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Review

Membranes for solubility-based gas separation applications

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Abstract

The use of membranes in gas separations has grown at a very rapid pace in recent times. One particularly interesting application of gas separation with membranes is the removal of dilute heavy organics from light gas streams such as the removal of solvents from the exhaust of different process industries. For such applications separations are achieved using the solubility-selective mode in which preferential permeation of the heavier organic molecules is desired. This article aims to review some of the recent advancements in the field of membranes for solubility-based gas separations. The development of different inorganic, polymeric and hybrid membrane materials in light of the opportunities and challenges are presented.

Keywords: Membrane; Diffusion; Solubility-based gas separation; Gas and vapor permeation

1. Introduction

Gas separation is an important unit operation employed widely throughout the chemical industries. Examples include the separation of air into oxygen and nitrogen and the removal of volatile organic compounds from effluent streams. The traditional methods used for such separations include cryogenic distillation and adsorbent bed processes. In recent times, however membrane-based gas separation is becoming increasingly popular due to its inherent advantages over the more traditional methods. These include low capital and operating costs, lower energy requirements and generally ease of operation.

A membrane may be simply defined as an interphase between two bulk phases [1]. During the last 30 years, the use of membranes in separation processes has grown at a very rapid pace. Presently membrane-based processes are being used in a wide array of applications, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis [1,2]. Gas separation in membranes occurs due to differences in permeabilities of the species flowing through the membrane. With a few exceptions, membranes used for gas separation can be broadly categorized into two major classes: porous inorganic and dense polymeric.

Porous membranes have a well-defined static pore structure, which depending on the formation process can be highly connected and torturous or non-connected and straight. Pores in inorganic membranes can be classified according to their size as macropores (>500 Å), mesopores (500–20 Å) or micropores (<20 Å) [3].

Across these pore size regimes, gas transport in inorganic membranes may occur via a host of different mechanisms. A brief description of the commonly occurring mechanisms is given below:

(a) *Molecular diffusion*: In molecular diffusion, the mean free path of the gas molecules is smaller than the pore size and diffusion occurs primarily through molecule–molecule collisions. In molecular diffusion, the driving force is the composition gradient. If a pressure gradient is applied in such pore regimes bulk (laminar) flow occurs, as given by Poiseuille's equation. Such transport is often referred to as *Poiseuille flow* or viscous flow.
(b) *Knudsen diffusion*: This mode of transport is important when the mean free path of the gas molecules is greater

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than the pore size. In such situations the collisions of the molecules with the pore wall are more frequent than the collisions among molecules. Separation selectivities with this mechanism are proportional to the ratio of the inverse square root of the molecular weights. This mechanism is often predominant in macroporous and mesoporous membranes [4–7].

(c) *Surface diffusion*: Surface diffusion occurs when the permeating species exhibit a strong affinity for the membrane surface and adsorb along the pore walls. In this mechanism, separation occurs due to differences in the amount of adsorption of the permeating species. Surface diffusion often occurs in parallel with other transport mechanisms such as Knudsen diffusion [5,6].

(d) *Capillary condensation*: Capillary condensation is one form of surface flow where one of the gases is a condensable gas. Typically in mesopores and small macropores, at certain critical relative pressures (that may be determined by the Kelvin equation), the pore gets completely filled by the condensed gas. Due to the formation of menisci at both ends of the pore, transport can take place through hydrodynamic flow driven by capillary pressure difference between the two ends. This mechanism of gas transport can be thought of as the ultimate limit of the process of adsorption as pressure is increased. In theory, capillary condensation can be used to achieve very high selectivities, as the formation of the liquid layer of the condensable gas will block and prevent the flow of the non-condensable gas [6–8].

(e) *Configurational or micropore diffusion*: This type of diffusion may be considered as surface diffusion in the limit where the pore size becomes comparable to the molecular size. In this mechanism, diffusion is perceived as an "activated" process and separation is a strong function of molecular shape and size, pore size, and interactions between the pore wall and gas molecules. This type of mechanism is dominant in microporous zeolite membranes and carbon molecular sieves [4,7].

