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ABSTRACT

IMMOBILIZED LIQUID MEMBRANES FOR FACILITATED TRANSPORT AND GAS SEPARATION

by

Anjaneya Sarma Kovvali

Separation and purification of gas mixtures is a major area of activity in chemical engineering. Gas separation using facilitated transport membranes has been the subject of considerable research for many years. Immobilized liquid membranes (ILMs) are an important class of facilitated transport membranes. Despite their potential to provide superior performance, they could not achieve commercial success so far due to their instability. Recent research addressed the issue of stability of ILMs by replacing water as the solvent successfully with glycerol. In the present thesis, the relevance of glycerol as an ideal solvent for developing stable ILMs is demonstrated using the separation of olefin-paraffin gas mixtures with silver nitrate-glycerol ILMs.

It would be ideal if the use of solvent in forming the ILM can be completely eliminated. Such a radically different concept of forming ILMs was demonstrated with Polyamidoamine (PAMAM) dendrimer as the liquid membrane in its pure form. The pure dendrimer ILMs studied in the present thesis functioned as CO₂-selective molecular-gate membranes. It was also demonstrated that a judicious use of glycerol as a solvent in dendrimer solutions results in improving the performance of dendrimer membranes.

There is always a need for physical solvents with enhanced solubility for the gas species of interest, particularly for CO_2 . The present thesis identified one such solvent, glycerol carbonate, and demonstrated its unique features for CO_2 separation.

Enhancement of CO_2 fluxes with the addition of carriers such as dendrimers was also briefly explored to identify future directions for this new area of research.

For any membrane process to be commercially successful, the process should have higher fluxes for the gas species of interest (e.g. CO₂) without compromising on the selectivity of the membrane. The present thesis proposed and explored two novel concepts in preparing thinner liquid membranes. One approach uses the asymmetric nature of pores in the substrates to position the liquid membrane in a small section of the substrate. The other approach utilizes a traditional interfacial polymerization technique to form a thin support layer for immobilizing the liquid membrane on it. Both approaches have the potential to define the success of immobilized liquid membranes for solving the gas separation problems with efficiency and economy.

IMMOBILIZED LIQUID MEMBRANES FOR FACILITATED TRANSPORT AND GAS SEPARATION

by

Anjaneya Sarma Kovvali

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering

> Department of Chemical Engineering, Chemistry, and Environmental Science

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APPROVAL PAGE

Immobilized Liquid Membranes for Facilitated Transport and Gas Separation

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This thesis is dedicated to

All the *gurus* who taught me everything

and

My parents who taught me everything else

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NOMENCLATURE

- A Membrane area, cm^2
- C_{im} concentration of species i in the membrane phase, cc(gas)/cm³
- D_{im} diffusion coefficient of species i in the membrane phase, cm²/s
- J_i flux of species i, cc(gas)/cm².s or mol/cm².s
- p_i partial pressure of species i, cm Hg
- P pressure, cm Hg
- Q_i permeability coefficient, cc.cm/cm².s.cm Hg
- RH relative humidity, %
- S Solubility of gas, cc/cm³.cm Hg
- t_m membrane thickness, cm
- V_i volumetric permeation rate of species i, cc(gas)/s
- x_i mole fraction of species i
- y_{H2O} mole fraction of water

Subscripts/superscripts/Greek letters

- eff effective
- i,j species
- in inlet condition
- f feed condition
- lm logarithmic mean value
- out outlet condition

p permeate side condition

sat	saturation
t	total
true	true
ε _m	porosity of the substrate
τ _m	tortuosity of the substrate

- Δp_i partial pressure difference of species i across the membrane, cm Hg
- $\alpha_{i/j}$ Selectivity of the membrane for species i over species j

CHAPTER 1

INTRODUCTION

1.1 Background

Separation and purification of gas mixtures with energy efficiency and selectivity is vital to a broad array of industries and technologies. Regardless of the separation problem, most current developments in separation and purification of gas mixtures rely on developments in suitable adsorbents and membranes. Separation of different gas species in a mixture is usually achieved by either chemical or physical means. Such approaches include gas absorption into a solvent, pressure swing adsorption, cryogenic separation, distillation, membrane-based separation etc.

Membrane-based processes have some definite advantages over the traditional processes for gas separation as they are easy to scaleup because of their modularity, have low maintenance and labor costs associated with their operation and have low energy requirements. These advantages have helped membrane-based gas separation to become an established unit operation (Ho and Sirkar, 1992; Geankoplis, 1993) Although membrane-based gas separation has achieved major breakthroughs (Ho and Sirkar, 1992; Stern, 1994; Koros and Fleming, 1993), many more are needed for economic and efficient separation of mixtures of O_2 - N_2 , CO_2 - CH_4 , CO_2 -air, olefin-paraffin etc.

Gas separation using facilitated transport membranes (FTMs) has been the subject of considerable research for many years. Major advantages of FTMs over conventional polymeric membranes include higher fluxes for reacting gas species like carbon dioxide, olefins and the resultant high selectivities over nonreacting species like nitrogen, paraffins etc. This is possible due to the additional mechanism of a reversible chemical reaction of the preferred gaseous species with a reactive carrier present in the FTM in addition to the solution-diffusion mechanism. FTMs are particularly attractive at low reacting species concentrations where the concentration driving force for the solution-diffusion membranes is very low (Meldon et al., 1982; Ho and Dalrymple, 1994). Facilitated transport membranes include ion-exchange membranes, fixed-site carrier membranes, contained liquid membranes, and immobilized liquid membranes (Way and Noble, 1992).



Figure 1.1 Schematic of an immobilized liquid membrane for gas separation

Figure 1.1 shows schematically an immobilized liquid membrane in a microporous substrate. Immobilized liquid membranes (ILMs) contain a liquid solution immobilized in the pores of the polymeric substrate by physical forces. They are also referred to as supported liquid membranes (SLMs), particularly in the context when feed

and sweep side are liquid streams. The liquid solution consists of a carrier and a solvent. The carrier reacts reversibly with the gas species of interest.

ILMs can potentially provide the highest fluxes and selectivities for reacting species such as carbon dioxide and olefins particularly at low concentrations in gas separation. Despite the obvious advantages offered by the immobilized liquid membranes, commercialization of these membranes has not taken place due to the inherent limitation of stability of the liquid membranes. The main reasons for the instability of the ILMs are due to (Chen et al., 1999):

- absence of any chemical bonding of the carrier to the substrate matrix
- evaporation of the carrier species and/or the solvent liquid into the gas phases during the operation
- lower breakthrough pressures associated with the liquids.

The stability of aqueous-based ILMs is usually improved when the feed and sweep sides are completely humidified, minimizing the loss of solvent (water) due to evaporation (Teramoto et al., 1986). The long term stability of these membranes has not been established in literature and obviously these membranes can not withstand even temporary oscillations in the humidity conditions on either side of the liquid membranes. A major factor that limited the practical applicability of such an approach is that the sweep side always requires a sweep gas, essentially diluting the permeated gases. This limitation has serious implications in downstream processing of the permeate stream or when highest possible concentrations on the permeate side are required, either for economic or environmental reasons. For example, in the separation of carbon dioxide from gas mixtures for sequestration, the permeate side should be as concentrated as technically possible in carbon dioxide to reduce the gas volumes for further transport and storage.

Another alternative way to improve the ILM stability is to use low-volatile and hygroscopic solvents like polyethylene glycol for preparation of the ILM (Meldon et al., 1986; Davis and Sandall, 1993; Saha and Chakma, 1995). However, the performance of such a membrane has not been acceptable (Meldon et al., 1986).

Some of the possible approaches that can be considered to improve the stability of the ILMs are:

- to select a carrier which itself is highly viscous and non-volatile and does not require a solvent,
- to select a solvent which is highly viscous and non-volatile, and can accommodate carrier species for efficient transport of reacting gas species,
- to select a solvent which is viscous and non-volatile and may not require the presence of water for the selectivity.

If the presence of water is needed for the reversible chemical reaction to occur, then, in the first approach the carrier should be also hygroscopic while the solvent should be hygroscopic in the second approach.

1.2 Development of Stable, Highly Selective ILMs

The present thesis focuses on these three approaches towards improving the stability and performance of the ILMs for gas separation for two applications, namely CO_2 separation and olefin-paraffin separation.

The first approach of improving the ILM stability by employing a liquid membrane system where a carrier is the only component in the ILM is studied using a new class of hyperbranched polymers called dendrimers. This class of polymers has molecular weights ranging from 518 to several thousands depending on their generation. They also offer the needed properties like non-volatility, good chemical and thermal stability, reversible complexation capability etc. (Tomalia et al., 1990). The selective separation of CO_2 from CO_2 -N₂ mixtures using a generation zero poly(amido amine) dendrimer is studied in Chapter 2.

For the second approach of selecting a suitable solvent, glycerol is an ideal solvent for containing the carriers needed for the facilitation reactions for the gas separation systems studied here. Glycerol possesses excellent characteristics: it is highly hygroscopic; its highly variable viscosity with water content may be of considerable utility; it is essentially non-volatile (Chen et al., 1999). The contribution of glycerol as the solvent toward stability of the ILMs for carbon dioxide separation has been demonstrated (Chen et al., 1999) by dissolving carriers such as sodium carbonate. In the present thesis, the concept of using glycerol as the solvent in place of water for forming a stable ILM is extended to other facilitated transport systems in gas separations. The ILMs for the separation of olefins from paraffins are studied here by incorporating silver nitrate as the facilitating agent for olefins in glycerol. The stability and the performance of such an ILM are demonstrated. Selective separation of 1-butene from a mixture of 1-butene (olefin) and n-butane (paraffin) in nitrogen is studied as an example system through silver nitrate-glycerol ILM in microporous flat membranes. An introduction to the problem and

prior approaches have been provided in Chapter 3. The experimental details and results are also presented and discussed in Chapter 3.

Facilitated transport membranes provide very good selectivities and permeances for the reacting species (e.g. CO₂, olefins) when they are present in low concentrations in the feed gas mixture. However, their performance at high feed side concentrations of the reacting gases is usually compromised due to carrier saturation. The presence of glycerol in the present ILMs does not prevent this deterioration in performance at higher CO₂ concentrations as it is essentially non-selective to carbon dioxide (Chen et al., 1999). (The same observation is true in the separation of 1-butene/n-butane mixtures.) There is always a need for better solvents which have selectivities for the gas of choice (third approach). Glycerol carbonate is explored in Chapter 4 of the present thesis as a possible CO₂-selective physical solvent for carbon dioxide separation. Whether glycerol carbonate can be used as solvent for carriers such as sodium glycinate, dendrimers for carbon dioxide separation has also been explored in Chapter 4.

1.3 Formation of Thinner ILMs for Enhanced Permeation

The permeances of gas species across a liquid membrane are dependent on its thickness. The reduction in thickness of the ILM reduces the diffusional path lengths for the reacting species or its complexes as well as for non-reacting species. The ILMs formed with thickness smaller than that of the substrate employed in the present thesis are referred to as "thin ILMs" in the present context whereas the ILMs filling the entire porous region of the substrates are referred to as "full ILMs". Because of the higher viscosities of glycerol or dendrimers, the fluxes of the reacting species like carbon dioxide or an olefin can be lower than those obtained in water-based ILMs. Correspondingly, the fluxes of non-facilitated species e.g. N₂, paraffins etc., can also be considerably lower. Therefore, the selectivities of these ILMs may be much higher than those obtained by the water-based ILMs (Chen et al., 1999). So it is logical to try to improve the fluxes for these glycerol-based or dendrimer-based ILMs. However, thin ILMs are likely to yield lower selectivities for most of the partial pressure range of the reacting species as the increased fluxes due to the facilitating reactions are considerably reduced in comparison to the solution-diffusional transport rates.

Most of the literature on thin ILMs involved essentially a singular feature. The thin films were formed on top of a substrate by forming gel membranes with polymers such as poly (acrylic acid) (Matsuyama et al., 1996) or polyvinyl alcohol (PVA) (Ho and Dalrymple, 1994). While polyacrylic acid gel-based thin films are formed via plasma polymerization, the PVA membranes were formed via coating and subsequent crosslinking and heat treatment. Other thin films (ILMs and non-ILM facilitated transport membranes) followed similar routes (Quinn and Laciak, 1997; Quinn et al., 1997). In most of these cases, the thickness of the thin film is usually anywhere from 2.9 μ m (Ho and Dalrymple, 1994) to 50 μ m (Matsuyama et al., 1996) depending on the difficulties involved in the membrane formation.

Thin ILMs were also formed by immobilizing the aqueous-based liquid membrane through only part of the thickness of the substrate pores (Bhave and Sirkar, 1986) of hydrophobic Celgard films of polypropylene. The ILM thickness was reduced by evaporating the water from the ILM from one side of the substrate membrane leading to an ILM thickness less than that of the substrate. This approach can lead to thinner ILMs with higher fluxes. However, the substrate studied was a microporous Celgard film with essentially uniform pore dimensions across the thickness of the substrate. Because of this reason, it is not possible to form thin ILMs with any non-volatile solvent other than water employing this approach.

A recent effort to form thin glycerol-based ILMs in microporous PVDF substrate met with limited success (Chen et al., 2000). The glycerol-based thin ILMs were formed by contacting one side of the substrate with the liquid solution for a finite amount of time. The time of contact was always less than that would normally be observed to completely wet the substrate. Even though an increase in CO₂ permeances by as much as a factor of 3 was observed with thinner ILMs, the CO₂/N₂ selectivity suffered drastically and the stability of the liquid membrane was also not encouraging. The reason for this behavior was the relatively uniform characteristics of the substrate membrane across its thickness and pore size distribution. In addition, the thin liquid film was exposed to the feed gas pressure on the coating side which allowed the solution to spread to larger pores under gas pressure and thereby introduce tiny defects. Even though this technique is inherently practical, its applicability to liquid with different viscosities and wetting characteristics is not known.

The present thesis investigates two novel techniques for forming thin ILMs for CO_2 -N₂ separation; they are illustrated in Chapter 5. These techniques are expected to be particularly advantageous for higher partial pressure ranges of the reacting gas species

where commercially available polymeric membrane processes tend to have low selectivities. Broadly, the two techniques can be described as:

- 1) forming an ILM in a thin section of the substrate membrane
- forming a support layer on top of a substrate membrane and the liquid membrane is immobilized in this support layer.

There are differences between the first technique investigated in the present thesis and some of the thin films studied in literature (Bhave and Sirkar, 1986; Chen et al., 2000). The present technique utilizes the asymmetry of the pores in a given substrate. In other words, the present technique is applicable to asymmetric substrate membranes and/or composite membranes. It can also be applied to non-aqueous systems. The perceived advantage of the present technique is that it can lead to stable and thin ILMs within a small section of the substrate.

If an ILM is located in a thin support film on top of a substrate matrix, it can be expected that the thickness of the ILM is the same as that of the support film. It can be very small compared to that of a full ILM formed in the substrate. One such way to form thin porous films is attempted here by interfacially polymerizing the support film for the ILM on a porous substrate matrix. Interfacial polymerization occurs between a water soluble reactant A and an organic soluble reactant B at the aqueous-organic phase interface. The polymeric films formed through interfacial polymerization generally are very thin and have been primarily used as reverse osmosis membranes (Cadotte et al., 1981). Applicability of such films for immobilizing liquid membranes is not studied in literature so far. The support layers formed in the present study via the approach of interfacial polymerization immobilized with glycerol are pure carbonate,

 Na_2CO_3 -glycerol to study their performances for CO_2 - N_2 separation. The feasibility of forming functional thin films was also explored with dendrimers.

1.4 Theoretical Understanding of Non-aqueous ILMs

The use of non-aqueous solvents or carriers for facilitated transport has been a relatively recent activity. Because of this reason, there are no data on various aspects of transport of gases through such liquids. A significant difference between the liquid membranes studied in the present thesis and those studied in literature is that in the present thesis the sweep side always employs a dry gas stream. In addition, the geometry of the flat membranes introduces additional uncertainties in the hydrodynamics and concentration profiles in the liquid membrane. A preliminary theoretical analysis is performed in Chapter 6 for a pure glycerol ILM to predict the permeabilities of nitrogen and carbon dioxide under conditions of different relative humidities. The objective of this exercise is to identify the parameters that are needed to theoretically describe the ILM performance and to highlight the uncertainties involved in using existing theories to describe various phenomena that occur in a non-aqueous liquid solution.

CHAPTER 2

CARBON DIOXIDE REMOVAL FROM GAS STREAMS USING ILMS

2.1 Introduction

Separation of CO_2 from gas mixtures is vital for a wide range of applications. Removal of carbon dioxide from gas streams is of importance both in terms of its impact on environment and process economics. At low concentrations of carbon dioxide in the gas streams or atmosphere, its removal has been receiving renewed attention because of its dominant role among gases responsible for global warming. Highly selective removal of carbon dioxide at very low concentrations is essential in critical applications such as Mars Mission, space suit and breathing apparatus (Chen et al., 1999). It could also be of economic significance to remove carbon dioxide at low concentrations if the process requires it.

