ₄ H ₈	
2.8	2.0	–1.7	48
3	2.3	–1.4	40
3.15	2.35	–1.1	33
3.25	2.4	–0.8	25
3.35	2.41	–0.7	23

to very low separation performances initially. However, as the permeation time increases, both the selectivity and the permeance increase continuously to finally reach equilibrium values. These unusual permeation properties are likely to be due to the conversion of the initially inactive silver ionic aggregates into the more active free ions through the coordination of propylene to the silver ions under a propylene environment [124]. The membrane was composed of a co-polyimide from equimolar portion of 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) with 3,7-diamino-2,8(6)-dimethyl-di-benzo-thiophene-sulfone (DBBT) carbonized membranes [114]. Polysulfone hollow fibers are capable of functioning under high trans-membrane pressure differential [125]. Moreover, the effect of some polymers on the performance of C₃H₆/C₃H₈ properties is given in Table 19.

3.3. C₄ gas separation

Yang and Hsiue compared the permeability coefficients and separation factor in various membranes for separation of C₄ olefin/paraffin (Table 20) such as silicone rubber-graft-poly (acrylic acid) (SR-g-AA) incorporated with silver ion (SR-g-AA-Ag⁺) [114].

Hu et al. used a hydrous AgI-doped PSM to separate feed gases comprised C₂ and C₄ olefin/paraffin. The PSM, consisting of a perfluorinated polyethylene backbone with pendant side chains terminating in sulfonic acid groups. They asserted that the higher upstream gas pressure, the higher will be the permselectivity of alkenes relative to their corresponding saturated alkanes [127] (Table 21).

Kraus and Stern did studies on the interaction of butadiene with AgNO₃ [128]. While, HO described that poly(vinyl alcohol)-containing silver nitrate membranes. Selectivities

Table 13

Separation performance of propylene/propane mixtures through two mixed silver salt membrane [118].

POZ + x + y		Permeance (GPU)		Selectivity C ₃ H ₆ /C ₃ H ₈
[x] = [AgNO ₃]	[y] = [AgBF ₄]	C ₃ H ₆	C ₃ H ₈	
1.0	0	0.2	0.2	1
0.7	0.3	4	0.04	100
0.3	0.7	4.5	0.04	95
0	1.0	11	0.24	45

POZ + x + y		Permeance (GPU)		Selectivity C ₃ H ₆ /C ₃ H ₈
[x] = [AgNO ₃]	[y] = [AgCF ₃ SO ₃]	C ₃ H ₆	C ₃ H ₈	
1.0	0	0.2	0.2	1
0.7	0.3	0.1	0.1	30
0.3	0.7	0.3	0.01	28
0	1.0	4.6	0.31	15

POZ + x + y		Permeance (GPU)		Selectivity C ₃ H ₆ /C ₃ H ₈
[x] = [AgBF ₄]	[y] = [AgCF ₃ SO ₃]	C ₃ H ₆	C ₃ H ₈	
1.0	0	10	0.25	45
0.7	0.3	9	0.3	35
0.3	0.7	7	0.5	22
0	1.0	5	0.7	15

Table 14

Performance of pure PHMV and PHMV/silver salt physically dispersing.

Membrane	Permeance(pure gas) (GPU)		Selectivity (α) C ₃ H ₆ /C ₃ H ₈
	C ₃ H ₆	C ₃ H ₈	
PHMV	54.1	45.5	1.2
PHMV/AgBF ₄	33.6	<0.1	>336
PHMV/AgClO ₄	6.8	<0.1	>168
PHMV/AgCF ₃ SO ₃	12.8	<0.1	>128

decrease in the order: 1,3-butadiene > 1-butene > isobutylene > trans-2-butene as the steric hindrance at the double bond of olefin increases [26].

3.4. C5 and C6 gas separation

From studies on the separation of pentene isomers (cis-2-pentene and trans-2-pentene), it is observed that in aqueous salt

Table 17

Different types of crown ether cross-linked membranes performance.