In dense polymeric materials, solution-diffusion is widely accepted to be the main mechanism of transport [4,9–11]. This mechanism is generally considered to be a three-step process. In the first step the gas molecules are absorbed by the membrane surface on the upstream end. This is followed by the diffusion of the gas molecules through the polymer matrix. In the final step the gas molecules evaporate on the downstream end. In glassy polymers, the sorption of gases becomes a complex process, which has been described by a combination of Henry's law and Langmuir expressions. This has been referred to as "dual mode sorption theory" [11]. Diffusion in glassy polymers is usually an activated process and, Arrhenius relations may be used to express the permeability, diffusivity, and solubility coefficients.

2. Theory of gas transport in membranes

In this section a simplified development of the theory of gas transport across a membrane is presented. The focus is on single gas species and several assumptions will be made to simplify the presentation, but these are discussed later.

The diffusion of gas through the membrane can be expressed by Fick's first law:

$$J = -D\left(\frac{\mathrm{d}C}{\mathrm{d}x}\right) \tag{1}$$

where J is the flux of the gas through the membrane, D, the diffusion coefficient, and $\mathrm{d}C/\mathrm{d}x$ is the concentration gradient of the gas across the membrane. At steady state, the flux is a constant. If D is assumed to be constant, Eq. (1) can be integrated to give:

$$J = D\frac{C_\mathrm{o} - C_\mathrm{l}}{l} \tag{2}$$

where C_o and C_l are the concentration of the gas on the upstream and downstream ends, respectively, and l is the thickness of the membrane. At low pressures, Henry's law is often adequate to express the concentration of the gas in the membrane:

$$C = Sp \tag{3}$$

where S is the Henry's solubility constant and p is the pressure of the gas. By substituting Eq. (3) into Eq. (2) we get:

$$J = DS\frac{(p_\mathrm{o} - p_\mathrm{l})}{l} = \bar{P}\frac{(p_\mathrm{o} - p_\mathrm{l})}{l} \tag{4}$$

where $\bar{P}$ is permeability of the gas and according to Eq. (4) can be defined as:

$$\bar{P} = DS \tag{5}$$

The permeability is therefore a product of the diffusivity and solubility coefficients of the gas species. In real systems, the diffusion coefficient D and the solubility coefficient S may both be function of concentration, so the theoretical analysis becomes more complicated. However, the idea of the permeability being the product of a solubility term and a diffusivity term is quite general.

In gas separation with membranes, selectivity is defined as the ratio of the individual gas permeabilities. Based on single gas permeabilities of species "A" and "B" we may write an ideal selectivity as:

$$\alpha_{\mathrm{A/B}} = \frac{\bar{P}_\mathrm{A}}{\bar{P}_\mathrm{B}} = \frac{D_\mathrm{A}}{D_\mathrm{B}}\frac{S_\mathrm{A}}{S_\mathrm{B}} \tag{6}$$

The selectivity can therefore be viewed as a function of differences in both the diffusivity and solubility coefficients of the two gases.

Diffusivity-based gas separation is generally employed for chemically similar species like O_2 and N_2, where separation occurs due to the preferential permeation of the smaller more mobile species. In fact most membrane gas separation systems in operation are diffusivity-based. However, in certain industrial and environmental applications, it is preferable to achieve separation based on solubility differences.

3. Solubility-based gas separations

Differences in solubility arise from differences in the molecular-level interactions of the membrane material with the permeating species. The exploitation of “chemically specific” energetic interactions such as hydrogen bonding may lead to greater selectivity; however, even simple van der Waals dispersion forces, which tend to be stronger for the larger molecules, may lead to significant selectivity. In certain applications, like the removal of volatile organic compounds (VOCs) from effluent streams or the removal of higher hydrocarbons from natural gas, process economics dictate that membranes should be designed to preferentially permeate the larger molecular weight species. In these examples the heavier species are present in dilute concentrations and preferential permeation of the heavier species translates into lower surface area requirements; furthermore, the “cleaned” lighter component is kept on the high-pressure side, which may be advantageous [10].

Freeman and Pinnau outlined the design criteria for solubility-selective polymeric membranes [10]. They point out that for separation of dilute heavy molecular weight species from light gases, such as the removal of organic vapors from air, generally the diffusivity selectivity is in favor of the smaller more mobile species. Therefore, to achieve separation in such cases with the preferential permeation of the larger species, one would like the polymer to have a high enough free volume so that the ratio of diffusivities of the two species is driven close to unity. The solubility-selectivity is greater for the larger species simply due to van der Waals interactions, resulting in an overall higher selectivity for the larger species.