The importance of carbon dioxide removal is not limited to low concentrations of CO_2 in gas mixtures. Most sources of carbon dioxide emissions are identified as energy generators where carbon dioxide is currently emitted at relatively high concentrations, around 10-15%. Similarly, other industrial process streams contain relatively high concentrations of carbon dioxide. Carbon dioxide removal is desired in processes such as synthesis gas production, upgrading of natural gas, landfill gas recovery and enhanced oil recovery (Quinn and Laciak, 1997). Natural gas and biogas contain high concentrations of carbon dioxide, where issues of corrosion and regulatory constraints play a major role in a determined effort to reduce carbon dioxide from these gas streams and sequester it. For CO_2 separation from these streams, it is desirable to achieve very high selectivity for CO_2 over other gases.

Some of the processes currently commercialized to remove carbon dioxide from gas streams are (Kohl and Riesenfeld, 1979):

- absorption with volatile carriers such as ethanolamines (mono- and di-), and ethylene diamines (EDA)
- pressure swing adsorption processes
- membrane-based processes.

Among these processes, membrane-based processes offer unique advantages. Membrane-based devices/processes are modular in nature, require low maintenance and are not energy intensive. So far, polymeric membranes have been used commercially for CO₂ separation. Current commercialized membranes have pressure normalized fluxes in the range of 10-40 GPUs (5-4500 Barrers) and low selectivities for CO₂ over N₂ around 10-40 (Way and Noble, 1992). Such low fluxes and selectivities for carbon dioxide are due to the solution-diffusion mechanism of transport for all gas species through these membranes. The low fluxes and selectivities associated with polymeric membranes make membrane-based carbon dioxide removal often unattractive compared to other conventional processes.

The permeation of a species i through a polymeric membrane can be written as

$$J_i = -D_{im} \frac{dc_{im}}{dt_m}$$
(2.1)

where J_i is the flux of the species *i*, D_{im} is the diffusion coefficient of the species in the membrane, c_{im} is the concentration of the species (related to its solubility in the polymer) and t_m is the membrane thickness. The same flux expression is applicable for all gas species, irrespective of their concentrations in the gas phase. This, in general, results in

lower selectivities for the gas species of interest as it is often removed from other gas species having similar diffusivities and solubilities through the polymer. The problem becomes particularly acute for nonporous polymeric membranes at lower CO_2 feed partial pressures; the CO_2 flux, a product of the CO_2 partial pressure difference across the membrane and the CO_2 permeance, becomes quite low. Hence, development of CO_2 selective membranes having high CO_2 permeance and selectivity would lead to higher energy efficiency and reduced capital costs. Facilitated transport membranes (FTMs) offer a solution to this problem. FTMs selectively permeate carbon dioxide by means of reversible reaction between carbon dioxide and a complexing agent in the membrane in addition to conventional solution-diffusion.

Facilitated transport membranes (FTMs) have been therefore investigated (Ward and Robb, 1967; Meldon et al., 1982; Bartsch and Way, 1996) wherein reactive carriers increase the CO₂ permeability drastically and CO₂ permeance significantly at low CO₂ partial pressures in the feed gas; CO₂ is transported not only as a free species but also as a carrier-complexed species. This is due to the facilitating reaction mechanism in FTMs compared to the solution-diffusion mechanism in polymeric membranes. Other gases such as N₂, O₂, and CH₄ permeate through the membranes by the simple solution-diffusion mechanism. FTMs are particularly attractive at low reacting species concentrations where the partial pressure driving force is very low. This is especially advantageous for removal and sequestration of carbon dioxide when it is present in the feed at low concentrations. FTMs can be in the form of (Noble and Way, 1994):

- a solvent-swollen polymer film,
- a solid polymer film having functional groups reactive with CO_2 (often called a fixed carrier membrane), and
- an appropriately immobilized thin liquid layer containing species reversibly reactive with CO₂ (ILM) and contained liquid membrane (CLM).

The simplified reaction scheme for carbon dioxide (A) with a carrier (C) in a facilitated transport membrane can be written as

$$A + C \iff AC \tag{2.2}$$

The reaction between carbon dioxide and the carrier should be reversible and fast for high removal rates for CO_2 . The reversible nature of the complexation reaction ensures that only a small amount of carrier is required for continuous removal of CO_2 from the feed gas mixtures.

Of these different configurations of FTMs, immobilized liquid membranes (ILMs) can potentially yield higher CO_2 permeances and selectivities, particularly at low CO_2 concentrations. Figure 2.1 shows schematically the transport mechanism of a reacting gas species A (e.g. carbon dioxide) and a non-reacting gas species B (e.g. nitrogen) through an immobilized liquid membrane having a facilitating carrier C (e.g. Na₂CO₃). Carbon dioxide dissolves in the ILM liquid at the feed side (high partial pressure) boundary and diffuses through the membrane; simultaneously it reacts with the carrier and the complex diffuses to the low pressure side. The flux of carbon dioxide from the high to the low partial pressure side of the membrane is enhanced by an additional flux of these reaction products. At the low partial pressure side of the membrane, the reaction is reversed,

carbon dioxide is released from the complexed species in the liquid and is swept away by a sweep gas or by applying vacuum. The physically dissolved carbon dioxide is also released at this surface.



Figure 2.1 Schematic of facilitated transport in immobilized liquid membrane.

Despite the obvious advantages offered by the immobilized liquid membranes, i.e., high permeances and selectivity, commercialization of these membranes has not taken place due to the inherent limitation of stability of the liquid membranes. Some of the main reasons for the instability or failure of the ILMs are due to:

- absence of any chemical bonding of the carrier to the substrate matrix,
- evaporation of the carrier species and/or the solvent liquid into the gas phases during the operation, and
- lower breakthrough pressures associated with the substrates and the liquids.

The problem of the ILM drying out when aqueous solutions are used is usually addressed by humidifying both the feed and sweep gas streams. This approach obviously imposes a limitation on the practical utility of these membranes, namely, vacuum can not be used on the low partial pressure side to remove carbon dioxide. Another alternative is to use low-volatility and hygroscopic liquids such as poly(ethylene glycol) (PEG). However, the performance level of such a membrane has not been high enough (Meldon et al., 1986).

Glycerol has been used successfully as the replacement for water as the solvent in the ILMs for separating CO_2 from N_2 streams (Chen et al., 1999, 2000). Glycerol is very viscous when dry and has higher viscosity than poly(ethylene glycol) (PEG) 400 at ambient temperatures. Because of the higher solution viscosities, the glycerol-based ILMs result in lower permeabilities for the non-reacting species like N_2 and hence higher selectivities for the reacting species like CO_2 . The permeation characteristics of CO_2 through glycerol-based ILMs using different carriers like sodium carbonate and sodium salt of glycine have been studied (Chen et al., 1999, 2000). These membranes were shown to be stable under different operating conditions due to a variation of relative humidity of the gas streams, transmembrane pressure and carbon dioxide partial pressures. Their performances were demonstrated to be stable for extended periods of time, up to 600 hours (Chen et al., 2000). Both carriers mentioned above require a solvent, glycerol, to dissolve them to be useful for CO_2 separation.

It would be interesting to study novel carrier liquids which do not require any additional solvent for separation of carbon dioxide from gas mixtures. These carrier liquids should be non-volatile and should have high densities of reactive functional groups for CO_2 separation. These carrier liquids can potentially eliminate the necessity of a solvent; the liquid membranes formed can be inherently stable. Such an approach has not been reported in the open literature for carbon dioxide separation.

2.2. Literature Review on Carbon Dioxide Removal by FTMs

A facilitated transport membrane can be prepared by swelling a polymer film with a solvent and subsequently introducing the carrier by diffusion or by ion exchange. The resulting membrane will be in an intermediate state between liquid and solid phases. If the solvent used to swell the polymer film is a good physical solvent for the gas of interest, solvent swollen polymer films can be used as gas separation membranes without a carrier species present (Matson et al., 1988). The solvents used in these membranes are mainly pyrrolidones. Fixed carrier (ion exchange) membranes have several advantages

as supports for facilitated transport membranes for subsequent introduction of the carrier by diffusion or by ion exchange. Once the charged carrier species is exchanged into the membrane, the carrier may not be lost unless it is replaced by another ion. Ion exchange membranes prepared by grafting acrylic acid and methacrylic acid to polyethylene and other substrates were used for carbon dioxide separation. CO₂ facilitation was carried out by using different amines as carriers such as diethylenetriamine and triethylenetetramine, ethylenediamine (Matsuyama et al., 1994, 1996). Ethylenediamine (EDA) was found to be the best carrier among various amines studied.

The thin liquid layer of the carrier and the solvent can be immobilized in the pores of a porous polymer film to create an immobilized liquid membrane (ILM) or between hollow fibers on the shell side to develop the contained liquid membrane (CLM) (Majumdar et al., 1988). The ILMs investigated employ generally an aqueous solution containing a carrier species such as carbonate and bicarbonate solutions (Ward and Robb, 1967; Otto and Quinn, 1971; Bhave and Sirkar, 1986), diethanolamine (DEA) (Guha et al., 1990; Teramoto et al., 1996), ethylenediamine (EDA) (Way et al., 1987) etc. which react reversibly with CO₂. Amines such as these are volatile and are generally considered toxic. Salts/salt hydrates, which are molten at low temperature, have also been used as carriers in the form of an immobilized liquid membrane (Laciak et al., 1990; Quinn et al., 1995) or as the membrane itself (Quinn et al., 1997; Quinn and Laciak, 1997). However, making defect-free membranes is difficult (Quinn, 1998).

The common features of many of the different configurations of facilitated transport membranes are:

- the solvent, if used, is usually water,

the membrane requires both feed and sweep sides to be humidified for the membrane not to fail.

These features place a severe limitation on the commercialization of facilitated transport membranes as vacuum can not be applied on the permeate side for collection of carbon dioxide. Application of vacuum on the permeate side has the potential advantage of producing the highest possible concentration of carbon dioxide. The presence of water as a solvent in most of these membranes essentially makes these membranes prone to instability due to evaporation and flooding. When amines like DEA, EDA are used as carriers, the FTMs are unstable due to the loss of carrier by evaporation.

2.2.1 Reaction Mechanisms for Carbon Dioxide Facilitation with Amines

In general, amines as carriers perform better than carbonate/bicarbonate solutions for carbon dioxide separation. Among various amines, sterically hindered ones have higher capacities for CO_2 than unhindered primary and secondary amines (Bosch et al., 1989).

In systems where amines are used as carriers, the reactions can occur with primary, secondary or tertiary amines. A primary amine reacts with carbon dioxide according to

$$CO_2 + 2RNH_2 \iff RHNCOO^- + RNH_3^+$$
 (2.3)

The secondary amines also react with CO_2 via the same reaction mechanism. The reaction of CO_2 with tertiary amines can be described satisfactorily with the base-catalysis reaction mechanism (Little et al., 1990; Versteeg and van Swaaij, 1988)

$$CO_2 + R_3N + H_2O \iff HCO_3^- + R_3NH^+$$
 (2.4)

Although the tertiary amine is not supposed to react directly with CO_2 like a primary or a secondary amine because they lack the proton needed in the de-protonation step, tertiary amines show considerable reactivity toward CO_2 ; further water is essential for this reaction. Most of these amines are volatile and are considered generally toxic. If the amine functional groups could be stabilized in a form where it is not volatile, it can be expected that such a carrier would perform on par with a solution containing volatile amines without the associated problems.

2.3 Significance of Dendrimers in Carbon Dioxide Separation

As discussed earlier, amine functional groups in a form where they are not volatile could lead to very stable ILMs with high carbon dioxide permeances and selectivities. One such class of carriers is dendrimers. Dendrimers are a novel class of polymers having some unusual properties. They essentially form the fourth major class of known macromolecular architecture. The traditional macromolecular architectures have been linear, crosslinked and branched. The term dendrimer comes from dendron, the Greek word for tree, refers to a general polymer architecture. The basic structural elements of a dendrimer are (Dvornic and Tomalia, 1995):

- a central molecular core (I)
- terminal surface groups (Z) which may be chemically reactive or inert
- interior branch junctures having various branching functionalities or multiplicities, and

connectors, divalent segments that covalently connect neighboring branching structures and provide internal molecular armature that holds together the entire dendritic molecular structure.

This concept is shown schematically in Figure 2.2.



Figure 2.2 Basic structural elements of dendritic molecular architecture (from Dvornic and Tomalia, 1995)

A major class of dendrimers which has been studied in a wide range of applications is Starburst[®] poly(amidoamine) (PAMAM) dendrimer. Depending on the interior core initiator, whether ammonia or ethylene diamine (EDA), 3 or 4 dendrons are contained in the dendrimer. This also influences the spatial distribution of the dendrons. It is possible to modify the surface groups of PAMAM dendrimers to obtain polymers

with unique properties. An interesting aspect of this surface modification of dendrimers through the amidation reaction is that a mixed-surface dendrimer (a dendrimer that contains two types of functional groups) can also be prepared. Different dendrimers have been synthesized in literature with about 30 different initiator core compounds and 100 different surface functional groups (Tomalia et al., 1990). As diverse as the dendrimers are, their applications are equally diverse. Their main applications are found in biomedical, pharmaceutical and industrial areas. Table 2.1 lists a few important applications involving dendrimers.

Application	Reference				
Biomedical					
CKMB immunoassay Singh et al., 1994					
Pharmac	eutical				
Controlled release of aspirin Tomalia et a., 1994					
Indust	rial				
Asymmetric catalysis	Bolm et al., 1996				
Reactions with proteins	Singh, 1998				
Homogeneous catalysis	Knapen et al., 1994				
Electrokinetic chromatography	Dubin et al., 1992; Tanaka et al., 1995, 1997				
Photoresponsive dendrimers	Junge and McGrath, 1997				

 Table 2.1 Current research and applications in dendrimers

In the present thesis, Starburst[®] polyamidoamine (PAMAM) dendrimers with ethylene diamine (EDA) core were studied for carbon dioxide separation. The present

study focused on generation zero dendrimer because of its very suitable characteristics for the application of CO_2 separation. The structure of PAMAM dendrimer of generation zero with EDA core is shown in Figure 2.3.



Figure 2.3 Schematic of the structure of EDA core PAMAM dendrimer of generation zero

The number of functional groups in a particular dendrimer molecule doubles with each generation. Generation zero PAMAM dendrimer with EDA core, the smallest of this class of dendrimers, has four amine functional groups. On a comparative basis, generation zero EDA core PAMAM dendrimer has 9.1M of primary amine functional groups and 4.6M of tertiary amine groups, whereas a 2M aqueous solution of EDA commonly used in industry has only 4M of primary amines. The functional group concentrations in various generations of PAMAM dendrimers with EDA core are shown

in Table 2.2.

Generation	MW	Prima	ry amines	Tertiary amines		
		Number	Concentration (M)	Number	Concentration (M)	
0	518	4	9.1	2	4.6	
1	1430	8	6.7	4	3.3	
2	3256	16	6.0	8	3.0	
3	6909	32	5.6	16	2.8	

Table 2.2 Functional group concentrations in various PAMAM dendrimershaving an EDA core

Dendrimers are non-volatile, and chemically and thermally stable. They are considered non-toxic for generations 5 or less (Roberts et al., 1996). PAMAM dendrimers have a very high density of primary amine functional groups on their surfaces.

2.4 Experimental Details

Dendrimer liquids used in the current work are hydrophilic and do not wet hydrophobic substrates. Hydrophilic or hydrophilized membrane substrates were used in the present study to immobilize the liquid membranes. Both flat membranes and hollow fiber membrane modules were employed. The flat membranes used were hydrophilic poly(vinylidene fluoride) (PVDF) membranes (Millipore, Bedford, MA) and hydrophilized Celgard 2500 membranes (Celgard LLC, Charlotte, NC). The hydrophilized Celgard 2500 membranes prepared from hydrophobic polypropylene

microporous substrates are not yet commercially available. The properties of these flat membranes are given in Table 2.3. Two types of hollow fibers membranes were also used in the present study. They are hydrophilized polyacrylonitrile (PAN) (Sepracor, Marlborough, MA) and polysulfone (Minntech, Minneapolis, MN). Hollow fiber modules were fabricated using these fibers by placing them in a transparent polyethylene shell casing. The tube and shell sides were separated with appropriate potting. The details of the hollow fiber membranes and membrane modules fabricated are provided in Table 2.4. All ILMs formed were full ILMs; they completely filled the pores of the substrate membrane resulting in the ILM thickness being equivalent to that of the substrate. The thickness, porosity and tortuosity of the substrates were obtained either from manufacturer's catalogs or from literature.