Total feed pressure (Pa)	Total permeance (Barrer) C ₃ H ₆ /C ₃ H ₈ Native	α	Total permeance (Barrer) C ₃ H ₆ /C ₃ H ₈ AgNO ₂	α	Total permeance (Barrer) C ₃ H ₆ /C ₃ H ₈ AgBF ₄	α
6FDA–4MPD/DABA 4:1 (crown ether crossl.) membranes						
140,000	4.5	8	1.4	14	1.2	16
300,000	3.8	7.5	1.5	13	1	15
450,000	3	7	1.6	11	0.8	12
6FDA–4MPD/15-crown-5/DABA 4:4:1 (crown ether crossl.) membranes						
140,000	0.56	15	0.23	36	0.25	48
300,000	0.48	14	0.20	32	0.20	41
450,000	0.40	13	0.18	23	0.18	28

Table 15

Effect of feed composition in TEG/AgBF₄ (43 wt %) [120].

Feed composition (C ₃ H ₆ mole fraction)	Permeability (cm ³ (STP) cm/ cm ² scmHg)		Separation factor
	Propylene	Propane	
0.04	3000	7	300
0.3	700	10	80
0.5	600	10	70
0.8	400	12	40

Table 16

Selectivity of propylene/propane through polymer/silver salt complex membranes as a function of the silver salt concentration.

Ligands type	Polymer/silver	Mole fraction of silver C ₃ H ₆ /C ₃ H ₈ selectivity				
		0	0.1	0.2	0.35	0.5
Ester	PMMA/AgBF ₄	1	15	19	24	40
	PMMA/AgCF ₃ SO ₃	1	12	13	15	18
	PBMA/AgBF ₄	2	3	8	9	35
	PBMA/AgCF ₃ SO ₃	2	3	7	8	14
Ketone	PVMK/AgBF ₄	1	1	10	28	54
	PVMK/AgCF ₃ SO ₃	1	1	2	5	12
Amide	PVP/AgBF ₄	1	1	3	14	50
	PVP/AgCF ₃ SO ₃	1	1	2	5	15
	POZ/AgBF ₄	1	1	2	15	48
	POZ/AgCF ₃ SO ₃	1	1	2	10	17

solutions one olefin increases the solubility of the other [43]. Son et al. studied on selective absorption of isoprene from n-pentane mixtures via reversible π -complexation with an aqueous solution of copper(I) nitrate. [129]. Sridhar et al. prepared a cuprous Diketonate (PPO, EC, CA, and PSF) membrane in a-Methylstyrene, for the separation of feeds included hydrocarbons such as C₂, C₃, C₄, and C₅ [122]. The separation of 1-hexene and hexadiene by a thin stationary Ag⁺ loaded Nafion membranes as a selective barrier between the olefin and the silver ion containing liquid was reported. A stationary (FTM) membrane formed a selective barrier between the olefin and the silver-ion-containing liquid. The polymeric dense layer of the membrane was placed in direct contact with the solvent, ensuring free diffusion of the olefin through the membrane, but inhibited diffusion of the solvent through the

Table 18
Experimental data for permeation of C₃H₆/C₃H₈.