Both inorganic and polymeric membranes can be designed to achieve solubility-based gas separations. Both materials have certain advantages and disadvantages and presently research effort is concentrating on designing membranes that provide high throughput and high selectivity.

3.1. Inorganic membranes

Microporous inorganic membranes are usually amorphous in nature and formed from metals, ceramics, or pyrolyzed carbon [12,13]. To obtain high enough permeances for the inorganic membranes to be practically useful, the membrane thickness needs to be quite small (on the order of microns). Amorphous inorganic materials do not typically have the inherent mechanical strength to form self-supported membranes in this size range, and therefore macroporous supports made of alumina, zirconia, glass, or stainless steel are used to provide the desired mechanical strength. There a number of processes employed for the formation of amorphous microporous inorganic membranes; however, among them the most widely used are sol–gel method, chemical vapor deposition (CVD) and pyrolysis method for the formation of carbon membranes [12–14].

Table 1
Permeability and selectivity data for N_2 and hydrocarbon gases through SSF membranes [26]

Gas	Permeability (mol m s^{-1} m^{-2} Pa^{-1} × 10^{10})	Selectivity (P_i/P_{N_2})
N_2	0.000251	
CH_4	0.00221	8.80
C_3H_8	0.000971	3.87
n-C_4H_{10}	0.000519	2.07

The sol–gel process involves the formation and deposition of a suitable sol, like a colloidal boehmite, onto a porous support, followed by drying and thermal treatment [13–19]. The sol–gel technique has been widely adopted for the formation of silica- and alumina-based inorganic membranes. Supported carbon membranes are created by heating precursors like polyfurfuryl alcohol (PFA) or phenolic resins at high temperature in an inert environment [12,20,21]. The heat treatment leads to the formation of non-graphitizing carbon, which is well cross-linked. Zeolite membranes are generally formed by a hydrothermal deposition method on suitable porous supports like α-Al_2O_3 [13,17,22–24]. The main advantages of this class of crystalline inorganic membranes are high chemical stability and very narrow pore size distribution; however, it is very difficult to create a defect-free zeolite membrane with practically useful thickness.

Inorganic materials like carbon molecular sieves and zeolites can be used to achieve separation based on diffusivity–selectivity [4,21]. In applications like the removal of hydrogen from hydrocarbons, high hydrogen/hydrocarbon selectivities can be achieved using carbon molecular sieves. However, one major problem associated with this type of membrane is that it is very fragile and prone to fouling by condensable species [4].

Microporous inorganic membranes have been modified and studied as possible materials for achieving solubility-based separation. The goals of these modifications have been to tune the pore size such that surface effects like surface flow and capillary condensation were enhanced, resulting in an increased flow for the larger species. Rao and Sircar developed nanoporous carbon membranes, which they called selective surface flow (SSF) membranes. Their aim was to separate hydrogen–hydrocarbon mixtures by preferential adsorption and diffusion of the hydrocarbons. The membranes had pore sizes in the range of 5–6 Å and achieved separation on the basis of selective adsorption and blocking. The permeability and selectivity data of the SSF membranes for nitrogen, and hydrocarbon gases is given in Table 1. Generally, as higher molecular weight species were selectively adsorbed, the membranes showed higher permeation factors for the hydrocarbons as compared to nitrogen and hydrogen. The membranes performance showed a significant improvement upon increasing the feed pressure due to higher adsorption of hydrocarbons at higher partial pressures [25,26].

Hassan et al. investigated the gas separation properties of silica hollow fiber membranes with pore size ranging between 5.9 and 8.5 Å [27]. They conducted both single and mixed gas experiments using light gases and hydrocarbons with kinetic diameters ranging from 2.6 to 3.9 Å. They observed large separation factors for carbon dioxide/methane mixtures, which was attributed to surface diffusion as being the primary transport mechanism. The mixed gas selectivity was higher than single gas, which they concluded was due to the competitive adsorption effects.