 Table 2.3 Characteristics of the flat substrate membranes used for immobilizing dendrimer liquid membranes

Membrane Type	Material	Porosity	Tortuosity	Thickness, μm	Pore diameter, μm
Durapore	Hydrophilized PVDF	0.7 ^a	2.58 ^b	100 ^a	0.1 ^a
Celgard 2500	Hydrophilized Celgard	0.45 ^c	2.54 [°]	25°	0.08 ^c

a From manufacturer's catalog

b Chen et al., 1999

c Prasad et al., 1986

Starburst[®] PAMAM (polyamidoamine) dendrimers of generation zero and three in methanol were obtained from Sigma Chemical Co. (St. Louis, MO). Starburst[®] PAMAM (polyamidoamine) dendrimer of generation zero is henceforth identified as "dendrimer" for convenience. Methanol from the dendrimer solution was removed by subjecting the solution to vacuum for several hours to several days; the resulting pure dendrimer solution was stored in a desiccator till used. 44% (1M) and 75% dendrimer solutions in glycerol were also prepared for particular experiments. All gas mixtures with CO_2 content varying between 0.5-10% in N_2 were obtained from Matheson (East Rutherford, NJ). Higher carbon dioxide concentrations were obtained by mixing pure carbon dioxide and nitrogen gas streams using Matheson electronic mass flow controllers (Model No 8272-0412) in required ratios. Gas mixtures containing toluene in N_2 and CO_2 in O_2 were obtained from Matheson in the required concentrations.

 Table 2.4 Details of hollow fiber substrates and modules used for immobilizing dendrimer liquid membranes

Membrane Supplier	Membrane material	Porosity	Tortuosity	Pore diameter, µm	Fiber i.d./o.d., µm
Sepracor	Polyacrylonitrile (PAN)	N/A	N/A	70,000 MWCO	200/300
Minntech	Polysulfone	0.3-0.4	N/A	0.1	280/360

Module No.	Membrane material	Module length, Cm	Number of fibers	Membrane Area, (A _{lm}) cm ²
1	Polyacrylonitrile (PAN)	30	50	116.4
2	Polysulfone (PS)	18	20	36.0

N/A Not available

2.4.1 Preparation of ILMs

The most common method for preparing ILMs is to wet the pores of a polymeric membrane with the solvent-carrier mixture-containing solutions having the desired composition (Way and Noble, 1992). Depending on the nature of the solvent-carrier solution and the membrane characteristics, it usually takes from a few minutes to a few hours to completely fill all the porous region of the membrane and wet it. By controlling this time of exposure, only part of the membrane can be filled with the liquid resulting in thinner ILMs (Chen et al., 2000). The ILMs in this work were prepared by the immersion technique. After immersing the membrane in the dendrimer solution (either pure or in a solvent), it was removed from the liquid, and the extra liquid from the surfaces was removed. If the immersion time was long enough, the ILMs thus prepared can be 100% wetted and translucent, which is a good indication that the pores are filled with the carrier solution. ILMs prepared by the immersion technique normally have thickesses comparable to that of the substrates.

2.4.1.1 ILM preparation in flat membranes. In the present work, ILMs filling the entire void fraction of the flat membranes were prepared by immersing the membranes in dendrimer solutions for at least 8 hours till the membranes were translucent. This was done to ensure that the wetting process was complete. After complete wetting, the membrane surfaces were carefully wiped with tissue paper to remove any excess solution. In some instances, any moisture absorbed by the liquid was removed by applying vacuum during the wetting process. The procedure was similar if 44% or 75% solutions of dendrimer in glycerol were used as the liquid to be immobilized.

2.4.1.2 ILM preparation in hollow fiber modules. Pure dendrimer ILMs were immobilized in hollow fibers by filling the entire void fraction of the fibers. The lumen side of the fibers was filled with the 20% solution of dendrimer in methanol for a minute with the other end closed. Nitrogen was passed at a low flow rate on the shell side to evaporate the methanol. The procedure was repeated from the other tube end. In the case of polysulfone fibers, because of their pore size and porosity, methanol was seen coming out on the shell side. No attempt was made to evaporate methanol from the shell side during immobilization as it could impede with the ILM preparation. After the ILM was immobilized in the pores, nitrogen at high flow rates (~50 cc/min) was passed from tube side for a few minutes to clear the lumen side of any possible blockage. This was verified by making sure all fibers were open. To remove any remaining methanol from the pores, house vacuum (~18 inch Hg) was applied from the shell side with a small flow of nitrogen on tube side overnight. Despite this elaborate procedure, it was necessary to repeat the immobilization procedure for both fibers in order to prepare leak-free hollow fiber modules.

2.4.2 Measurement of Equilibrium Water Uptake in Dendrimer and Glycerol

PAMAM dendrimer of generation zero is hygroscopic and has a finite solubility in water. Similarly, glycerol is strongly hygroscopic and 100% miscible with water. When the dendrimer-based ILMs are exposed to humidified feed gas, they could pick up significant amount of water from the feed stream and some of the water could be transported across the membrane as the sweep gas used was always dry helium. The water content in the liquid membrane has significant influence on the performance of the dendrimer-based ILMs. The amount of water sorbed by the liquid membrane influences the membrane performance as it:

- decreases in the viscosity of the liquid membrane, thus increasing the diffusivity of all the species
- changes in solubility of species due to the change in the concentration of the solution
- changes in facilitating reactions as water participates directly in the tertiary amine facilitation reactions.

However, the data on water uptake by pure dendrimers is not available in literature. Chen et al. (1999) reported preliminary data on water uptake by glycerol at different ambient relative humidity conditions. Since such data were not available for pure dendrimer liquid, experiments were done to determine the amount of water absorbed in dendrimer when exposed to the ambient conditions with known relative humidity and temperature.

Due to the hygroscopic nature of the liquid, fresh dendrimer liquid absorbs water from ambient air when exposed to it. If the contact time between the dendrimer liquid and ambient air is sufficient, it can be assumed that an equilibrium has been reached for water content between the dendrimer and ambient air. The change of weight of the dendrimer + water under different relative humidities was recorded using an electronic balance (Model PB 303, Mettler-Toledo, Cincinnati, OH) as the relative humidity of the balance environment was monitored by a humidity probe (Vaisala, Woburn, MA). The measurements with this technique gave reasonably reproducible results. It was also verified that the change of weight of the dendrimer + water does not show any signs of hysteresis with the direction of RH change. For comparison, the water uptake by glycerol was also studied. These measurements were done independent of the data reported by Chen et al. (1999) and covered wider RH conditions.

2.4.3 Experimental Setup and Procedure

Figure 2.4 shows the schematic of the experimental setup used for studying the permeation behavior of ILMs. The flat membrane was placed in between two half cells and was supported by a porous stainless steel screen (Pall Trinity Micro, Cortland, NY) in the bottom cell well. The support screen is made of SS304 and is highly porous with a thickness of 158 μ m. The gas space on top of the membrane was sealed by a Viton O-ring on the top half of the cell. The CO₂/N₂ permeation performance through the ILMs was measured by the sweep gas technique (Bhave and Sirkar, 1986).



Figure 2.4 Schematic of the experimental setup

The feed gas was allowed to flow through the top half of the cell at a rate controlled by an electronic mass flow controller. The feed gas was humidified with water in a gas bubbler before entering the cell. When measurements were conducted using dry feed gases, the humidifier was bypassed. For experiments involving partially humid feed gas, the feed gas through the bubbler was blended with dry feed gas proportionally to obtain the required inlet relative humidity. The feed gas outlet from the cell was connected to a pressure gauge and a back pressure regulator (Fairchild, Winston-Salem, NC) to control the feed side pressure. The relative humidities of the feed gas before and after the cell were monitored by two humidity probes (Model No. UT32, Vaisala, Woburn, MA) connected in-line. Dry helium, used as a sweep gas, was passed through the bottom half-cell.

The schematic for the experimental setup for studying the ILMs in hollow fiber modules was the same as the one used for flat membranes. The feed for all hollow fiber ILMs was introduced though the lumen side of the membrane with the sweep gas flowing on the shell side. Experiments with hollow fiber module ILMs were performed both in cocurrent and countercurrent modes.

The sweep gas outlet from the test cell or module was connected to a HP 5890 Series II Gas Chromatograph (GC) for analysis using a Porapak Column (Alltech, Deerfield, IL). The detector and the injector were at 200 °C; the oven temperature used was 50 °C for detection of gases with subsequent ramping up to 110 °C to remove any water vapor from the column. Figures 2.5 and 2.6 show representative calibration curves used in the present work for carbon dioxide and nitrogen respectively. The calibration of the GC was checked periodically to see any changes in the GC sensitivity and corrected

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Figure 2.5 Representative calibration curve for carbon dioxide analysis

The experiments were started by setting the feed side flow rate and pressure and the sweep side flow rate. The sweep side flow rates were kept relatively low, around 3-8 cc/min to allow effective detection of nitrogen. Feed and sweep gas streams for flat membranes were in cocurrent mode. Due to low permeation rates, the change in CO_2 , N_2 , or O_2 partial pressure along the feed side was negligible. All experiments were carried out at room temperature.



Figure 2.6 Representative calibration curve for nitrogen analysis

2.4.4 Calculation Procedure for Gas Permeances and the Separation Factor

Based on the GC calibration and the peak areas obtained, the mole fractions of the species in the sweep gas stream can be obtained. When multiplied by the sweep side gas volumetric flow rate, one can obtain the volumetric flow rate of the species through the membrane.

The effective permeance of a species through the membrane was calculated by

$$\left(\frac{Q_i}{t_m}\right)_{eff} = \frac{V_i}{A_i \Delta p_i}$$
(2.5)

where V_i is the volumetric permeation rate of species i, Δp_i is the partial pressure difference of species i across the membrane and A_t is the total membrane area. True permeance of the species $(Q_i/t_m)_{true}$ is obtained from

$$\left(\frac{Q_i}{t_m}\right)_{true} = \left(\frac{Q_i}{t_m}\right)_{eff} \frac{\tau_m}{\varepsilon_m}$$
(2.6)

The permeability of a gas species through the ILM is obtained by multiplying its true permeance through the ILM and the membrane thickness.

$$Q_i = \left(\frac{Q_i}{t_m}\right)_{true} t_m \tag{2.7}$$

Separation factor of species i with respect to species j , $\alpha_{i/j}$, is defined by

$$\alpha_{i/j} = \frac{\left(Q_i/t_m\right)_{eff}}{\left(Q_j/t_m\right)_{eff}} = \frac{\left(Q_i/t_m\right)_{true}}{\left(Q_j/t_m\right)_{true}}$$
(2.8)

In the case of analyzing hollow fiber module data, the partial pressure differences of the species and the membrane area for transport are based on logarithmic mean averages (see Appendix A). The subsequent reported values of permeances are denoted with subscript lm to highlight this aspect of the calculation. Water vapor flux was

calculated based on the temperature and the relative humidities of the inlet and outlet feed gas streams. At any given temperature, the saturation vapor pressure (p_{sat}) for water vapor was obtained from Perry et al. (1984).

Mole fraction of water vapor at saturation, $y_{H2O}^{sat} = p_{sat}/P_{f}$

where P_f is the feed side total pressure.

At feed inlet, $y^{in}_{H2O} = RH_{in} * y^{sat}_{H2O}$ At feed outlet, $y^{out}_{H2O} = RH_{out} * y^{sat}_{H2O}$ Water flux = $V_f (y^{in}_{H2O} - y^{out}_{H2O})/A_t$ (2.9)

where V_f is the feed side flow rate.

No corrections were made to the saturation vapor pressure to account for the above atmospheric conditions. Gas permeances are reported in units of $cc(stp)/cm^2.s.cm$ Hg. Wherever convenient, the gas permeances are also reported in the units of GPU which is equivalent to 10^{-6} cc(stp)/cm².s.cm Hg. Gas permeabilities are reported in the units of Barrer which is 10^{-10} cc(stp).cm/cm².s.cm Hg. Water fluxes are reported as cc(stp)/cm².min. Sample calculations for a typical experimental run are shown in Appendix A.

2.5 Results and Discussion

The dendrimer-based liquid membranes, as mentioned earlier, are unique in terms of their preparation and behavior. The generation zero polyamidoamine dendrimer was used in its pure form without any additional solvents as a facilitated transport liquid membrane. The effect of an additional non-volatile solvent on the behavior and stability of the dendrimer-based ILMs was also studied by adding glycerol to the dendrimer solution.

For convenience, whenever dendrimer is used in its pure form without any solvent as the ILM, the ILM is referred to as **<u>pure dendrimer ILM</u>**. All ILMs formed were full ILMs; they completely filled the pores of the substrate membrane resulting in the ILM thickness being equivalent to that of the substrate.

2.5.1 Generation Zero Pure Dendrimer ILMs in Flat Membranes

2.5.1.1 Effect of Δp_{CO2} **in PVDF substrates.** A total of up to four cells to hold flat membranes were used in series for studying generation zero pure dendrimer ILMs in PVDF substrates to increase the total membrane area available for permeation and detect the extent of nitrogen permeation. The addition of the test cells was done in stages. The total membrane area for four cells was 47 cm². The feed gas was completely humidified with water and the sweep gas was dry helium. The measured effective permeance of CO₂ and CO₂-N₂ selectivity obtained for a generation 0 dendrimer ILM in the hydrophilized PVDF substrate are shown in Figure 2.7 and Table 2.5 as a function of the CO₂ partial pressure difference, Δp_{CO2} , between the feed CO₂-N₂ gas mixture and the permeate. For selectivity, the separation factor, $\alpha_{CO2/N2}$, (Eqn. 2.8) was used. The feed gas mixture was at a total pressure of 91.5 cm Hg (3 psig). The N₂ permeances were so low that a total of up to four test cells had to be used in series to increase the membrane area to 47 cm² so that the N₂ permeating through the membrane could be detected by the GC.



Figure 2.7 Variation of effective permeance of carbon dioxide $(Q_{CO2}/t_m)_{eff}$ and separation factor $(\alpha_{CO2/N2})$ with partial pressure difference of carbon dioxide (Δp_{CO2}) in hydrophilic PVDF membrane. ILM: pure dendrimer (generation 0).

	Effective Permeance		Permeability		Separation	Water Flux
Δp _{CO2}	N ₂	CO ₂	N_2	CO ₂	Factor	
cm Hg	cc/cm ² .s.cmHg	cc/cm ² .s.cmHg	Barrer	Barrer	$(\alpha_{\rm CO2/N2})$	cc/cm ² .min
	x 10 ¹⁰	x 10 ⁶				x 10 ³
0.00	7.87	0.00	0.29	-	-	-
0.00	9.09	0.00	0.34	-	-	-
0.26	8.41	11.15	0.31	4100	13300	-
0.27	5.40	9.77	0.20	3600	18000	2.23
0.30	4.37	7.98	0.16	2900	18300	4.56
0.30	4.61	7.24	0.17	2700	15800	4.23
0.36	3.99	7.57	0.15	2800	19000	6.48
0.39	-	8.47	0.00	3100	-	25.00
1.70	3.39	2.29	0.13	840	6800	-
4.48	3.77	0.97	0.14	360	2600	6.17
8.95	6.32	0.82	0.23	300	1300	6.07
29.83	5.37	0.39	0.20	140	720	4.82
61.82	0.00	0.35	-	130	-	5.23
90.31	0.00	0.22	-	80	-	5.39

Table 2.5 The effect of the partial pressure difference of carbon dioxide onthe performance of PVDF-based full ILM with pure dendrimer.

Figure 2.7 illustrates that the separation factor $\alpha_{CO2/N2}$ could go very close to 19,000 at a low CO₂ feed partial pressure of 0.36 cm Hg. Depending on the CO₂ partial pressure, the value of the (Q_{CO2}/t_m)_{true} will change; at 0.26 cm Hg it was found to be 41 GPU. The corresponding CO₂ permeability (Q_{CO2}) is 4100 Barrers. The true N₂ permeance in the presence of small amounts of CO₂ in the feed gas was around 1.47 to 1.9 x 10⁻⁹ cc/cm².s.cm Hg. This value was increased to around 3.0 x 10⁻⁹ cc/cm².s.cm Hg for pure N₂. The separation factors are not reported for p_{CO2,f} exceeding 30 cm Hg since no N₂ peaks were detected in the GC due to lowered p_{N2,f}. At the highest Δ p_{CO2} of 90 cm Hg, (Q_{CO2}/t_m)_{eff} is 2.2 x 10⁻⁷ cc/cm².s.cm Hg. At the higher Δ p_{CO2}-s (~30 cm Hg), α _{CO2/N2} is around 700. This behavior reflects the classical carrier saturation behavior of facilitated transport membranes; as p_{f,CO2} or Δ p_{CO2} increases, Q_{CO2} decreases; therefore α _{CO2/N2} also

All data on the effects of Δp_{CO2} , RH_f, and transmembrane pressure difference were obtained with the same set of membranes. This set of membranes was used continuously for more than 35 days without any visible signs of any membrane leaks or instability. During this period, the membranes were subjected to varying Δp_{CO2} s, transmembrane pressures, RH_f conditions. As can be expected with facilitated transport membranes, very high separation factors were obtained at low carbon dioxide partial pressures. The CO₂-N₂ selectivity at the lowest Δp_{CO2} is about 5 times higher than the highest value reported anywhere (Chen et al., 2000). The pure dendrimer membranes appear to function almost as a molecular gate for CO₂ vis-a-vis other inert gases, N₂, O₂ etc. On a comparative basis, the pure dendrimer liquid provides a functional group density of 9.12M for -NH₂ and 4.56M for =N. Conventional aqueous solutions used as a membrane e.g., 2M of EDA, will provide a functional group density of 4M only for -NH₂. Thus, pure dendrimer liquid can create an environment possessing a very high concentration of facilitating species; such a high concentration will simultaneously decrease the gas solubilities drastically via salting-out effect.