References	Author	Polymer	T (K)	Feed pressure	pC ₃ H ₆ (Barrer)	Selectivity
[96]	Krol et al.	Matrimid [®]	299 ± 2	2–3 bar	0.10	16
[96]	Krol et al.	Matrimid [®] -Thermid 85/15	299 ± 2	2–3 bar	0.03	4
[96]	Krol et al.	Pyralin 2566	299 ± 2	2–3 bar	0.09	21
[96]	Krol et al.	Torlon AI-10	299 ± 2	2–3 bar	<0.02	–
[40]	Bai et al.	PPO	303 ± 2	2–4 bar	9	4.25
[122]	Sridhar and Khan	EC	303 ± 2	3–3.9 atm	52	3.25
[122]	Sridhar and Khan	CA	303 ± 2	3–3.9 atm	15.2	2.6
[122]	Sridhar and Khan	PSF	303 ± 2	3–3.9 atm	25	1.4
[123]	Staudt-Bickel and Koros	6FDA–mPD	308 ± 2	3.8 atm	0.13	10
[123]	Staudt-Bickel and Koros	6FDA–IpDA	308 ± 2	3.8 atm	0.58	15
[123]	Staudt-Bickel and Koros	6FDA–6FpDA	308 ± 2	3.8 atm	0.89	16
[5]	Burns and Koros	Matrimid [®]	308 ± 2	2 atm	0.10	10
[5]	Burns and Koros	6FDA–33'/DMDB	308 ± 2	1.1 atm	0.15	13.2
[70]	Tanaka et al.	6FDA–TeMPD	323 ± 2	2 atm	37	8.6
[70]	Tanaka et al.	6FDA–TrMPD	323 ± 2	2 atm	30	11
[70]	Tanaka et al.	6FDA–DDBT	323 ± 2	2 atm	0.76	27
[70]	Tanaka et al.	BPDA–TeMPD	323 ± 2	2 atm	3.2	13
[70]	Tanaka et al.	PPO	323 ± 2	2 atm	2.3	9.1
[70]	Tanaka et al.	P4MP	323 ± 2	2 atm	54	2
[70]	Tanaka et al.	1.2PB	323 ± 2	2 atm	260	1.7
[70]	Tanaka et al.	PDMS	323 ± 2	2 atm	6600	1.1
[70]	Tanaka et al.	6FDA–ODA	373 ± 2	2 atm	0.48	11

Table 19
Polymers' effect on the performance of C₃H₆/C₃H₈ properties.

References	Author	Polymer	pC ₃ H ₆ (cm ³ (STP) cm ² s cmHg)	C ₃ H ₆ /C ₃ H ₈ separation factor
[47]	Kim et al.	PVP/AgCF ₃ SO ₃ (%mol 0.5)	310,000	1000
[47]	Kim et al.	PVP/AgBF ₄ (%mol 0.5)	110,000	23
[115]	Kim et al.	PVA/AgSbF ₆ (%mol 0.9)	2,500	5
[119]	Kim et al.	PS/AgBF ₄ (%mol 0.5)	110,000	65
[119]	Kim et al.	PS/AgCF ₃ SO ₃ (%mol 0.5)	50,000	18
[63]	Sunderrajan et al.	PEO/AgBF ₄	18	260
[126]	Hong et al.	POZ/AgBF ₄ (40% humidity)	200	270
[88]	Park et al.	PAAm/AgBF ₄ (0.1M) ((dry Memb.))	15	170
[120]	Duan et al.	TEG/AgBF ₄ (dry feed)	80	25
[120]	Duan et al.	TEG/AgBF ₄ (wet feed)	900	70
[116]	Kang et al.	EPR/Ag ⁰ /pBQ 1:1:0.85	5,000	11

membrane. It was observed that, there was an increase in the solubility of 1-hexene in the ethylene glycol–Ag⁺ solution with a decrease in temperature (Table 22) [75].

In 1999, Goering et al. used a silver(I)-exchanged Naffion, Neosepta CM-1, and Neosepta CM-2 membranes to separate 1,5-hexadiene and 1-hexene [130]. The transport of cyclohexene, 1,5-hexadiene, 1-hexene, and styrene through sodium(I) and silver(I)-Nafion and Nafion-poly(pyrrole) composite membranes was also investigated [75]. For separating unsaturated hydrocarbons (carbon-carbon triple and double bonds),

such as acetylene, benzene also some researches have been conducted like the method provided by Pinnau et al. [92]. They have also conducted a comparison between olefin permeabilities and facilitation factors of Nafion and Nafion-poly(pyrrole) membranes (Table 23).