Huang et al. modified γ-alumina membranes for recovery of acetone from nitrogen by reducing the pore size to enhance multilayer diffusion and capillary condensation transport mechanisms [28]. The modified membranes showed higher acetone permeability and higher separation factors as compared to polymeric membranes; however, the performance was strongly influenced by temperature and feed composition. Depending on the temperature and the feed composition, the separation factor varied from being less than 10 to as high as 1200.

Inorganic membranes typically have the advantage of higher permeabilities as compared to polymeric membranes, and selectivities are high when certain transport mechanisms are dominant. Inorganic membranes also exhibit good resistance to harsh chemical conditions and can withstand high-pressures and temperatures. However, one major drawback of inorganic membranes is that selectivity tends to be a strong function of process conditions, especially temperature, pressure, and mole fraction of the condensable species in the feed.

3.2. *Polymeric membranes*

The use of polymer membranes has generated an ever-increasing interest in the field of gas separation [9,11]. Polymers are available in a wide array of chemistries that can be used to suit particular applications. As with inorganic membranes, one would like to form the polymer layer with minimum possible thickness. Polymeric membranes are therefore cast on supports to form integrally skinned membranes. Phase inversion is one of the commonly used processes to form integrally skinned polymeric membranes. In this process a sol is inverted to form a porous three-dimensional macromolecular network. There are four major categories of the phase inversion process depending on whether the casting procedure is wet or dry, and whether the phase inversion is carried out in a dry or wet medium [4,11].

For gas separation, the most desirable polymers are those that provide both high permeability and selectivity. For diffusivity-based separations, polymers however show what has been commonly termed in literature as the “inverse permeability/selectivity” behavior. Robeson investigated this inverse relationship and suggested that there exists a hypothetical “upper bound” in the relationship between permeability and selectivity [29]. Much of the present research has focused on pushing the polymer performance above the upper bound and into the economically attractive region currently enjoyed by inorganic membranes.

Table 2
Permeability and selectivity data for N_2 and hydrocarbon gases through PDMS [31]

Gas	Permeability ($\text{mol s}^{-1}\,\text{m}^{-2}\,\text{Pa}^{-1} \times 10^{10}$)	Selectivity (P_i/P_{N_2})
N_2	0.00154	
CH_4	0.00486	3.15
C_3H_8	0.0287	18.65
C_2H_4	0.0126	8.18
C_2H_6	0.0151	9.81

For solubility-based separations, Freeman and Pinnau have suggested the possibility of having a positive correlation between permeability and selectivity, which is in contrast to diffusivity-based separation [10]. By observing propane/methane selectivity as a function of propane permeance through a number of polymers they demonstrated the polymers that exhibited higher permeabilities for propane were also more selective for propane.

For solubility-based separation, polydimethysiloxane (PDMS) and poly(1-trimethylsilyl-1-propyne) have shown promising results, primarily because they exhibit diffusivity selectivity near unity for a wide range of gas species [10,30]. PDMS is a rubbery polymer silicone polymer that has one of the lowest glass transition temperatures. PDMS therefore has a very flexible backbone and exhibits diffusivity selectivity near unity.

PDMS has been investigated extensively as a suitable material for removal of different solvents from air or nitrogen. Stern et al. carried out permeability studies of a number of different gases through unmodified and structurally modified PDMS [31]. Table 2 details the permselectivity data obtained by Stern et al. for nitrogen and hydrocarbon gases. Baker et al. studied the permeabilities of different solvents and nitrogen through a number of polymers including PDMS [32]. Their study showed that all the polymers selected showed high solvent/nitrogen selectivity. Considering the different factors involved in membrane formation, they concluded the PDMS was the best material among the polymers tested for achieving solubility-based separations. Blume et al. studied the permeation and sorption of a number of different gases through PDMS [33]. Their study showed a strong dependence of solvent permeabilities on the solvent concentration and they concluded that the solvent permeation was largely dependent upon the sorption of the solvent into the polymer. Kimmerle et al. studied the fluxes and separation factors for acetone–air mixture through PDMS–polysulfone composite membrane at different solvent feed mole fractions and permeate pressures [34]. They also worked out the economics of building a solvent recovery system based on their membrane

Table 3
Permeability and selectivity data for N_2 and hydrocarbon gases through PTMSP [40]

Gas	Permeability ($\mathrm{mol\,s^{-1}\,m^{-2}\,Pa^{-1}} \times 10^{10}$)	Selectivity (P_i/P_{N_2})
N_2	0.0211	
CH_4	0.0516	2.44
C_3H_8	0.101	4.81
n-C_4H_{10}	0.264	12.51

system and calculated the time return of investment to be less than 2 years.