The carbon dioxide permeances for pure dendrimer ILMs were lower compared to those obtained using sodium glycinate salt in glycerol ILMs (Chen et al., 2000). The selectivities, however, were about 4-5 times those obtained for glycine sodium saltglycerol ILM. This could be due to lower mobility of dendrimer-carbon dioxide complexes. The molecular weight of dendrimer of generation zero is about 518 whereas the molecular weights of glycine salt and glycerol are about 100. Hence it can be expected that the diffusivities of the dendrimer-CO₂ complex could be much less than those in glycine salt-glycerol system. The pure dendrimer solution could also be facilitating the transport of carbon dioxide through an alternative mechanism of carbon dioxide jumping from one dendrimer molecule to another dendrimer molecule. This mechanism is possible at high carrier concentrations (Cussler et al., 1989).

Another reason for relatively low carbon dioxide permeances in pure dendrimer ILMs is due to reduced solubilities of all gas species due to salting out effect. No direct data are available for solubilities of carbon dioxide and other gases in pure dendrimer solutions of different generations. However, it can be extrapolated from aqueous amine solutions that increased amine concentrations induce lowered carbon dioxide loading per mole of amine at the same carbon dioxide partial pressure. For example, at a carbon dioxide partial pressure of 1 kPa (0.75 cm Hg), 0.5M triethanolamine (TEA) (corresponding to 7.37 wt%) aqueous solution can load up to about 0.8 mole CO₂

per mole of TEA. As the TEA concentration increases, the CO_2 loading decreases. At 5M TEA concentration (corresponding to 67 wt%), the CO_2 loading is reduced to about 0.1 mole CO_2 per mole of TEA (Li and Mather, 1994, 1996).

Because of the lower permeances observed in pure dendrimer liquid membranes, there is a need to improve the CO_2 permeances while retaining the high selectivities from pure dendrimer solutions. One way to achieve this objective is to use thinner substrate membranes. Hydrophilized Celgard 2500 is a suitable substrate having a thickness of 25 µm compared to the 100 µm thick PVDF substrate.

2.5.1.2 The effect of Δp_{CO2} in hydrophilized Celgard substrate. Figure 2.8 and Table 2.6 show the variation of carbon dioxide effective permeance and separation factor for a hydrophilized Celgard 2500 membrane. The data were obtained using a single membrane of area 12.56 cm². The feed gas was completely humidified with water and the sweep gas was dry helium. CO₂ effective permeances observed as a function of Δp_{CO2} are close to those observed in the PVDF substrate. This is encouraging as the porosity of Celgard substrate is only about 65% of that of PVDF substrate.

However, the N_2 permeabilities were 3-4 times larger; therefore only one test cell was used in this series. The increased nitrogen permeabilities are due to inherent or residual hydrophobicity of the developmental Celgard polypropylene substrate. This could lead to higher nitrogen permeabilities through the membrane. Similar behavior was also observed by Chen et al. (2000). The highest separation factor obtained for a feed gas mixture of 0.5% CO₂-rest N₂ was close to 3900 and carbon dioxide permeability was 1040 Barrers.



Carbon dioxide partial pressure difference, $\Delta p_{\rm CO2}$, cmHg

Figure 2.8. Variation of effective permeance of carbon dioxide $(Q_{CO2}/t_m)_{eff}$ and separation factor $(\alpha_{CO2/N2})$ with partial pressure difference of carbon dioxide (Δp_{CO2}) in hydrophilized Celgard 2500 membrane. ILM: pure dendrimer (generation 0).

	Effective	Permeance	Perme	ability	Separation	Water Flux
Δp _{CO2}	$\frac{N_2}{cc/cm^2.s.cm}$	CO ₂ cc/cm ² .s.cm	N_2	CO ₂	Factor	
cm Hg	нд x10 ⁸	нд х10 ⁶	Barrer	Barrer	$(\alpha_{CO2/N2})$	$x 10^3$
0.43	0.19	7.39	0.27	1000	3900	-
1.86	0.36	4.27	0.51	600	1200	7.26
4.95	0.32	1.68	0.45	240	530	5.87
7.91	0.47	1.03	0.67	150	220	10.94
9.87	0.34	0.96	0.48	140	280	7.62
10.62	0.59	0.57	0.83	80	100	12.58

Table 2.6 The effect of partial	pressure difference of carbon dioxide on the
performance of hydrophilized	Celgard-based full ILM with pure dendrimer

2.5.1.3 Effect of transmembrane pressure difference. ILMs consist of liquids immobilized in the pores of the substrates. The maximum transmembrane pressure differences (TMP) for an ILM depends on the pore size of the substrate and the surface tension of the ILM liquid. For practical application of the liquid membranes, the ILM should be able to withstand the transmembrane pressure difference. The PVDF film used in the present work has a water bubble point pressure of 4.8 atm (360 cm Hg). Figure 2.9 shows the variation of carbon dioxide permeability for different transmembrane pressures for both hydrophilic PVDF and hydrophilized Celgard 2500 based pure dendrimer ILMs.



Figure 2.9. Schematic of transmembrane pressure difference in pure dendrimer ILMs.

transmembrane pressures of 1.7 atm (120 cm Hg). It should also be noted that the PVDF membrane-based ILM was tested for TMPs with a 0.5% CO₂-N₂ feed gas mixture. The steep behavior of the ILM performance with transmembrane pressure is due to

the sensitivity of the carbon dioxide permeability at low Δp_{CO2} s. This trend could be seen in Figure 2.9. Data for Celgard 2500 membrane were obtained with a 5.2% CO₂-N₂ feed gas mixture where the effect of facilitation will not be very evident at the relatively higher carbon dioxide partial pressures.

2.5.1.4 Effect of feed gas relative humidity on the ILM performance. The facilitation reactions of amines and carbonates with carbon dioxide require the presence of water. Most of the studies in the literature on carbon dioxide reaction with the amines were carried out in an aqueous medium. Immobilized liquid membranes studied recently (Chen et al., 1999, 2000) employed glycerol as the solvent for the carrier instead of water. It was found that absence of water vapor in the feed stream resulted in a complete loss of facilitation and drastically reduced the permeabilities for both nitrogen and carbon dioxide. In the case of pure dendrimer membranes, water is also required for creating a charged environment for effective rejection of nitrogen for achieving high CO_2-N_2 selectivities in addition to implementing the CO_2 facilitation reactions.

Figure 2.10 shows the effect of a variation of the feed side relative humidity on the separation behavior of dendrimer-based ILMs in a PVDF substrate. The separation factor ($\alpha_{CO2/N2}$) of the ILM is plotted on a logarithmic-normal scale against the variation of average feed side relative humidity. The feed inlet relative humidity was adjusted by mixing completely humidified feed stream with dry feed stream before it entered the cell. As can be seen in the case of pure dendrimer ILM, the reduction in relative humidity of the feed stream increased nitrogen permeation tremendously resulting in a loss of selectivity by the ILM for carbon dioxide over nitrogen. However, the selectivity was



Figure 2.10. Effect of variation of feed side average relative humidity on the ILM performance. ILM: Pure dendrimer (generation 0) in PVDF substrate.

regained as the feed was completely humidified. It should be stressed that in all these experiments, dry helium was used as the sweep gas.

To observe the effect of an absence of humidity in the feed stream on the ILM performance, the humidification of the feed gas stream was stopped in between. The nitrogen permeance of the ILM increased drastically: nitrogen permeability across

the membrane increasing 6300 times resulting in a CO_2/N_2 separation factor of around 5. But as the feed gas humidification was started again, the performance of the ILM returned to its original of high CO_2-N_2 selectivity and very low N₂ permeability. For a completely humidified feed inlet stream, the feed exit relative humidities were usually around 70%.

For pure dendrimer membranes, there appears to be a sharp transition around an average feed RH (RH_{f,avg}) of 82% (feed exit RH of 64%) below which the CO₂-N₂ selectivity decreases continuously as the N₂ permeance shoots up. The CO₂ permeance decreases first and then rises slightly. This behavior of carbon dioxide permeation is essentially the result of a change of mechanism of transport for carbon dioxide. As the RH decreases, the amount of sorbed water in the dendrimer liquid decreases. The ionic concentrations of carbamates and other species decrease just as the local aqueous ionic envelopes around the functional groups shrink. These lead to increased N_2 permeance through the intermolecular and intramolecular space with a decrease in RH. However, for CO₂, initially the permeance is reduced due to reduced facilitation; without moisture, CO₂ does not react with the amine functional groups. When, however, the RH is reduced considerably, the inherent high mobility through a low molecular weight liquid, namely, the dendrimer, becomes dominant and it results in a higher CO₂ permeability. The observed selectivity, 5, for dry feed gas represents the performance of pure dendrimer liquid membrane unaffected by the radical effects of water.

2.5.2 The Effect of Glycerol on the Performance of Dendrimer-based ILMs

The selective transport of CO_2 is considerably aided by the activation of various amine groups in the presence of water and by a reduction of N_2 transport due to the ionic environments around the primary and tertiary amine functional groups in the dendrimer. The ionic environment may be maintained over a broader RH range if an extremely viscous polar low molecular weight hygroscopic liquid like glycerol is incorporated in the pure dendrimer ILM. Under absolutely dry conditions, glycerol present in the intramolecular and intermolecular spaces could reduce the transport rates of gaseous species by orders of magnitude and drastically reduce any membrane leakage since Chen et al. (1999) have shown that pure glycerol has very low permeabilities for N_2 , CO_2 , etc. in the absence of any water. In essence, addition of glycerol to dendrimer liquid is expected to increase the range of feed side relative humidities over which the ILM is effective in preventing nitrogen leakage through it.

Figure 2.11 illustrates these results for an ILM containing 44% (1M) and 75% generation zero dendrimer in a glycerol solution in the hydrophilized PVDF substrate under completely humidified feed gas conditions. For comparison, the pure dendrimer behavior is also plotted. The substrate membranes were soaked in the dendrimer solutions for 8 hours and vacuum was applied for about 5 hours to remove any absorbed moisture.



Carbon dioxide partial pressure difference, cmHg

Figure 2.11. Variation of permeance of carbon dioxide and separation factor with partial pressure difference of carbon dioxide in hydrophilic PVDF substrates for different dendrimer concentrations in the ILM
The removal of the absorbed moisture proved to be important for successful operation of the ILM under dry or partially humid feed conditions. When the ILM based on 44% (1M) dendrimer solution in glycerol was formed without removing any ambient moisture that was absorbed by the solution/support membrane, the ILM tended to perform poorly under dry feed gas conditions: N₂ permeability was 1260 Barrers. However when the ILM was formed by vacuuming for about 5 hours, N₂ permeability dropped to about 8 Barrers. Once feed side humidification was started, N₂ permeability dropped to about 1 Barrer and CO₂ permeability increased drastically. The highest CO₂ permeability observed was about 5400 Barrers for a 0.5% CO₂ feed gas.

The 75% dendrimer ILM achieved a separation performance much closer to the pure dendrimer ILM than 44% dendrimer ILM. The highest selectivity obtained for a 0.76% CO₂-N₂ gas mixture (Δp_{CO2} of 0.82 cm Hg) was about 16,300 (compare 18,000 for a pure dendrimer at a lower Δp_{CO2} of 0.27 cm Hg). The corresponding CO₂ and N₂ permeabilities were 3160 Barrers and 0.19 Barrers respectively. The increase in nitrogen permeability from an average value of 0.17 Barrers to 0.19 Barrers is not very significant.

This behavior indicates that the addition of small amounts of glycerol did not affect the CO₂-selective molecular-gating behavior of PAMAM dendrimers. It should be mentioned that nitrogen was detected by the GC in only a few experiments for 75% dendrimer ILM even though three test cells were used in series for the experiments. This behavior is strongly suggestive of molecular gating observed with pure dendrimer ILMs.

Table 2.7 presents the data for dendrimer-based ILM performance under dry and completely humid feed gas conditions. Data obtained for pure glycerol ILM under similar

conditions was also presented for comparison (Chen et al., 1999). It should be stressed that for all the experimental data presented here, the sweep gas was dry helium. Pure glycerol ILM has a CO₂ permeability of 5.62 Barrers under dry feed gas conditions with a $\alpha_{CO2/N2}$ of 1.5. When 100% RH feed gas was introduced, CO₂ transport was facilitated 20 times resulting in a $\alpha_{CO2/N2}$ of around 39, which is that of water. For pure dendrimer membranes, under completely humidified feed conditions, the CO₂ permeability was 3600 Barrers with a $\alpha_{CO2/N2}$ of 18,000. But the significant feature of the pure dendrimer ILM was that its N₂ permeability was about 0.2 Barrer. This value was 15 times lower than that of pure glycerol ILM, essentially functioning as a CO₂-selective molecular gate in blocking the nitrogen transport.

	Dry feed gas			100% RH Feed gas			
ILM	Q _{CO2} Barrer	Q _{N2} Barrer	$\alpha_{\rm CO2/N2}$	Q _{CO2} Barrer	Q _{N2} Barrer	α _{CO2/N2}	
Pure glycerol ^a	5.62	3.79	1.48	111	2.85	39	
44% (1M) dendrimer (generation 0) in glycerol ^b	17.0	7.54	2.25	900	0.94	940	
75% dendrimer in glycerol ^c	5800	860	6.7	3200	0.19	16300	
Pure dendrimer (generation 0) ^d	4700	930	5.05	3600	0.2	18000	

Table 2.7 Performance of dendrimer-based ILMs⁺ under dry and 100% humid feed gas conditions

+ Substrate: PVDF

a Chen et al., 1999

b Feed 5.2%CO₂-rest N₂ mixture at 7 psig feed pressure.

c Feed 0.76% CO₂-rest N₂ mixture at 12 psig feed pressure.

d Feed 0.5% CO₂-rest N₂ mixture at 3 psig feed pressure.

When this membrane was exposed to dry feed conditions, the membrane tended to lose its gating ability, with the selectivity of only 5. The nitrogen permeability increased 4600 times, mainly as the membrane was leaking. Addition of glycerol to the pure dendrimer has the effect of preventing the membrane from leaking nitrogen under dry feed conditions. 44% dendrimer-balance glycerol ILM under completely dry feed gas conditions has a CO₂ permeability of 17 Barrers with almost no selectivity for carbon dioxide over nitrogen. But in the presence of humidified feed gas, carbon dioxide transport was facilitated about 52 times, while reducing nitrogen permeation rate by 8 times. It should be mentioned that the data presented in the table was obtained with 5.2% CO₂-balance N₂, where effects of carrier saturation were evident in the low values of the carbon dioxide permeabilities.

The addition of a small amount of glycerol to pure dendrimer solution (75% dendrimer solution) did not prevent the excessive nitrogen transport through the liquid membrane under complete dry feed gas conditions. However, as seen from Figure 2.12, the addition of glycerol in such quantities improved the operating range of feed side average relative humidity tremendously while retaining the molecular gating ability of pure dendrimer liquids. It should be pointed out that the improvement of the operating range of relative humidity by 75% dendrimer liquid brings the dendrimer-based ILMs to the range usually observed in practical situations.

2.5.3 Equilibrium Water Uptake by Dendrimer Liquid

It is necessary to compare the equilibrium water uptake by the dendrimer liquid and glycerol. Chen et al. (1999) measured the equilibrium water concentration in glycerol in the ambient RH range of 48% to 85%. The equilibrium water uptake by generation zero dendrimer liquid was measured here in the ambient RH range of 17% to 75%. The water uptake by glycerol membranes was also measured in this RH range; they are found to be consistent with the reported data (Chen et al., 1999). Figure 2.13 shows the variation of water content in both dendrimer and glycerol as a function of the ambient RH. The measurements of water uptake did not show any signs of hysteresis with the direction of RH change. For all RH levels studied here, glycerol holds much more sorbed water than the pure dendrimer liquid. This phenomenon explains the nitrogen rejection behavior of the pure dendrimer liquids at high feed inlet relative humidities and poor selectivities observed at low feed side relative humidities. This also explains why the performance of a 75% dendrimer membrane decreases with a decrease in RH much more slowly than that of a pure dendrimer membrane (Figure 2.12).

For all RH levels studied here, glycerol will hold much more sorbed water than pure dendrimer liquid. This phenomenon explains the nitrogen rejection behavior of the dendrimer liquids at high feed inlet relative humidities and poor selectivities observed at lower relative humidities.