4. Modeling

Recent studies of transport mechanism in the carrier mediated membrane has led to a basic and more precise understanding of the effect of the major parameters involved, including the reaction kinetics, equilibrium (binding constant), diffusivities, membrane thickness, etc.

FTMs can be distinguished by two limiting steps (diffusion controlling step (fast reaction), and Reaction controlling step (slow reaction)). The latter case does not occur frequently and only the former case will be considered [104]. In a simple

Table 20
Comparison of the permeability coefficients (*p*) and separation factor (*α*) in various membranes at 1.5 atm and 298 K.

Sample	<i>p</i> × 10 ²⁰ (Barrer)		<i>α</i>
	i-C ₄ H ₈	i-C ₄ H ₁₀	
SR-g-AA-Ag ⁺	2400	825	2.91
PE-g-AA-Ag ⁺	5.25	0.58	9.01

Table 21

Total permeability coefficients and Ideal separation factor of ethylene/ethane, 1-butene/*n*-butane in anhydrous AgI-doped PSM as a function of upstream gas pressure [127].

Feed gas pressure (Pa)	Permibility (Barrer)		α , separation factor	
	$(C_2H_4/C_2H_6) \times 10^{21}$	$(1-C_4H_8/n-C_4H_{10}) \times 10^{10}$	C_2H_4/C_2H_6	$1-C_4H_8/n-C_4H_{10}$
26,664	2.4	2.0	6	10
53,329	2.2	4.0	8	300
79,993	2.6	5.2	11	1,000
133,322	3.4	13	18	4,000
159,987	3.8	17	23	2,500
186,651	4.8	23	20	6,250
213,316	5.0	32	29	13,500

Table 22

Results of 1-hexene solubility in ethylene glycol or 1,3-propanediol/Ag⁺ solution [75].

Temperature (K)	Concentration of Ag ⁺ (mol/l)	Solubility of 1-hexene in Ag ⁺ solution (mol/l)	Specific solubility of 1 hexane in Ag ⁺ solution (mole olefin/mole Ag ⁺)
Ethylene glycol			
288	2	0.88	0.44
298	2	0.7	0.35
308	2	0.52	0.26
1,3-Propanediol			
288	1.25	0.97	0.77
298	1.25	0.82	0.66
308	1.25	0.58	0.46

FTM with a uniform thickness and composition, the following reversible chemical reaction, takes place in the facilitated transport membrane.



where M = solute being transport; L = carrier; ML = solute-carrier complex. In the case, say, of homogeneous reaction, the local species balance will generally read

$$\frac{\partial C_i}{\partial t} = \vec{\nabla} \cdot \vec{N}_i - r_i; \quad i = M, L, LM \quad (5)$$

Carrier-mediated diffusion-reaction equations of the following forms have considered for this system of transportation. For one-dimensional diffusion the results is restricted to the usual

steady state experiment on membranes.

$$D_i \frac{\partial^2 C_i}{\partial x^2} = \eta(C_1, C_2, \dots), \quad i = M, L, LM \quad (6)$$

$$r_M = -k(C_L, C_{ML}) \left[C_M C_L^n - \frac{C_{ML}^m}{K} \right] \quad (7)$$

Here, x measures normal distance through the membrane, from one of its interfaces $x = 0$ to the other $x = L$, both of which then serve as system boundaries.

At very low driving force conditions, the flux due to the solution-diffusion pathway is very small. And the majority of diffusion is due to diffusion of the carrier-gas complex. As the driving force decrease further, the flux of the uncomplexed gas

Table 23

A comparison between olefin permeabilities and facilitation factors of Nafion and Nafion-poly(pyrrole) membranes.