Leemann et al. in a similar study investigated the performance of PDMS membrane in the removal of toluene from nitrogen. Their study showed that within certain regimes of purity and flow the PDMS membrane system could be an economical alternative to the conventional processes [35]. PDMS is currently being used commercially for the separation of VOCs from air.

PTMSP is a glassy polymer that was first synthesized by Masuda et al. in 1985 [36]. PTMSP has one of the highest free volume known of any glassy polymers, which has been attributed to it unique structure [9,37–39]. PTMSP has shown very high permeabilities and very low selectivities for lighter gases. For this reason initially PTMSP was considered by Kesting and Fritzsche and by Stern as having little use in gas separation [9,11]. However, the low diffusivity–selectivity property of PTMSP makes it a good candidate for solubility-based separation. Pinnau and Toy studied the transport of light gases and organic vapors through PTMSP [40]. They observed higher permeability coefficients for the more condensable gases than the lighter non-condensable gases (Table 3). This behavior was attributed to the dominance of the solubility effects in the transport of gases through PTMSP. The mixed gas selectivities in general showed higher values as compared to ideal selectivities suggesting blocking effects by the condensable species during mixed gas permeation. Merkerl et al. performed mixed gas permeation of synthesis gas (syngas) on both PDMS and PTMSP [41]. Their study again showed that both PDMS and PTMSP exhibit higher permeability for the more condensable gas (carbon monoxide and hydrogen sulfide) as compared to hydrogen, and demonstrated the suitability of these materials for solubility-based separations.

There are certain disadvantages in using polymeric membranes. Polymers exhibit high selectivities, but they tend to have low throughput (compared to porous materials) due to their low free volume. Generally, polymers cannot withstand high temperatures and harsh chemical environments as well as inorganic membranes. PDMS has been shown to be prone to plasticization, which may greatly reduce its selectivity when exposed to actual gas mixtures [30]. A major drawback of PTMSP is that this polymer, like most glassy polymers, is prone to aging effects and shows a decrease in permeability over time. This has been attributed to relaxation of the polymer chains and possible attack by impurities on the unsaturated double bonds in the polymer backbone [42].

3.3. Hybrid membrane materials

Another approach is to design organic–inorganic hybrid membranes that combine the best characteristics of both polymeric and porous materials. Different types of hybrids have been proposed to enhance membrane performance. Organic–inorganic hybrids have been formed by incorporating inorganic particles into a polymer matrix, covering a porous substrate with organic–inorganic sol–gel materials, forming layers of polymeric material on the surface of a porous substrate, and by plasma polymerization on the surface of an inorganic support [43–50].

One approach for generating organic–inorganic hybrids is based on the tethering of organic compounds to the porous surfaces of inorganic substrates. The chemical derivatization of inorganic substrates to form self-assembled monolayers (SAMs) has been a field of interest for a number of applications, such as wetting, electrochemistry, bioactive surfaces, and catalysis [51]. More recently this approach has been applied to membranes. Miller and Koros modified commercially available mesoporous alumina membranes by chemical vapor deposition of trichlorosilane oligomers on the membrane surface [52]. Their aim was to reduce the pore size for a sieving (diffusivity-based) application and therefore they used aliphatic oligomers with a high degree of fluorine substitution. They observed a permeability drop for all gases of one to two orders of magnitude, and also a decrease in the selectivity for the lighter gases over the heavier, upon modification.

Paterson and co-workers published a series of papers on the surface modification of inorganic membranes [53–59]. Their modifications were based on wet chemistry routes rather than the vapor deposition as employed by Miller and Koros. In the first paper titanium membranes with an average pore size of 2 nm were modified with phosphoric acid and alkyl phosphonic acid derivatives [53]. They investigated the effects of such modification on bovine serum albumin (BSA) filtration and found an increase in the rejection with the modified membranes without loss in flow. They concluded that with such modifications it was possible to change the nature of the inorganic surface from hydrophilic to hydrophobic.