Figure 2.12 Effect of feed side average relative humidity on dendrimer ILM performance. Feed CO₂ concentration: 0.27-1.03 cm Hg



Figure 2.13. The equilibrium sorption of water by dendrimer and glycerol

2.5.4 Comparison of the Performance of Dendrimer Membranes

It would be useful to compare the performances of the dendrimer-based ILMs in PVDF substrates with some of the promising membranes in literature at both low and high carbon dioxide partial pressures. The carbon dioxide permeances for pure dendrimer ILMs were lower compared to those obtained by glycine sodium salt in glycerol ILMs (Chen et al., 2000) in PVDF substrates. The selectivities, however, were about 4-5 times those obtained for glycine sodium salt-glycerol ILM. Table 2.8 compares the performance of dendrimer-based membranes at a low CO₂ feed gas concentration of around 0.5%. At low $\Delta p_{CO2}s$, the pure dendrimer membranes are highly selective for CO₂ over N₂. The pure dendrimer membranes offer about the same effective permeance of CO₂ as 1M sodium carbonate-glycerol ILM, but are about 13 times more selective for CO₂. Similarly, glycine sodium salt-glycerol membranes offer the trade off of higher effective permeance for CO₂ and about one-fourth of the pure dendrimer membrane selectivity for carbon dioxide. The presence of a small amount of glycerol in the dendrimer (25%) liquid does not affect either the permeances or $\alpha_{CO2/N2}$ very much. However, further increase in the glycerol content in the ILM reduces the selectivity of the ILM for carbon dioxide without offering any significant advantages in terms of carbon dioxide permeance.

Carrier	CO ₂ effective permeance, GPU	CO ₂ permeability, Barrer	α _{CO2/N2}	Reference
PAMAM pure dendrimer, generation zero	9.8	3,600	~ 18,000	Current work
75% Dendrimer – balance glycerol	8.58	3,200	16,300	Current work
44% Dendrimer – balance glycerol	10.2	3,800	3,000	Current work
2.25M glycine sodium salt-glycerol	27.5	10,100	≥ 4,000	Chen et al., 2000
1M Na ₂ CO ₃ -glycerol	8.4	3,100	1,400	Chen et al., 1999
Plasma grafted AA with EDA	100	~4,000	4,000	Matsuyama and Teramoto, 1996

Table 2.8 Performance of dendrimer membranes $^+$ at low CO2 concentrations.Feed CO2 concentration: ~0.5%

+ Substrate: PVDF

The plasma-grafted thin membrane soaked with EDA (Matsuyama and Teramoto, 1996) offers by far the highest effective permeance for carbon dioxide of 100 GPUs and a selectivity that is comparable to or somewhat less than that of glycine sodium salt-glycerol ILM. It should be stressed that these thin membranes were tested under humidified conditions on both feed and sweep sides of the membranes. There was no study performed on the loss of EDA with time. EDA is a volatile and toxic amine and it could lead to process stream contamination. However, dendrimer membranes have similar permeability for carbon dioxide at these CO₂ concentrations. This confirms that the dendrimer membranes facilitate carbon dioxide on par with other facilitated transport membranes, whereas the high selectivities are mainly due to the high density of charged functional groups present under humidified feed conditions.

At higher partial pressures of carbon dioxide, the selectivity of dendrimer membranes is comparable to the highest levels of selectivity reported in literature by polyelectrolyte salt membranes (Quinn and Laciak, 1995). Table 2.9 summarizes the comparison of dendrimer-based ILMs with various membranes studied in literature at higher feed CO_2 concentrations. The Q_{CO2} offered by dendrimer membranes are comparable to or higher than those of polyelectrolyte membranes. The selectivity and permeances offered by the polyelectrolyte membranes were achievable within a narrow range of the feed and sweep relative humidities. It should also be mentioned that making a pinhole-free membrane from these salts is difficult (Quinn and Laciak, 1997, Quinn, 1998).

Carrier	Δp _{CO2}	CO ₂ effective permeance, GPU	CO ₂ permeability, Barrer	α _{CO2/N2}	Reference
PAMAM dendrimer, generation zero	30	0.4	150	720	Current work
75% Dendrimer- balance glycerol	26	0.8	300	760	Current work
44% Dendrimer- balance glycerol	32	0.64	240	250	Current work
2.25 Glycine sodium salt- glycerol	30	1.1	400	195	Chen et al., 2000
1M Na ₂ CO ₃ - glycerol	59	2.5	920	100	Chen et al., 1999
Polyelectrolyte membrane	36	9.0	90-180 ^a	835	Quinn and Laciak, 1997
PEI/PVA blend membrane	30	2.0	~440	70	Matsuyama et al., 1999

Table 2.9 Performance of dendrimer membranes⁺ at high concentrations of CO₂ in the feed gas

+ Substrate: PVDF

a The range based on the range for thickness of 10-20 μ m. Membrane tortuosity and porosity not accounted for in the calculation.

Polyethyleneimine/polyvinyl alcohol blend membranes (Matsuyama et al., 1999) provide about 5 times higher permeance than dendrimer membranes, but the selectivity of the blend membranes for CO_2 was an order of magnitude lower than that of dendrimer membranes. This indicates that the dendrimer membranes are in the right direction for commercialization of membrane processes for CO_2 removal from flue gases, as Haraya et al. (1993) indicated that a $\alpha_{CO2/N2}$ of more than 210 and Q_{CO2} of more than 100 Barrers are required to recover CO_2 efficiently by a single stage permeator. On the other hand, the pure dendrimer membranes spanning the full thickness of the thick PVDF substrates offer significantly lower effective permeance for carbon dioxide. Obviously, thinner ILMs are called for. At high feed CO_2 concentrations, both 75% dendrimer and 44% dendrimer solutions in glycerol behave in a manner similar to that for low CO_2 feed concentrations.

2.5.5 Performance of Dendrimer Membranes in Hollow Fiber Substrates

Generation zero PAMAM dendrimer was immobilized in two types of hydrophilic hollow fibers potted in a module. Completely humidified feed gas was introduced in all experiments from the lumen side while the sweep gas (dry helium) was passed on the shell side. Figures 2.14 and 2.15 show the effective CO₂ permeance and the $\alpha_{CO2/N2}$ for the PAN and polysulfone fiber modules respectively. Logarithmic mean average values for the membrane areas, and the partial pressure differences across the ILM were employed for calculating the permeances of both species (see Appendix A).

The experiments with PAN fiber module were done in both cocurrent and countercurrent mode for transmembrane pressure differences up to 139 cm Hg (1.8 atm) on the feed side. Higher permeances for both carbon dioxide and nitrogen and higher separation factors were observed in the countercurrent mode. However, higher water fluxes (not reported here) were observed in countercurrent mode of operation for the same reason, resulting in lower feed side exit relative humidities. The highest CO₂ effective permeance obtained with PAN fibers was about 13 GPU, resulting in a separation factor of 1335 for a Δp_{CO2} of 0.28 cm Hg when the feed and sweep gases were flowing countercurrently.



 CO_2 partial pressure difference (Δp_{CO2Jm}), cm Hg

Figure 2.14 Performance of pure dendrimer ILM in poly(acrylonitrile) (PAN) fiber module.

The experiments with polysulfone fiber modules were conducted only in the cocurrent mode. The effective permeances and water fluxes observed were higher compared to those observed in the PAN fiber module at comparable Δp_{CO2} values. This is expected as the PAN fibers, used for ultrafiltration, have a lower porosity whereas polysulfone fibers, used for microfiltration, have a significantly higher porosity.



Figure 2.15 Performance of pure dendrimer ILM in a polysulfone fiber module.

The highest effective permeance for the polysulfone fibers was about 9.7 x 10^{-6} cc/cm².s.cm Hg for a feed CO₂ partial pressure of 0.45 cm Hg.

Even though the effective permeances for carbon dioxide in these hollow fiber modules were comparable to those obtained in flat membrane ILMs, the effective permeances for nitrogen are in general higher in the case of both hollow fiber modules. The effective permeance of nitrogen through the PAN module was between $6.8-9.3 \times 10^{-9}$ cc/cm².s.cm Hg. These permeances for pure dendrimer membranes were 2 to 3 times

higher than those obtained with sodium carbonate-glycerol ILMs in the PAN fibers (Chen et al., 2001). Similarly, the pure dendrimer ILMs in polysulfone hollow fibers have a nitrogen effective permeance in the range of $3.9-5 \times 10^{-9} \text{ cc/cm}^2$.s.cm Hg. These values are comparable to those obtained in polysulfone fibers with sodium carbonate-glycerol ILMs (Chen et al., 2001).

The discrepancy in N₂ permeation rates between ILMs in hollow fibers and flat membranes is expected because of the differences in the procedure for forming the dendrimer ILMs in flat membranes and hollow fibers and the very nature of dendrimer liquids. The dendrimer liquid was introduced as a solution in methanol into the hollow fibers and methanol was subsequently evaporated by applying a mild vacuum (5-15 in Hg) from the shell side, leaving pure dendrimer behind in the pores of the hollow fibers. The dendrimer in methanol solution was applied at atmospheric pressure from the lumen side as application of higher pressures may result in a loss of the dendrimer to the shell side. It is possible that some of the fine pores of the hollow fibers may not be filled with dendrimer but will permeate some nitrogen, resulting in a loss of selectivity for carbon dioxide vis-à-vis N2. The reason could also be the inherent hydrophobic nature of the substrates. This is particularly true in the case of PAN fibers which were hydrophilized, as polyacrylonitrile is inherently hydrophobic. Better techniques of hydrophilization of hydrophobic fibers to ensure uniform and permanent hydrophilization could improve this situation. Better approaches for immobilization of the dendrimer in the pores should result in higher separation factors by hollow fiber membrane ILMs. An additional reason for higher N₂ permeance is the somewhat lower exit gas relative humidity on the feed side compared to that for flat membranes which will increase the N₂ permeance.

2.5.6 Dendrimer Liquid Membranes for Separation of CO₂/O₂ Mixtures,

Toluene-N₂ Mixtures

Table 2.10 presents limited data on the performance of the generation zero dendrimerbased liquid membranes for separation of carbon dioxide/oxygen mixtures using relatively low Δp_{CO2} -s of up to 0.99 cm Hg. At a Δp_{CO2} of 0.74 cm Hg, the pure dendrimer ILM has a Q_{CO2} of 1970 Barrers and a $\alpha_{CO2/O2}$ of 2276. The carbon dioxide permeability was comparable to that obtained using a humidified CO₂-N₂ gas mixture under similar CO₂ partial pressures. The permeability of oxygen through the pure dendrimer ILM was about 0.87 Barrers compared to the nitrogen permeability of 0.17 Barrer. This is partly because of a significantly higher solubility of oxygen in water compared to nitrogen. As the feed gas stream was completely humidified, water sorbed by the dendrimer liquid yielded higher transport rates for oxygen than for nitrogen. The addition of glycerol to generation zero dendrimer increases the permeabilities of both carbon dioxide and oxygen with a reduction in the selectivity of the ILM for carbon dioxide over oxygen to about 1000. This trend was seen with both 75% dendrimer and 44% dendrimer ILMs. The presence of glycerol in the liquid membrane increases the effective permeance of oxygen more than the increase in the effective permeance of carbon dioxide for similar carbon dioxide partial pressures. As a result, the CO_2/O_2 separation factors are lower for dendrimer-glycerol mixture ILMs than for pure dendrimer liquid membranes.

An experiment was done to study the separation capabilities of dendrimer ILMs for toluene-N₂ mixtures. The data are presented in Table 2.10. The effective permeance observed for 548 ppm toluene feed concentration was 1.71×10^{-7} cc/cm².s.cm Hg.

Nitrogen permeance was not analyzed. Based on the average nitrogen effective permeance value of 5 x 10^{-10} cc/cm².s.cm Hg obtained during CO₂-N₂ separation, the toluene-N₂ separation factor would be about 350. This value is considerably higher than what would be observed for silicone coated gas permeation membranes commercially available. Such a reasonably high selectivity for toluene is possible due to the high solubility of toluene in the organic dendrimer liquid membranes and molecular gating behavior vis-à-vis nitrogen.

Table 2.10. Gas transport of dendrimer-based ILMs for CO₂-O₂, toluene-N₂ mixtures and CO₂-N₂ mixtures for higher generation dendrimers^a

ILM	∆p _i cm Hg	(Q _i /t _m) _{eff} GPU	(Q _j /t _m) _{eff} GPU	Q _i Barrer	Q _j Barrer	α _{i/j}	
$CO_2(i) - O_2(j)$ mixture							
Pure Generation 0	0.74	5.34	2.35e-3	2000	0.87	2300	
75% Generation 0	0.56	11.8	1.16e-2	4400	4.28	1000	
44% Generation 0	0.99	7.59	8.41e-3	2800	3.10	920	
$CO_2 (i) - N_2 (j)$ mixture							
Pure Generation 3	0.51	0.9	N/D	330	-	-	
Pure Generation 3	2.0	0.27	N/D	100	-	-	
Toluene (i) – N ₂ (j) mixture							
Pure Generation 0	0.05	0.17	N/D	-	-	~350 ^b	

a PVDF substrate; feed gas completely humidified

b Estimated based on nitrogen permeance for CO₂-N₂ system

N/D Not detected

A few exploratory studies conducted with generation 3 PAMAM dendrimer are also presented in Table 2.10. Generation 3 dendrimer is more viscous and sticky than generation zero dendrimer. Due to higher viscosity of the liquid, lower carbon dioxide permeances were observed. No nitrogen was detected by the GC for the membrane area provided. Due to the difficulty in handling of the liquid, further experiments could not be performed to determine the effect of higher generation dendrimers on the molecular gating behavior of PAMAM class dendrimers.

2.6 Conclusions and Recommendations

From the above discussion, the following conclusions can be drawn:

- Under high feed relative humidity conditions, pure dendrimer liquid behaves as a molecular gate permitting CO₂ to pass through but blocking N₂, O₂ etc. When the feed relative humidity is reduced, the selectivity drops drastically.
- 2) The CO₂-selective molecular gating ability of pure dendrimer liquid membranes are preserved over a wide range of feed gas relative humidity by adding 25% glycerol to the dendrimer liquid. The addition of small amounts of glycerol does not seem to affect the CO₂ permeances.
- 3) The dendrimer-based liquid membrane provides the highest selectivities reported in literature among all membrane-based processes so far for CO₂-N₂ separation both at low and high Δp_{CO2}-s.
- Hydrophilized Celgard membranes having a thickness lower than that of PVDF substrates improved the CO₂ effective permeances.

- 5) The dendrimer liquid membranes were able to withstand transmembrane pressure differences (TMP) up to 52 cm Hg in 0.1µm PVDF substrate and 120 cm Hg in 0.04 µm hydrophilized Celgard substrate.
- 6) The water uptake of pure dendrimer liquids was experimentally determined and compared with pure glycerol liquid at different ambient RH. Dendrimer liquid absorbs less water than glycerol at comparable ambient RH values.
- 7) The use of hollow fiber substrates for containing the ILMs was explored with two types of hollow fibers. Their performances were consistent with the observations made with glycerol-based ILMs conducted separately.
- There is a need to improve the CO₂ permeances, particularly at high CO₂ partial pressures.

CHAPTER 3

OLEFIN-PARAFFIN SEPARATION WITH FACILITATED TRANSPORT ILMS

3.1 Introduction

Simple olefins are important petrochemical feed stocks and are usually produced by dehydrogenation of corresponding alkanes (paraffins). Olefin/paraffin gas/vapor mixtures are encountered in the production and purification of various unsaturated hydrocarbons. According to one estimate, about 1.2×10^{14} BTU of energy is used yearly for olefin/paraffin separation (Eldridge, 1993). Major portion of the capital cost in an ethylene plant is for the olefin/paraffin separation train (Eldridge, 1993). In addition to the large refineries, small plants producing olefin using natural gas liquids (NGL) are the main industries involved in olefin/paraffin separation. Clean Air Act and other federal regulations have become more stringent in monitoring and mandating the emissions from refineries and other hydrocarbon-based industries. Hence, there is a huge incentive, both in terms of economics and environmental regulation, to look for efficient and benign processes for separating olefin/paraffin mixtures.

Currently available for olefin/paraffin separation are (Eldridge, 1993):

- cryogenic (low temperature) distillation
- extractive distillation
- physical adsorption
- chemisorption
- physical absorption
- reactive absorption
- membrane separation.

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Olefin/paraffin mixtures are conventionally separated mainly by cryogenic distillation, which is highly energy and capital intensive (Eldridge, 1993). Therefore, they are economically attractive for gas streams with high quantities of olefins (Eldridge, 1993; Safarik and Eldridge, 1998). In extractive distillation, however, the thermodynamic characteristics of the high boiling point polar solvents have a major impact on the process economics. On the basis of a computer simulation, extractive distillation does not offer any advantage over traditional distillation for some of the hypothetical solvents studied for the separation of propane and propylene (Kumar et al., 1972). Extractive distillation is unlikely to be economical unless novel solvents are designed (Eldridge, 1993).

Molecular sieve based physical adsorption would incur lower energy costs compared to distillation processes, but capital costs are higher. Molecular sieves were used to separate propane from propylene using equilibrium adsorption followed by a variable temperature stepwise desorption. An "Olex" process licensed by UOP Inc. uses a proprietary adsorbent fluid in combination with moving bed adsorption. Chemisorption of an olefin by a complexing agent, typically a copper and silver salt, was studied for ethylene adsorption (Hirai et al., 1986; Pearce, 1988). Selectivities for ethylene from ethane were low and regeneration could be accomplished by pressure swing adsorption (Pearce, 1988).

Separation of olefin/paraffin mixtures based upon reversible chemical complexation is selective and less expensive (Safarik and Eldridge, 1998). An olefin/paraffin separation process based on reactive adsorption has two major potential benefits. Utilizing a mass-separating agent rather than an energy-separating agent could substantially reduce energy requirements. Further, a selective facilitating agent having

a large olefin capacity and fast reaction rates would permit the use of smaller contactors.