Olefin	Permeability of silver(I)-form membrane (mol cm M ⁻¹ cm ⁻² s ⁻¹ × 10 ¹⁵)	Permeability of sodium(I)-form membrane (mol cm ⁻² s ⁻¹ × 10 ¹⁵)	Facilitation factor
Nafion membranes			
Cyclohexene	14.2	<0.05	>296
1,5-Hegzadiene	73.9	0.58	127
1-Hegzene	153	0.59	259
Styrene	3.28	1.19	2.8
Nafion-poly(pyrrole) composite membranes ^a			
Cyclohexene	1.39	0.38	3.6
1,5-Hegzadiene	107	8.62	12.4
1-Hegzene	234	12.9	18.1
Styrene	2.95	8.72	0.34

^a Properties were measured at 298 K in CCl₄/water containing silver nitrate at ionic strength $\mu = 1$.

molecules decrease much faster than the carrier transport

$$N_A = -D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} \quad (8)$$

4.1. Facilitation factor

A useful quantity, called the facilitation factor, can be defined as the ratio of the flux of a component across a membrane with carrier, divided by the transmembrane flux of the same component across the identical membrane without carrier [131].

$$F = \text{facilitation factor} = \frac{\text{solute flux with carrier present}}{\text{solute diffusion flux}} \\ = (-D_M dC_M/dx|_{x=0}) / (D_M \cdot C_{M,0}) \quad (9)$$

The total flux in facilitated transport membranes is not directly proportional to the concentration gradient due to the existence of two transport mechanisms in the membrane: solution–diffusion and diffusion of carrier–solute complex. As noted above, the solute flux with carrier present can be obtained by multiplying the solute diffusion flux of Knudsen diffusion mechanism by facilitation factor F . It can be viewed as a measure of increased selectivity for multi-component feed mixtures. Ward provided analytical solutions for the facilitation factor under diffusion-limited and reaction-limited regimes. His solution for the diffusion-limited regime is [132].

$$F = 1 + \frac{\alpha K}{1 + K} \quad (10)$$

To obtain this solution, the diffusion coefficient of the carrier and solute–carrier complex are assumed to be equal. This is usually justified when the carrier is normally much larger than the solute. The result of facilitation factor has been improved by Smith and Quinn. They extended the range of analytical solution and assumed a large excess of carrier to linearize the differential equations describing the transport across the membrane. Their result is as in Eq. (11):

$$F = \frac{1 + (\alpha K / (1 + K))}{1 + (\alpha K / (1 + K)) (\tanh \lambda / \lambda)} \quad (11)$$

where,

$$\lambda = \frac{1}{2} \left(\frac{1 + (\alpha + 1)K}{\varepsilon(1 + K)} \right)^{1/2} \quad (12)$$

They showed that their solution had the proper behavior in both the diffusion-limited and reaction-limited regimes Hoofd and Kreuzer applied a combined Damkohler technique to obtain the solution [133,134]. Noble, way and Power extended this model further to incorporate external mass transfer effects adjacent to the membrane boundaries. This external mass transfer effect is described by a Sherwood number. Assuming reaction equi-

rium $\tanh(\lambda/\lambda) \rightarrow 0$,

$$(F - 1)^{-1} = E^{-1} \\ = \left(1 + \frac{2}{Sh} \right) \alpha^{-1} + \left[\left(\frac{2}{Sh} \right) \left(1 + \frac{1}{\alpha K} \right) + \frac{1}{\alpha K} \right] \quad (13)$$

where α^{-1} is directly proportional to the solute feed concentration (C_{A0}). In a plot of E^{-1} versus C_{A0} , as C_{A0} is reduced, the plot should be linear and Eq. (12) is valid. For the straight-line portion of the curve, the slope and the intercept can be used to estimate two unknown quantities if all other properties have been independently measured or estimated. Typically, the two unknown quantities are Sh and D_{ML} .

A more rigorous numerical study of facilitated transport membranes and modules was presented by Basaran [135], Burban, and Auvil to investigating the effect of differing carrier and carrier–solute complex diffusivities. Relative to the case when the $D_M = D_{ML}$, the facilitation factor F increases if $D_M < D_{ML}$, and F decreases if $D_M > D_{ML}$. An optimization was also carried out to determine the maximum facilitation factor and dimensionless equilibrium constant extending the results of Kemena [136] to cases where $D_M \neq D_{ML}$.