In Part II of Paterson et al.'s work, 5 nm alumina membranes were surface derivatized with PDMS silicone oil [54]. Due to the presence of surface hydroxyl group on the inorganic substrate they were able to chemically attach the silicone oil; infrared spectroscopy studies confirmed the presence of siloxane derivative on the alumina surface. Permeation studies were conducted using light gases, carbon dioxide, methane and propane. After treatment the permeance of all gases went down about 4–5 orders of magnitude. The modified membrane in some cases (e.g. CO_2/N_2) exhibited selectivities similar to a dense PDMS film, while in other cases (e.g. CH_4/N_2) showed significantly higher selectivity.

Table 4
Permeability and selectivity data for N_2 and hydrocarbon gases through hybrid membranes [57,58]

Gas	Permeability (mol s^{-1} m^{-2} Pa^{-1} $\times 10^{10}$)	Selectivity (P_i/P_{N_2})
N_2	0.000480	
CH_4	0.00116	2.42
C_3H_8	0.00872	18.17
n-C_4H_{10}	0.018	37.50

They concluded that the membrane after modification no longer remained porous and gas permeation was occurring predominantly due to the solution-diffusion mechanism.

Octadecyltrichlorosilane (OTS) was used to modify 5 nm alumina membranes in Part III of Paterson et al.'s study [55]. Trichlorosilane is a highly reactive functionality and reacts readily with the surface hydroxyl groups of the alumina membrane. Infrared spectroscopy again confirmed the attachment of the oligomer, and gas permeation experiments similar to ones conducted in Part II showed about three orders of drop in permeance for all gases. Interestingly, however, no improvement in propane/nitrogen selectivity was observed after this modification.

In another study, Randon and Paterson modified 5 nm alumina membranes with *n*-butyl phosphonic acid and *n*-dodecyl phosphate [56]. Gas permeation experiments were conducted using nitrogen and propane. By repeated treatments with the C10 oligomer they were able to increase C_3H_8/N_2 selectivity to 16, which was a slight improvement compared to polyethylene, the chemical analogue of the alkyl chains.

However, what was very significant was that the modified membrane exhibited significantly higher propane permeance. Their conclusion was that the modification had made the membrane hydrophobic and improved the membrane's solubility-based separation characteristics.

Javaid et al. modified 5 and 12 nm alumina membranes using different alkyl trichlorosilanes with chain lengths ranging from C4 to C28 [57]. Their study showed a significant increase in propane/nitrogen selectivity accompanied, by a loss in permeance, after modification of the 5 nm membranes (Table 4). The selectivity increase was positively correlated with chain length and was attributed to the effective filling of pores with oligomer. The membrane surface became hydrophobic, and solution-diffusion becoming the dominant mechanism of transport in the modified membrane. In comparison to PDMS, one of the best-known polymers for solubility-based separations, the hybrid membranes exhibited equal or greater propane/nitrogen selectivity although at lower propane permeance. These results were in contrast to the similar modification done by Leger et al. in which they did not observe any increase in propane/nitrogen selectivity [55]. This difference was attributed to differences in the synthesis conditions, especially the trichlorosilane reagent concentration. Javaid et al. employed a concentration that was almost 30 times lower than the one used by Leger et al. X-ray photoelectron spectroscopy (XPS) characterization confirmed the attachment of the oligomer to the membrane surface, and results from the XPS depth profile showed the oligomer covering mainly concentrated near the membrane surface.

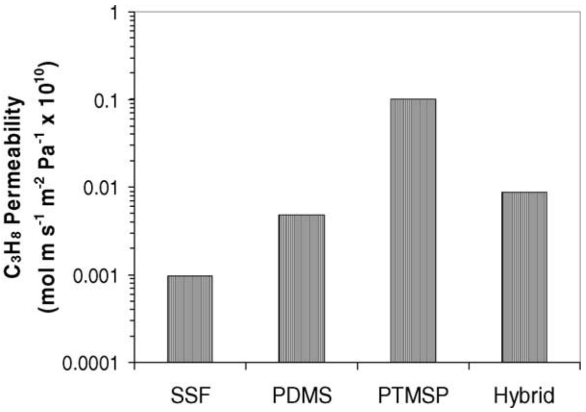

Fig. 1. Propane permeability comparison for different types of membranes [26,31,40,57–58].