For industrial-scale application of reactive absorption, a metallic salt solution should exhibit the following properties (Safarik and Eldridge, 1998):

- large absorption capacity and high selectivity for olefins
- rapid complexation and de-complexation reactions
- absence of side reactions.

These properties depend on various factors like the nature of the facilitating agent, nature of the solvent, concentration of the facilitating agent, nature of the olefin, additives in the solution, and temperature and pressure of operation.

Some transition metals form electron donor/acceptor complexes with alkenes (olefins). The metal-olefin bonding described by Dewar-Chatt model is commonly known as π -complexation. The Dewar-Chatt description of π -complexation is shown in Figure 3.1. The complex is formed between the metal and the olefin via a double bond. Both the metal and the olefin act as an electron donor and acceptor in the complexation process. Due to the reversibility of the complex, most suitable transition metals are Ag(I) and Cu(I). Other transition metals such as Pd(II), Hg(II) and Pt(II) are not practical for complexing with olefins due to their toxic nature and cost. Hence, most of the work has focused on silver and copper compounds. Silver nitrate, silver tetrafluoroborate, silver perchlorate, silver trifluoroacetate are amongst of the silver compounds studied for olefin separation.

Due to the reversibility of their complexes and relatively low cost, silver(I) and copper(I) are the most suitable transition metals in literature for olefin/paraffin separation (Keller et al., 1992; Blytas, 1992). The solvent, water, participates in the complexation

process by forming a weak bond with the complexing agent. This weak bond stabilizes the complexing agent in the absence of a reactive olefin [prevents Cu(I) from becoming Cu(II)]. Ho and co-workers (1988) obtained separation factors of 17 and 10 for ethylene/ethane and propylene/propane mixture systems respectively with cuprous diketonate in a α -methylstyrene solvent.



Figure 3.1 Schematic of π -complexation between silver ions and olefins (Safarik and Eldridge, 1998)

Silver nitrate in aqueous solution is the most commonly used facilitating system for separation of olefins from paraffins, while cuprous chloride has also been investigated to a limited extent (Hughes et al., 1986). In general, desorption occurs at a higher pressure in copper-based systems (Safarik and Eldridge, 1998). There are a few studies on non-aqueous solution based separation of olefin/paraffin mixtures like Tenneco Chemical's COSORB and ESEP (Safarik and Eldridge, 1998).

3.2 Membrane-based Processes for Olefin-Paraffin Separation

Most olefin-paraffin separation processes mentioned above are energy and capital intensive. Moreover, they perform the required separation in two steps. Membrane processes have been studied to either combine these two steps into one and/or improve the performance of the overall separation.

Research in membrane-based olefin separation can be broadly classified into following main categories:

- polymeric membranes and modified polymeric membranes
- carrier/polymer blend membranes
- ion exchange membranes with carrier impregnation
- membrane contactors with thermal desorption
- immobilized liquid membranes.

Polymeric membranes are in general considered to be the most stable configuration of all the membrane processes. But the permeabilities and selectivities offered by polymeric membranes tend to be very low as the mechanism of transport is the same for all species involved, namely, solution-diffusion. Usually olefins and paraffins have similar molecular sizes and solubilities, resulting in poor separation. For example, a polyimide membrane displayed a propylene permeability of about 20 Barrers and a propylene/propane selectivity of about 6 (Tanaka et al., 1996). For this reason, polymeric membranes have not received much attention for olefin/paraffin separation. To improve the olefin fluxes, facilitating agents like silver salts can be impregnated into the polymeric membrane and thereby achieve facilitated transport. However, polymeric materials such as polyimides can not solubilize the carriers effectively, but can provide the necessary mechanical strength. As a first step, acrylic acid is usually grafted on the polymeric substrates. As acrylic acid can be swollen under appropriate conditions, the membrane can be loaded with higher concentrations of the carrier. Hsiue and Yang (1993) grafted acrylic acid on polyethylene substrates. The resulting AA-grafted-PE film was immersed in 1M silver nitrate/glycerol solution. The role of glycerol was to swell the acrylic acid to incorporate higher loadings of silver nitrate. These membranes tend to have low selectivity (about 15) and permeability (12.5 Barrers) for 1-butene over iso-butane with about 111.7% AA grafting. The amount of grafting is defined here as the weight of the grafted membrane to that of the original ungrafted membrane. Among various swelling agents studied, the authors found that swelling by glycerol yielded the highest possible selectivity (Yang and Hsiue, 1998).

A similar grafting technique on a PTMSP substrate yielded a selectivity of only 6 for isobutene over iso-butane with an isobutene permeability of 1000 Barrers (Yang and Hsiue, 1996). However, the authors did not offer any explanation for the apparently high permeabilities with PTMSP substrates compared to polyethylene substrates. They also observed that the 'wet complex membrane' with glycerol exhibited excellent isobutene permeabilities and selectivities for the initial stages of operation; however, these values drop by about 60% during the first day, possibly due to loss of free glycerol. It may be that the authors observed the drop in the performance due to loss of water absorbed by glycerol and attributed it to glycerol. It is rather inconceivable that glycerol, with its very low vapor pressure (Chen et al., 1999), would be lost in any noticeable way within one day.

A variation of the above method of carrier impregnation is to form membranes using casting solutions containing the mixtures of the carrier and polymer. Additional crosslinking agents could be added to provide the necessary mechanical integrity to the thin membranes usually cast on microporous substrates. Ho and Dalrymple (1994) formed thin membranes on microporous teflon[®] substrates by casting with aqueous solutions containing polyvinyl alcohol (PVA) and silver nitrate. Pinnau and Toy (1997) cast solid polymer membranes with silver tetrafluoroborate dissolved in polyethylene oxide (PEO) to form thin membranes. PEO was supposed to form coordination bonds with the metal ion. One such membrane with 80 wt% Ag in the membrane provided a selectivity of ethylene over ethane of 120 and an ethylene permeance of 3.7×10^{-6} cc/cm².s.cm Hg under dry gas conditions. Interestingly, these membranes do not have facilitation of the olefin transport if the silver ion concentration in the membrane is below 50 wt% suggesting some sort of percolation threshold.

In addition to preparing polymeric films containing silver salts, ion exchange membranes and resins were also used for the same purpose of anchoring silver salts. The preferred ion exchange material is perfluorosulfonic acid (Nafion[®]) ionomer. Two approaches were followed in using the Nafion[®] ionomers:

- exchanging the cation of the existing Nafion[®] membranes with silver ions
- forming membranes with solutions of Nafion[®] and silver salts.

Eriksen et al. (1993) used Nafion-117 membranes for impregnation with silver tetrafluoroborate solutions. They found that heat drying Nafion[®] membrane at 340 °C

and soaking them in hot glycerol at 225 °C prior to impregnation increased the permeances of both ethane and ethylene by an order of magnitude with selectivity for ethane over ethane remaining constant at around 500. A 170 µm thick Nafion[®] membrane exchanged with 6M $AgBF_4$ solution tended to give very high permeability and selectivity for ethylene over ethane under completely humidified feed and sweep gas conditions (Eriksen et al., 1993). The permeability of ethylene was about 27000 Barrer (permeance is equal to 8×10^{-5} cc/cm².s.cm Hg) and a selectivity of 1900. They observed that pretreatment of the Nafion[®] membranes with glycerol and heat treatment increased the permeances by an order of magnitude. However, when dry purge gas was used, ethylene permeability was only 3-4 Barrer and the selectivity was only 30. This indicates that the membranes were stable only under a narrow relative humidity conditions. Yamaguchi et al. (1996) also observed that the hydration of AgBF₄ played an important role in olefin transport. However, a recent study with a polymer electrolyte membrane composed of poly(2-ethyl-2-oxazoline) and $AgBF_4$ indicated that $AgBF_4$ could facilitate without water (Hong et al., 2001).

Funke et al. (1993) studied the Nafion-117 membrane without any heat treatment steps for the separation of c-2-butene/t-2-butene. Their approach yielded selectivities in the range of 1.9-2.7 depending on the feed composition. Thoen et al. (1994) studied such an approach to study the separation of C_5 - C_{10} dienes from monoenes. The separation factors tended to be higher for higher dienes. However, the selectivities of these membranes were below 40.

To avoid some of the problems associated with the above membrane configurations, membrane-based gas-liquid contactors were used for olefin-paraffin separation. In this configuration, usually absorption of olefin in aqueous silver nitrate solution occurs in a membrane contactor, while desorption of olefins from the aqueous solutions is performed via conventional devices like flash pot (Valus et al., 1991; Davis et al., 1993; Tsou et al., 1994). The combination of membrane-flash devices ensures constant regeneration of the aqueous solution (preventing the drying of the fibers) and an independent control on both steps of olefin-paraffin separation, i.e., absorption and desorption. Tsou and coworkers (1994) studied the separation of ethylene/ethane mixtures in such a membrane-based absorber. With polysulfone fibers, they obtained an ethylene/ethane separation factor close to 400 and an ethylene permeance of about 1.4x 10⁻⁵ cc/cm².s.cm Hg for a 5M silver nitrate solution. Other researchers claimed similar results as well (Valus et al., 1991). However, the membrane contactor configuration has certain limitations, especially a decrease in species flux along the absorber due to carrier saturation. Even though it improves overall energy efficiency of the separation process, there is considerable energy requirement in the desorption stage.

The ideal configuration in terms of simplicity, compactness and higher fluxes for olefins would be a single membrane unit incorporating simultaneous absorption and stripping of olefins. This is possible with supported liquid membranes. The membrane phase, usually aqueous silver nitrate solutions, is immobilized in the pores of polymeric substrates. On high pressure feed side of the liquid membrane preferential absorption of olefin takes place while the desorption of olefin takes place on the low pressure (sweep) side. One of the earliest studies (Steigelmann and Hughes, 1973) for ethylene/ethane separation using aqueous silver nitrate solutions immobilized in cellulose acetate membranes demonstrated the applicability of supported liquid membranes. Teramoto and coworkers (1986) employed a 170 μ m thick cellulose filter as the substrate for immobilization of aqueous silver nitrate solutions. However, their experimental results showed that the liquid membrane fails after about 3 hours of operation, even with humidification of both feed and sweep streams. When 4M AgNO₃ solution was used, the permeability ratio of ethylene to ethane was 1000. Hughes et al. (1986) studied the supported liquid membrane configuration using both flat (cellulose acetate) and hollow fiber (cellulose ester reverse osmosis) membranes. The liquid membranes used in their work had to be regenerated periodically for stable operation. A separation factor between 125-170 was obtained for a feed mixture of 33% each of methane, ethane and ethylene. When larger permeators were tested over a period of 25 days, the performance was decreased with time due to loss of water and/or Ag⁺ from the fibers. They have also found that a minimum pressure differential across the fiber wall was necessary to maximize the permeator lifetime.

Davis and coworkers (1993) developed hybrid membrane-distillation processes to reduce the capital and operating costs of conventional distillation columns. The authors demonstrated in a pilot plant study the cost savings and stability of the hollow fiber based supported liquid membrane of aqueous silver nitrate. However, the regeneration methods for the liquid membrane were not mentioned.

As can be discerned from literature, the separation of olefin-paraffin mixtures is an important application of facilitated transport with huge economic incentive. Membrane processes, in spite of their numerous advantages, at their current state of research, still suffer from perceived shortcomings.

3.3 Objectives and Scope of Present Work

Thus, there have been numerous studies on the feasibility of various carriers for the facilitation of olefins in olefin-paraffin mixtures. As discussed earlier, membranes and membrane processes have been studied in literature to study the feasibility of membrane processes. However, the main objectives had been to utilize the existing carriers studied in conventional olefin-paraffin processes, and verify the usefulness of the membrane processes. Most commonly used carriers are silver salts. More importantly, silver nitrate appears to be the carrier of choice for olefin-paraffin separation, because of its economics and good complexation characteristics with olefins. In general, $AgNO_3$ and $AgBF_4$ are two of most commonly used agents in literature, even though other silver salts like silver perchlorate, silver trifluoroacetate were also studied (Safarik and Eldridge, 1998). Among these silver salts, AgBF₄ is found to form π -complexes with olefins more easily than silver nitrate. This is presumed to be due to highly hydrated state of boron atom which effectively frees more Ag+ ions to complex with olefins (Safarik and Eldridge, 1998). However, AgBF₄ is more expensive. In the present thesis, silver nitrate was used as the carrier for the selective separation of 1-butene from a mixture containing 1-butene, n-butane and nitrogen. The main objectives are to study:

- the feasibility of using glycerol as the solvent for silver nitrate for the facilitation of 1-butene;
- whether stable immobilized liquid membranes can be formed in hydrophilic substrates and whether some of the conclusions drawn in other glycerol-based ILMs for CO₂ separation can be extended to the present system;
- 3) the effect of silver nitrate concentration in glycerol on the ILM performance;

 the stability of the ILMs under humid-dry-humid feed gas stream cycles and their long-term stability.

In essence, the present work is not directed towards finding the best possible carrier for 1butene/n-butane separation. Rather, it is focused on the applicability of glycerol as a solvent for silver nitrate and whether such solutions can be used as stable liquid membranes for olefin/paraffin separation.

3.4 Experimental Details

Glycerol is highly hygroscopic in nature and sorbs water to a great degree. It is ideal to use hydrophilic or hydrophilized microporous substrates to immobilize the liquid membranes. In the present thesis, flat membranes were used to demonstrate the efficacy of using glycerol for the olefin/paraffin separation. The flat membranes used were poly(vinylidene fluoride) (PVDF) and hydrophilized Celgard 2500. These substrates were also used in the ILM studies for carbon dioxide separation. The characteristics of these substrates were presented earlier in Table 2.3.

3.4.1 Immobilized Liquid Membrane Preparation

The liquid membrane solutions were prepared by dissolving the appropriate amount of silver nitrate powder (Fisher Scientific, Springfield, NJ) in glycerol (Fisher Scientific, Springfield, NJ). Liquid membrane solutions up to 7.5M silver nitrate in glycerol were prepared by this approach. The solutions in general were homogeneous and clear. For some of the solutions, a small amount of black/gray precipitate was observed when exposed to atmospheric conditions for longer periods of time. This is presumed to be due

to the conversion of silver nitrate into other compounds like silver carbonate and silver oxide due to exposure to common gases like carbon dioxide and oxygen present in the atmosphere. However, the amount and the presence of the precipitate in the solutions were not significant compared to the volumes of the solutions. The solutions were stored under room conditions.

There is one major difference between the glycerol solutions prepared by dissolving silver nitrate and the solutions prepared by dissolving salts like sodium carbonate and sodium glycinate (Chen et al., 1999, 2000). When sodium carbonate or sodium glycinate was added to glycerol, the solution viscosity was observed to increase with increasing salt concentrations. At higher salt concentrations, the solutions appeared paste-like. Compared to this behavior, addition of silver nitrate does not appear to increase the glycerol solution viscosity. The hydrogen bonding ability of glycerol (Shchipunov and Shumilina, 1995) and the effects of addition of ionic salts (Hammadi and Champeney, 1998) are known. The viscous nature of 7.5M silver nitrate-glycerol solution appears to be similar to that of a 1M solution of silver nitrate-glycerol. The viscous nature of the silver nitrate-glycerol solutions was observed to change somewhat with time. It is assumed that this behavior is due to sorption of water from surroundings. In general, it was observed that ILMs made from freshly prepared solutions resulted in lower permeances for both 1-butene and n-butane. For most of the experiments reported here, freshly prepared solutions (up to a few weeks old) were used in forming the liquid membrane. For the experiment to study the long-term stability, the 5M AgNO₃ in glycerol solution was stored in a desiccator connected to house vacuum immediately after it was prepared.

Immobilized liquid membranes were prepared by placing the flat membrane on top of the silver nitrate-glycerol solution for sufficiently long periods of time so that the substrate was completely wetted by the solution. Using this approach, it can be assumed that the thickness of the ILM is equal to the thickness of the substrate. After the immobilization, the surfaces of the substrate were carefully wiped with kimwipes to remove any excess solution.

3.4.2 Experimental Setup

The experimental setup used for studying the olefin-paraffin separation capabilities of ILMs is essentially same as the one used for studying the separation of CO₂-containg gas mixtures using ILMs. The schematic of the setup is shown in Figure 2.4. The feed gas used was a mixture of 10% n-butane, 10% 1-butene-balance nitrogen (Matheson Gas, E. Rutherford, NJ). The presence of any trace impurities in the feed gas cylinders, if any, was not known. Whenever gas mixtures having lower concentrations of 1-butene, n-butane were required, the feed gas mixture from the gas cylinder was blended with pure nitrogen to obtain the required compositions. The sweep gas used in all experiments was dry nitrogen.

The experiments were conducted inside a fume hood for reasons of safety in handling the flammable gas mixture. All feed side connections were made with copper tubing. Gas alarm probes were placed both outside and inside of the fume hood to detect any gas leaks beyond permissible levels. The gas concentrations in the fume hood and the surroundings were continuously monitored using a Gas Alarm (Mining Safety Appliances Co., Pittsburgh, PA). The probes were periodically calibrated and tested against a standard propane calibration gas mixture. All experiments were conducted at room temperature, 23 ± 2 °C.