4.2. Numerical methods

Among various researches on the modeling and solution of the system of equations related to FTMs, Recently The mathematical models representing both once-through mode operation and recycling mode operation have been proposed for the hollow fiber SLM have been developed considering aqueous-layer diffusion in feed and stripping side, interfacial chemical reaction and membrane diffusion and relevant parameters affected on the removal efficiency of copper ion have been studied and discussed. It was found that the developed models can provide the removal efficiency of copper-ion in good agreement with the experimental data [137]. Furthermore, in the equilibrium regime, the limiting solutions of transport equations can be derived by rather simple algebra by Smith, Meldon, and Colton [131] for the very fast and slow reaction limit, used perturbation analysis to obtain solutions. Yung and Probstien [138] used a similarity transform to simplify the differential reactions and obtain a numerical solution. Schultz et al. [91] mentioned that it is generally difficult to decide which solution results in the accurate facilitation factors. Smith and Quinn [139] developed an approximate solution under the assumption of large excess of carrier. They linearized the basic equations by assuming that the carrier concentration is uniform throughout the membrane. However, as pointed out by Jemaa and Noble [140], this solution does not accurately predict facilitation factors at large values of the chemical equilibrium constant. Jemaa and Noble proposed an improved method for evaluating the facilitation factor in which a small nonzero permeate concentration at the membrane exit is assumed. Therefore, their solution needs empirically determined parameters. Basaran et al. [135] presented the approximate solution by the perturbation analysis. Furthermore, these methods except a few reports by Basaran et al. [135] are restricted to the case of equal carrier and complex diffusivities.

Teramoto, [141] developed an approximate solution of the facilitation factors assuming that the concentration of carrier is constant. However, these studies represent special cases in which simplifying assumptions could be made, making it possible to describe the performance of these systems. As the nonlinear reaction kinetics causes the governing differential equations of this system to be nonlinear, a general analytical solution is not available. Goddard [18] provided a further survey that focused on the system near the reaction equilibrium limit.

In 2006, Coutelieis et al derived the effective mass-transfer coefficient between two fluid phases in a porous medium, one of which was flowing and the other was immobile. They used traditional volume-averaging methods to obtain a unit-cell boundary-value problem for the calculation of the effective mass-transfer coefficient. Then, they used numerical methods that solve the flow velocity field under Stokes flow conditions, and the transport problem. In particular, they focused on the effect of shape factors for practical applications [142]. All the analytical treatments of facilitated diffusion that have been developed to date are based on one or more special simplifications of the problem. It is perhaps not surprising that these simplifications are associated with the physical regimes of fast or slow reactions, and of weakly perturbed systems with linearized kinetics.

One might expect that exact solutions are always possible through the use of numerical methods. However, in this system, numerical methods have also met with limitations. Bassett and Schultz [16] used a Runge–Kutta technique but found that convergence was difficult to realize even in the near-diffusion, non-equilibrium regime. Ward [132] and Smith et al. [131] have presented numerical solutions, but their algorithms were not given in detail. Smith et al. [131], Suchdeo et al. [143], Goddard et al. [91], on the semi-infinite interval $0 \leq x < \infty$ and subject to the exact boundary conditions at $x = 0$ solved the system. Jain and Schultz [144] solved the system by the method of successive substitutions or Picard iteration. Moreover, it is now well known that Picard-type iterative schemes can lead to divergent iteration in certain ranges of the parameters.

5. Summary

In the present review article, the basic fundamentals, advantages, methods and general mechanisms of facilitated transport membrane technology have been highlighted. The effects of different parameters on the degree of facilitated factor, permeance, and selectivity in the facilitated transport membrane are thoroughly discussed. In addition a number of potential applications of the FTMs in a variety of modules are highlighted. At last, some reviews have been conducted for the modeling as well as numerical solution to the governing system of equations.

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