In Part II of their study Javaid and Ford described the performance of OTS-modified with gas mixtures. Propane/nitrogen and butane/methane gas mixtures were used to evaluate the performance of the 5 nm OTS-modified membrane. In general their study showed higher mixed gas selectivities, which were attributed to competitive effects of heavier species [58].

McCarley and Way, in a study similar, modified 5 nm alumina membranes with C18 trichlorosilane [59]. They conducted both single gas and mixed gas permeation experiments at fixed trans-membrane pressures. The C18-treated membrane showed a significant increase in ideal selectivity for heavier gases (*n*-butane) over lighter gases (nitrogen and methane) as given in Table 4. By measuring pure gas permeances as a function of critical temperature they showed the relationship between the permeance and solubility of the

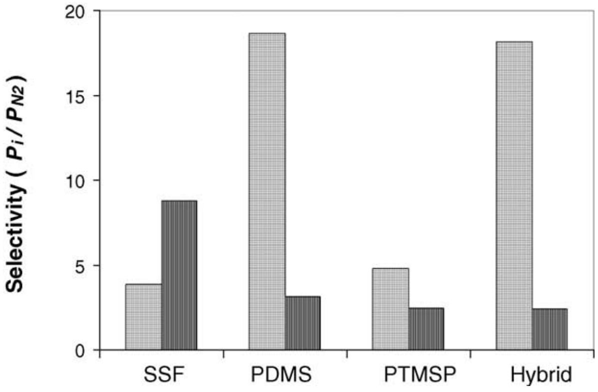

Fig. 2. Hydrocarbon/nitrogen selectivity for different membrane materials: ▨ represents C_3H_8/N_2 and ▥ represents CH_4/N_2 [26,31,40,57,58].

gases in the membrane, concluding that transport across the membrane was strongly dependent on preferential sorption. The mixed gas analysis also in general showed an increase in selectivity as compared to single gas measurements.

In general, all three membrane materials have shown potential in achieving solubility-based gas separation. As a comparison, propane permeability and propane/nitrogen selectivity for inorganic SSF, polymeric (PDMS & PTMSP) and hybrid membranes are plotted in Figs. 1 and 2. The permselectivity data for PDMS and hybrid membranes is comparable. The permeability for PTMSP is nearly an order of magnitude higher than both PDMS and hybrid membranes; however, the selectivity for propane/nitrogen is much lower. The performance of the SSF membranes is much lower as compared to the other membranes but the SSF membrane due to their inorganic structure can easily sustain harsh industrial environments.

4. Industrial applications

Membrane Technology and Research Inc., (MTR) has developed a solubility-based membrane system, VaporSep, for the recovery of VOCs from remediation off gases [60]. The membrane system consists of a rubbery polymer attached to a microporous support layer and a fabric support layer. Additionally VaporSep system has also been installed to recover hydrocarbons such as in the petrochemical refining and natural gas industries. In the recovery of VOCs the major drawbacks of this system are it's fouling due to oil and water present in the feed streams and reduction in the system capacity due to presence of CO_2. Currently the cost of the system for the removal of VOCs is higher as compared to some of the other technologies like catalytic conversion [60].

5. Future direction

The main challenge with solubility-based gas separation as with other gas separation membrane application is the achieving higher selectivity at acceptable production levels. The cost-effectiveness of this technology especially in the removal of VOCs from effluent streams is strongly dependent on overcoming this major challenge. Furthermore these properties of high flow and high selectivity need to be maintained consistently over long period of time under complex and harsh feed conditions. Future research must focus on the development of new materials and modification of the existing materials that overcome these challenges.

Another major problem with such types of application is the presence of liquid contaminants such as water and oil which cause fouling. Research must therefore also be directed in developing solubility-based membrane systems that resolve the problems occurring due to fouling.

6. Summary

Solubility-based gas separations for applications such as the removal of VOCs from air, in recent times have become important due to environmental and economic driving forces. The main objective is to obtain membranes that exhibit high permeability and high selectivity for the heavier species over the light gases. Previous work has shown that a huge potential exists for research and development in the field of membrane technology with regards to solubility-based gas separations, especially environmentally relevant gas separations.

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