The feed gas mixture was humidified prior to entering the test cell. Whenever partially humidified feed was desired, the feed gas mixture was split into two streams, one stream flowing through the humidifier and the other, dry stream. These two streams were blended to obtain the required inlet feed relative humidity. The sweep gas used in most of the experiments was dry nitrogen. In a few experiments, the sweep gas was humidified to study the effect of complete humidification of both the streams on the ILM performance.

The permeances of 1-butene and n-butane were calculated based on their concentrations on the sweep side. The sweep gas outlet was directly connected to a GC; the GC outlet was vented into the fume hood. The concentrations of 1-butene and n-butane in the sweep were analyzed using a Carbograph 1AC 60/80 mesh packed column (Alltech, Deerfield, IL) using a FID detector. The injector and detector temperatures were set at 200 °C. The oven temperature was maintained at 40 °C for 25 minutes for the duration of the run. After the analysis, the oven temperature was raised to 105 °C and held there for about 8 minutes to remove any moisture adsorbed by the column. 1-butene and n-butane peaks appeared approximately at 15.65 and 21 minutes respectively for the above column conditions. Representative calibration curves for 1-butene and n-butane are shown in Figures 3.2 and 3.3 respectively.



Figure 3.2 Representative calibration curve for 1-butene



Figure 3.3 Representative calibration curve for n-butane

3.4.3 Calculation Procedure for 1-Butene, n-Butane Transport and

Separation Factor

The mole fractions of the 1-butene and n-butane in the sweep gas stream can be obtained from the peak areas reported by the gas chromatograph. The volumetric flow rate of the species through the membrane can be obtained by multiplying the sweep side mole fraction with the sweep side gas volumetric flow rate. In the present thesis, nitrogen is present both as the sweep gas and as a component of the feed gas mixture. It is assumed that the presence of nitrogen in the feed gas mixture and its permeation through the membrane do not affect the permeation behavior of either 1-butene or n-butane. This is so since the N_2 permeation rates in glycerol-based ILMs are extremely small compared to the flow rate of the sweep N_2 . In this context, species i always refers to either 1-butene or n-butane.

Effective permeance of a species through the membrane was calculated by

$$\left(\frac{Q_i}{t_m}\right)_{eff} = \frac{V_i}{A_t \Delta p_i}$$
(3.1)

where V_i is the volumetric permeation rate of species i, Δp_i is the partial pressure difference of species i across the membrane and A_t is the total membrane area. True permeance of the species $(Q_i/t_m)_{true}$ is obtained from

$$\left(\frac{Q_i}{t_m}\right)_{true} = \left(\frac{Q_i}{t_m}\right)_{eff} \frac{\tau_m}{\varepsilon_m}$$
(3.2)

The permeability of a gas species through the ILM is obtained by multiplying its true permeance through the ILM and the membrane thickness.

$$Q_i = \left(\frac{Q_i}{t_m}\right)_{true} t_m \tag{3.3}$$

Separation factor of species i with respect to species j, $\alpha_{i/j}$, is defined by

$$\alpha_{i/j} = \frac{\left(Q_i/t_m\right)_{eff}}{\left(Q_j/t_m\right)_{eff}} = \frac{\left(Q_i/t_m\right)_{true}}{\left(Q_j/t_m\right)_{true}}$$
(3.4)

Water vapor flux was calculated based on the temperature and the relative humidities of the inlet and outlet feed gas streams. At any given temperature, the saturation vapor pressure (p_{sat}) for water vapor was obtained from Perry et al. (1984).
Mole fraction of water vapor at saturation, $y_{H2O}^{sat} = p_{sat}/P_{f}$

where P_f is the feed side total pressure.

At feed inlet,
$$y_{H2O}^{in} = RH_{in} * y_{H2O}^{sat}$$

At feed outlet, $y_{H2O}^{out} = RH_{out} * y_{H2O}^{sat}$
Water flux $= V_f (y_{H2O}^{in} - y_{H2O}^{out})/A_t$ (3.5)

where V_f is the feed side flow rate.

No corrections were made to the saturation vapor pressure to account for the above atmospheric conditions. Gas permeances are reported in units of $cc(stp)/cm^2.s.cm$ Hg. Wherever convenient, the gas permeances are reported in the units of GPU which is equivalent to 10^{-6} cc(stp)/cm².s.cm Hg. Gas permeabilities are reported in the units of Barrer which is 10^{-10} cc(stp).cm/cm².s.cm Hg. Water fluxes are reported as cc(stp)/cm².min.

3.5 Results and Discussion

3.5.1 The Effect of Silver Nitrate Concentration on the ILM Performance

Figure 3.4 and Table 3.1 present the effect of the concentration of silver nitrate in glycerol on the permeances of 1-butene and n-butane and the selectivity of the ILM for 1-butene over n-butane in a PVDF substrate. The feed gas was a mixture of approximately 10% of 1-butene and n-butane with balance nitrogen. The feed gas was completely humidified and dry nitrogen was used as the sweep gas for most of the data presented.



Figure 3.4 The effect of silver nitrate concentration on the performance of glycerol-based ILMs in PVDF substrates. $\Delta p_{1-butene} \sim 10$ cm Hg. Feed: ~10% 1-butene -10% n-butane -balance nitrogen mixture.

AgNO ₃ conc., M	Δp _{1-butene} , cm Hg	(Q _{1-butene} /t _m) _{eff} , cc/cm ² .s.cm Hg	Δp _{n-butane} , cm Hg	(Q _{n-butane} /t _m) _{eff} , cc/cm ² .s.cm Hg	α _{1-butene/n-} butane			
Hydrophilic PVDF substrate								
Feed humidified; dry sweep gas								
0	11.99	4.11E-08	11.85	4.99E-09	8.3			
1	11.15	2.25E-07	10.8	2.27E-09	99			
4	11.15	7.09E-07	10.8	1.27E-09	557			
4	11.15	6.76E-07	10.81	1.22E-09	554			
5	9.88	1.02E-06	9.67	2.54E-09	401			
7.5	11.15	7.15E-07	10.8	8.49E-10	842			
5	9.88	1.07E-06	9.68	2.45E-09	435			
5	5.70	1.25E-06	5.60	3.01E-09	417			
5	2.44	1.74E-06	2.38	3.1E-09	564			
5	1.28	2.44E-06	1.25	2.47E-09	987			
Feed and sweep gases humidified								
4	11.05	1.47E-06	10.81	4.16E-09	353			
7.5	11.05	1.16E-06	10.81	1.70E-09	682			
Hydrophilized Celgard								
Feed humidified; dry sweep gas								
5	10.56	7.93E-06	10.55	1.03E-07	77			
5	5.1	4.08E-06	5.02	5.46E-08	75			
5	4.26	4.85E-06	4.19	5.16E-08	94			
5	10.97	5.00E-06	10.55	8.61E-08	58			

Table 3.1 Performance of silver nitrate-glycerol ILMs in hydrophilic PVDF andhydrophilized Celgard substrates

Pure glycerol without any carrier has a very low selectivity of 8.3 for 1-butene. The effective permeance of pure glycerol ILM for 1-butene was a very low 4.11 x 10^{-8} cc/cm².s.cm Hg. When the ILM was formed with 1M AgNO₃, the effective permeance of 1-butene increased more than 5 times to 2.25 x 10^{-7} cc/cm².s.cm Hg with the selectivity of the ILM increasing to 99. This increase in selectivity was mainly due to two factors:

- increase in 1-butene effective permeance due to the augmentation of 1-butene flux from the reversible reaction between 1-butene and silver ion; and
- reduction in n-butane effective permeance due to reduced solubility of n-butane in the 1M AgNO₃ solution. This is simply the salting-out effect.

When the concentration of silver nitrate in glycerol was increased to 4M in the ILM, there was further increase in $(Q_{1-butene}/t_m)_{eff}$ to 7.09 x 10⁻⁷ cc/cm².s.cm Hg and further decrease in $(Q_{n-butane}/t_m)_{eff}$ to 1.27 x 10⁻⁹ cc/cm².s.cm Hg with an increase in the selectivity to about 557. Further increase in silver nitrate concentration to 7.5M did not appear to proportionally enhance the permeance of 1-butene, with $(Q_{1-butene}/t_m)_{eff}$ of 7.15x 10⁻⁷ cc/cm².s.cm Hg. This could be due to the increased viscosity of the 7.5M AgNO₃ solution in glycerol. However, due to the increased viscosity, n-butane permeance decreased, increasing the selectivity of 7.5M AgNO₃ ILM to about 842.

A few experiments were done with complete humidification on both sides of the ILM to observe any drastic changes in the ILM performance. There appears to be a general increase in the effective permeances of both 1-butene and n-butane with additional humidification of the sweep side. This is expected as the viscosity of the liquid membrane is expected to decrease with increased water content. This also results in reduced concentration of silver nitrate in the ILM. Due to these factors, there is a marginal decrease in the selectivities of the ILMs compared to their corresponding ILMs with only feed side humidification.

3.5.2 Comparison of Glycerol-based ILMs for Olefin/Paraffin Separation

It would be useful to compare the performances of glycerol-based immobilized liquid membranes with those of various membrane configurations studied in literature. There are a few main differences between the ILMs studied here and other membrane configurations. Various olefin-paraffin gas mixtures were also studied in literature. The predominant olefin-paraffin separation system studied was the ethylene-ethane system. As ethylene and ethane are smaller molecules compared to 1-butene and n-butane, the fluxes for the earlier system can be expected to be higher than those of 1-butene and n-butane. Similarly various silver salts were studied as facilitating agents for olefins. The ILMs studied in the present work always employed dry sweep gas except in a few experiments. There are very few studies in literature employing the liquid membrane in this mode. The concentration of silver nitrate in glycerol was studied up to 7.5M without observing any problems with the dissolution of the salt in glycerol.

Table 3.2 compares the performance of glycerol-based ILMs with those from literature. A 7.5M silver nitrate-glycerol ILM has 1-butene permeability of about 260 Barrers with a $\alpha_{1-butene/n-butane}$ of 850 when a mixture of 10% each of 1-butene and n-butane in nitrogen was used. The current ILMs perform essentially on par with the best available membrane configurations available in terms of their selectivity of 1-butene over n-butane.

Configuration Olefin-paraffi		$\mathbf{Q}_{\mathbf{Olefin}}$	$\mathbf{Q}_{Paraffin}$	α	Remarks	Reference
	system	Barrer	Barrer			
PE-AA grafted-	i-butane/1-	12.5	0.82	15	Dry gas	Hsiue and
Ag+	butane				streams	Yang, 1993
Thin	Mixture of	500 ^a	2.6	96 ⁶	Humid	Ho and
membrane,	butanes and n-				gas	Dalrymple,
PVA-AgNO ₃	butane				streams	1994
Thin	Ethylene/ethane	11.1	0.09	120	Dry gases	Pinnau and
membrane,						Toy, 1997
PEO-AgBF ₄						
Nafion-6M	Ethylene/ethane	26800	14	1900	Humidifie	Eriksen et
AgBF ₄					d gases	al., 1993
Nafion-6M	Ethylene/ethane	3-4	0.1	30	Dry purge	Eriksen et
AgBF4					gas	al., 1993
10M AgNO ₃	Ethylene/ethane	5100	5	1000	SLM	Teramoto
aqueous						et al., 1986
solution						
6 M AgNO ₃	Ethylene/ethane	5130 ^c	9.4	890-	SLM	Hughes et
aqueous	-			1350 ^d		al., 1986
Solution						ŕ
7.5M AgNO ₃ -	1-butene/n-	260	0.3	850	SLM/	Present
glycerol	butane				Dry	work
					sweep gas	
7.5M AgNO ₃ -	1-butene/n-	420	0.6	680	SLM/Hu	Present
glycerol	butane				mid	work
					Gas	
					streams	

Table 3.2 Comparison of various membrane configurations for olefin-paraffinseparation with the present ILMs.

a based on a 2.9 µm film with 40 wt% silver nitrate content

b based on a mixture containing 20% 1-butene and 40% n-butane, balance isobutylene and t-2-butene.

c permeability of ethylene calculated based on the permeation rate and average ethylene pressure on feed side.

d selectivity of ethylene over ethane calculated based on the data for stirred solutions atop porous Teflon films.

For example, a supported liquid membrane formed with 10M aqueous silver nitrate solution in a 170 µm cellulose filter provides an ethylene/ethane selectivity of about 1000 (Teramoto et al., 1986). However, the high permeability of ethylene (5100 Barrers) and high selectivity of the aqueous-based ILM were calculated based on the measurements taken at 30 minutes of the experiment. The stability of the ILMs after 3 hours of operation was highly questionable. Given these constraints, it is doubtful whether the reported values were that of steady state. In addition, both the feed and sweep gas streams employed in the study were completely humidified and at atmospheric pressure.

Similarly, aqueous silver nitrate ILMs formed in commercial reverse osmosis hollow fibers made of cellulose esters were studied for ethylene/ethane separation (Hughes et al., 1986). In spite of the dense nature of the RO membrane skin and resultant low water fluxes (and hence losses), the hollow fibers had to be re-impregnated with silver nitrate solution from time to time. A typical ethylene permeability of about 5130 Barrers was obtained at 21 °C with an equimolar feed gas mixture of methane, ethane and ethylene. The associated selectivity (defined as the ratio of concentrations of ethylene over non-reacting species in the permeate side over feed side) was about 150. In a separate experiment where the aqueous silver nitrate solution was placed as an immobilized liquid membrane film (depth of the liquid was 1-2 cm) on top of a porous Teflon[®] film, the ratio of permeation rates (which will be approximately equal to the ratio of permeances) was between 900-1350 for a 6M AgNO₃ in water solution. Needless to say, this configuration is not practical and only an indicator of the selectivities that can be obtained from aqueous solutions containing silver nitrate.

various membrane compositions/configurations attempted for Among olefin/paraffin separation, silver ions anchored to polyethylene-grafted with acrylic acid (PE-g-AA-Ag⁺) tended to yield low selectivities (Hsiue and Yang, 1993). For a 111.7% AA grafted of PE, the highest selectivity for 1-butene over iso-butane was 15.2 with a 1butene permeability of 12.5 Barrers. The authors observed a constant decrease in 1butene permeability and a simultaneous increase in iso-butane permeability with time, with the selectivity of the membrane for 1-butene over iso-butane dropping to about 2 from 15.2 within 30 days of operation. They concluded that this loss in selectivity was due to redox reaction of silver ions with oxygen to form silver and silver oxide. (The problem of silver ion becoming silver was also addressed by Hughes et al. (1986) by adding 1 wt% hydrogen peroxide to the aqueous solution).

When the membrane was formed with silver ions present in the casting solutions, the performance of the resulting membrane was better than the impregnation method. Ho and Dalrymple (1994) formed a thin membrane consisting of polyvinyl alcohol (PVA) and silver nitrate on top of a Teflon[®] support. The cast membranes were dried first at room temperature and then heated at 75 °C for 3 days for crosslinking of PVA. In the membrane, silver nitrate was supposedly dispersed in the PVA matrix and silver ion stabilized via coordination with oxygen atoms in the membrane. A 2.9 μ m PVA-silver nitrate thin film with 40 wt% silver nitrate resulted in a 500 Barrer permeability for 1-butene with a separation factor (ratio of olefin/paraffin concentration ratio in the permeate over that in the retenate) of 96. These membranes need to be exposed to completely humidified gas streams both on feed and sweep sides. The effect of dry gas streams on the membrane performance, if any, is not known for such a membrane.

A similar procedure was adopted by forming a blend membrane of polyethylene oxide and silver tetrafluoroborate for ethylene/ethane separation (Pinnau and Toy, 1997). These membranes were stable and gave reasonable performance even under dry feed gas conditions. For a 3 μ m thick membrane, the ethylene permeance was about 10⁻⁶ cc/cm².s.cm Hg with a ethylene/ethane selectivity of below 30 when the AgBF₄ concentration in the membrane was 50 wt%. However the selectivity increased to about 120 when AgBF₄ concentration was increased to about 80% in the membrane. This behavior is indicative that the mechanism of transport for ethylene is due to percolation.

The functional groups in ion exchange membranes like Nafion[®] were exchanged with silver salts for facilitating the transport of olefins (Eriksen et al., 1993). Nafion membrane was ion-exchanged with sodium and heated in glycerol and immersed in water to increase the water content of the membrane prior to exchanging the sodium ions with silver ions by soaking the membrane in aqueous 6M AgBF₄ solution. A very high selectivity for ethylene over ethane was observed (about 1900) with these membranes along with an ethylene permeability of about 26,800 Barrers. Both feed and sweep streams were completely humidified during the experiments. However, a control membrane (prepared with the same procedure) soaked in 1M AgBF₄ in glycerol solution instead of aqueous solution resulted in a selectivity of only 30 with ethylene permeability of only 3-4 Barrers when dry feed and sweep streams were employed. This clearly indicates that these membranes do require water, either at the stage of impregnation of silver ions and/or during the experiments. No data were presented about the stability of these membranes. Based on the above comparisons, the glycerol-based immobilized liquid membranes studied in the present work are highly selective for 1-butene over n-butane and their selectivities are on par with the highest achievable in literature. The permeances obtained with the current ILMs appear to be lower than those obtained in the thinner membranes reported in literature. It should be pointed out that the substrates used in the present study are 100 μ m thick and there is considerable room for improvement in permeances of olefins by using thinner substrates and/or thinner liquid membranes.

3.5.3 Silver Ion Coordination in Glycerol and Membranes

Silver ion forms hydrated structures in aqueous solutions (Yamaguchi et al., 1984, cited in Antonio and Tsou, 1993). There have been studies to determine the coordination of silver in aqueous and non-aqueous solutions (Antonio and Tsou, 1993). Silver ions are known to coordinate with four water molecules to form a stable, hydrated cation, $Ag(OH_2)_4^+$, with tetrahedral stereochemistry in aqueous solutions. This is true for both aqueous AgNO₃ and AgClO₄ solutions. (Antonio and Tsou, 1993). Analysis of silver K-edge EXAFS (extended X-ray absorption fine structure) reveals the presence of four oxygen atoms about the silver ion indicating that the coordination number for Ag⁺ in aqueous solution is 4 with Ag-OH₂ bond length of 2.40 ± 0.02 °A. Further, the hydrated silver ion has a total of 18 valence electrons about silver (10 from Ag⁺ and 8 from water molecules). The empirical "18-electron rule" predicts that this solvated, 18-electron Ag⁺ complex is a stable one. Antonio and Tsou (1993) observed that there is a decrease in silver coordination number from 4 to 3 in the membrane pores. The three oxygen atoms that form the first coordination sphere of Ag⁺ in membranes can come from either water molecules or the membrane matrix material. The bonding between water molecules and Ag⁺ is weak. Environmental perturbation such as going from the feed gas stream into membrane phase could affect the silver (I)-OH₂ interaction. Antonio and Tsou (1993) concluded that the aqueous environments in the membranes studied were sufficiently different from that of bulk water. It is not conceivable that hydrophilized PVDF films would contribute any oxygen atoms to silver coordination. (However, it should be mentioned that original polymer PVDF is hydrophobic and it is rendered hydrophilic via an acrylate grafting through some unknown process.) An additional variable in silver nitrate-glycerol liquid membranes in hydrophilized PVDF membranes is glycerol itself. Glycerol is known to absorb water from the surroundings. However, the nature of water absorbed is not known. The competitive behavior for water, if any, between glycerol for sorption and silver nitrate for coordination is at present unknown.

3.5.4 Effect of Olefin Partial Pressure on the ILM Performance

The effect of 1-butene partial pressure difference across the liquid membrane, $\Delta p_{1-butene}$, on the permeances and selectivity of 1-butene-n-butane is shown in Figure 3.5. The original feed cylinder contained a gas mixture of about 10% 1-butene and 10% n-butane in nitrogen. To obtain lower olefin concentrations in the feed gas contacting the liquid membrane, a non-reacting gas, nitrogen (occasionally helium) was blended with the above feed gas. Using this procedure, 1-butene concentrations down to 1% with balance nitrogen (occasionally helium) were obtained. The data with PVDF substrate presented in Figure 3.5 were obtained during a "long term" experiment where the ILM formed with 5M silver nitrate in glycerol solution was exposed to the original feed gas mixture of 10%



Partial pressure difference of species i (Δp_i) , cm Hg

Figure 3.5 The effect of partial pressure difference of the species on the ILM performance in a PVDF substrate. Feed side at 5 psig. ILM: 5M silver nitrate in glycerol solution.

each of 1-butene and n-butane for about 80 hours before the feed gas was blended with helium. More details about the long-term experiment and the ILM will be presented in section 3.5.7.

As can be seen from Figure 3.5, at the silver nitrate concentration of 5M in glycerol and 100% feed inlet RH, 1-butene effective permeance decreased considerably with increasing 1-butene concentration in the feed gas mixture. At the same time, n-butane permeance in the concentration range studied did not show any particular trend and was almost constant within the range of experimental deviations.

This characteristic of increased 1-butene permeance at lower partial pressure difference and decreased permeances at higher partial pressure difference is known as "carrier saturation", and is intrinsic to facilitated transport systems (Way and Noble, 1992). The total flux of 1-butene is composed of two parts, that of physically dissolved 1-butene and that of 1-butene-silver ion complex. The relative proportion of 1-butene transported in physically dissolved form and in chemically combined form is dependent on, among others, the carriers available for facilitation reaction. The higher the concentration of dissolved 1-butene, the greater is the formation of 1-butene-silver complex, saturating the membrane with the complex. This lowers the concentration of silver ions available for further 1-butene uptake, thereby decreasing any increase in flux with an increase in 1-butene partial pressure.

Since the ILMs display the partial pressure dependency for the permeances, high separation factors were obtained at lower 1-butene partial pressure difference. At an 1-butene partial pressure difference of 1.28 cm Hg, the selectivity of the ILM for 1-butene was as high as 987 with an effective permeance of 2.44 x 10^{-6} cc/cm².s. cm Hg for 1-butene. As 1-butene partial pressure difference increased to about 9.88 cm Hg, the effective permeance was reduced to 1.07 x 10^{-6} cc/cm².s.cm Hg with the resulting selectivity dropping to about 435.

An immobilized liquid membrane consists of liquid held in the capillary-like pore structure of the substrate. The maximum transmembrane pressure (TMP) differential an ILM can withstand depends on the pore size of the substrate and the surface tension of the ILM liquid. For the ILM configuration to be of any practical utility, ILMs should be able to withstand TMPs reasonably greater than those for intended applications. Most of the data in the present work were generated using 0.1 μ m hydrophilized PVDF films having a water bubble point pressure of 4.8 atm (360 cm Hg) (Millipore, 1997). The results of the experiments when a 5M AgNO₃ in glycerol ILM was subjected to TMPs upto 2 atm are shown in Figure 3.6. The feed gas mixture used was around 10% each of 1-butene and n-butane in nitrogen. The sweep side was dry nitrogen.

At lower TMPs of about 0.8 atm (equivalent to 12 psig feed side pressure), the effective permeances of 1-butene and n-butane were about 2.3 x 10^{-6} and 9.3 x 10^{-9} cc/cm².s.cm Hg respectively with a selectivity for 1-butene of about 245. However, as the TMP was increased to about 2 atm (corresponding to 28.5 psig), the effective permeances of both 1-butene and n-butane decreased marginally to 1.4 x 10^{-6} and 4.4 x 10^{-9} cc/cm².s.cm Hg respectively with the selectivity increasing to about 314. This behavior is expected. The water flux through a 5M silver nitrate-glycerol ILM subjected to a feed pressure of about 5.5 psig was typically about 1.6×10^{-2} cc/cm².min (water flux measured in a different experiment where the effect of feed side relative humidity on the ILM performance was studied, section 3.5.6). This value is significantly higher than those through sodium carbonate-glycerol ILMs (Chen et al., 1999) and sodium glycinate-glycerol ILMs (Chen et al., 2000) for carbon dioxide transport.



Figure 3.6 The effect of transmembrane pressure difference on the ILM performance in a PVDF substrate. ILM: 5M silver nitrate in glycerol Feed: ~10% 1-butene-10% n-butane- balance nitrogen. Permeate pressure: atmospheric

The water fluxes through silver nitrate-glycerol ILMs subjected to 5.5 psig feed pressure range from $1.6 \ge 10^{-2}$ to $7.94 \ge 10^{-2}$ cc/cm².min depending on feed and sweep flow rates. As the feed pressure increases, the TMP increases, resulting in higher water fluxes. Due to higher water fluxes, it can be expected that feed outlet RH will be substantially lower, resulting in a lower average RH for the ILM. Due to this reason, the permeances of both 1-butene and n-butane tend to be lower at higher TMPs.

3.5.6 Stability of ILM with Changing Feed Relative Humidity

The stability of the silver nitrate-glycerol ILM was studied in a 7-day-long experiment when the ILM was subjected to different feed inlet RH conditions. The performance of a 5M silver nitrate-glycerol ILM subjected to such RH conditions is shown in Figure 3.7. The variations of feed inlet RH and the effective permeance of 1-butene were plotted as functions of the duration of experiment. For convenience, the effective permeance of 1-butene is plotted on a logarithmic scale. At the start of the experiment, the ILM was exposed to completely humidified feed gas at the inlet. Then the fully humidified feed gas stream was blended with dry feed gas to yield a feed gas inlet stream of about 34%. Due to a decrease in the average RH of the ILM (due to lowered RH on the feed side and the resulting RH gradients across the ILM), the effective permeances of both 1-butene and n-butane decreased simultaneously, with the effective permeance of 1-butene decreasing to 3.27×10^{-7} cc/cm².s.cm Hg. However, the selectivity remained essentially constant during the period studied.

Then the ILM was subjected to completely dry nitrogen gas as feed stream for about 3 days to simulate dry feed gas conditions. When the dry feed gas mixture of 10%



Figure 3.7 ILM stability in a PVDF substrate with changing feed inlet relative humidity. ILM: 5M silver nitrate in glycerol. Feed: ~10% 1-butene- 10% n-butane- balance nitrogen.

each of 1-butene and n-butane was introduced, the effective permeance of 1-butene decreased by about 25 times, to about $6.92 \times 10^{-8} \text{ cc/cm}^2$.s. cm Hg and n-butane could not be detected. This behavior is quite similar to what was observed in CO₂-N₂ separation with glycerol-based ILMs (Chen et al., 1999).

When feed gas blended with humidified feed gas was reintroduced at about 29.3% RH, the performance of the ILM was restored to comparable levels. When the ILM was subjected to completely humidified feed gas, the effective permeance of 1-butene increased to approximately the initial levels. The non-reacting species n-butane could not be detected in the GC with confidence during this period. Hence the final selectivity of the ILM is not reported. It appears that it takes a longer time for steady state to reach for n-butane, an observation made by other researchers as well (Ho and Dalrymple, 1994). As seen for facilitated transport ILMs for carbon dioxide, the low volatility and highly hygroscopic nature of glycerol are responsible for the observed stability.

3.5.7 Long-term Stability of Glycerol-based ILMs for Olefin-Paraffin Separation

The main limitation of immobilized liquid membranes having facilitated transport has been their stability over extended periods of time, the principal reason being the loss of solvent water due to evaporation. However, as shown elsewhere (Chen et al., 1999; 2000), the replacement of water by glycerol has a dramatic effect on the stability of such ILMs. It was shown in the case of CO_2-N_2 separation with glycerol-based ILMs, the ILM was stable for over 600 hours studied without showing any signs of failure or deterioration in performance. For glycerol-based ILMs to be practical for olefin-paraffin separation, such ILMs should provide stable permeances and selectivities over an extended period of time. It should be pointed out that some of the data reported here (for example studies on the effect of relative humidity or partial pressure differences) were obtained using the same ILM over an extended period of time (up to 3 weeks) and subjecting them to continuous feed and sweep flow conditions. For safety reasons, the olefin-paraffin feed gas mixture was turned off during the night and nitrogen was passed on the feed side. In this sense, silver nitrate-glycerol ILMs were studied for their long-term stability on various occasions. However, to study the stable performance of such an ILM exposed continuously to olefin-paraffin feed gas mixture, a long-term experiment was carried out. Figure 3.8 and Table 3.3 present the data for such an experiment.

Duration,	Δp _{1-butene} , cm Hg	(Q _{1-butene} /t _m) _{eff} , cc/cm ² .s.cm Hg	∆p _{n-butane} , cm Hg	(Q _{n-butane} /t _m) _{eff} , cc/cm ² .s.cm Hg	α _{1-butene/}
h	U U		Ű	_	
16	9.88	1.02E-06	9.68	2.54E-09	402
38	9.88	1.05E-06	9.68		
60	9.88	1.06E-06	9.68	3.07E-09	345
82 ^a	9.88	1.07E-06	9.68	2.45E-09	435
107	5.70	1.25E-06	5.60	3.01E-09	417
119	2.44	1.74E-06	2.38	3.1E-09	564
131	1.28	2.44E-06	1.25	2.47E-09	987
148	9.88	1.3E-06	9.68	2.39E-09	544
152 ^b	9.88	1.31E-06	9.68	2.38E-09	549
511	9.88	2.28E-06	9.68	4.59E-09	497
559	9.88	2.62E-06	9.68	6.83E-09	384

Table 3.3 Long-term stability of silver nitrate-glycerol ILMs^{*}

* ILM: 5M silver nitrate-glycerol in 100 µm thick PVDF substrate.

a The ILM was exposed to lower olefin-paraffin concentrations between 82-148 hours.

b The ILM was exposed to humidified helium as feed gas between 152-500

A freshly prepared 5M silver nitrate in glycerol solution was immobilized in PVDF substrates (2 test cells connected in series to increase the membrane area). During the initial 82 hours of operation, the performance of the liquid membrane was stable. The effective permeances of 1-butene and n-butane were about 1.05×10^{-6} and 2.5×10^{-9}

cc/cm².s.cm Hg respectively with the selectivity remaining constant around 400. After 82 hours, the feed olefin-paraffin mixture was blended with humidified helium, which



Figure 3.8 Long term stability of glycerol-based ILMs for olefin-paraffin separation. ILM: 5M silver nitrate in glycerol. 82-148h: ILM was exposed to lowered partial pressures. 152-500 h: ILM was exposed to helium as feed.

resulted in lower olefin, and paraffin feed concentrations. With the decrease in olefin concentrations, there was an increase in 1-butene effective permeance while n-butane permeance remained constant. This is expected due to the facilitation reaction between 1-butene and silver nitrate. After 148 hours, blending with helium was stopped exposing the ILM to original feed gas concentrations. While the n-butane permeance remained constant, the permeance of 1-butene showed an increase to $1.3 \times 10^{-6} \text{ cc/cm}^2$.s.cm Hg. This was a clear indication that 1-butene permeance was changing with the duration of exposure to humidified feed gas. For safety reasons, the stability of the ILM was further studied by exposing it to humidified helium as feed gas under the same conditions of flow rate and pressure. After 500 hours, olefin-paraffin mixture was re-introduced as the feed gas mixture. There was a simultaneous increase in permeances of both 1-butene and n-butane almost by a factor of 2. However, these increases in the permeances compensated each other with the ILM maintaining essentially a constant selectivity during the entire 560 hours of operation.

It is known that both silver nitrate and glycerol are hygroscopic. However, their behavior in solutions is not known. As silver ions co-ordinate with water (Yamaguchi et al., 1984) it is possible that there is competition/co-operation between silver ions and glycerol for sorbed water during the experiment. The liquid membrane at the beginning of the experiment can be expected to be almost dry as extra precautions of not exposing the solution to ambient conditions and keeping it under constant house vacuum were taken. So, the behavior of the ILM during the initial stages of the experiments can be considered pseudo-steady state, while at the later stage of the experiment the ILM would have reached steady state with respect to moisture concentration along and across the liquid membrane. Ho and Dalrymple (1994) also observed that even a thin 2.9 μ m film PVA-silver nitrate film took almost 5 days to reach steady state in spite of humidifying both feed and sweep gas streams. Based on the above observations, it is possible that the behavior of silver nitrate is strongly influenced by the presence of solvent like glycerol and also by the polymer substrate. A further complication in our configuration was that there would be concentration gradient for moisture also in the liquid membrane, both in parallel and perpendicular directions. There is a need to study the behavior of silver ions in glycerol solution at various concentrations of moisture present to gain insight into the transport mechanism of silver nitrate-glycerol ILMs for olefin-paraffin separation.

3.6 Conclusions and Recommendations for Future Work

Based on the above observations, the following observations and recommendations can be made.

- Glycerol is a suitable solvent for silver nitrate and is effective in olefin-paraffin separation.
- 2) Silver nitrate is soluble in glycerol at least up to 7.5M. The solubility of silver nitrate in glycerol is high and the solution behavior appears to be similar to that of aqueous solutions. This is a marked difference from the highly viscous behavior of other glycerol-based solutions containing carriers such as sodium carbonate and sodium glycinate.
- 3) The silver nitrate-glycerol ILM showed facilitated transport behavior at low concentrations of 1-butene yielding higher 1-butene permeance and a high

selectivity close to 1000. As 1-butene concentration increased, the 1-butene permeance and selectivity decreased, the latter to about 400.

- 4) There was a general increase in 1-butene permeances when the ILM or the solution was exposed for prolonged periods to humidified gases or ambient conditions. A possible reason for this behavior could be sorption of water. However, the selectivity of the liquid membrane for 1-butene over n-butane was essentially constant over the duration of the experiment.
- 5) The behavior of silver ions in glycerol solutions is not studied and needs to be understood better for successful application of the present ILM configuration.
- 6) The effective permeance of 1-butene can be improved by forming thinner liquid membranes in a given substrate. Alternately, the ILMs can be formed in thinner substrates.
- 7) ILMs formed with AgBF₄ in glycerol solutions could be studied as it may not require the presence of water for facilitation of olefins. However, the role of water in facilitation of olefins by AgBF₄ is not conclusive.

CHAPTER 4

CARBON DIOXIDE SEPARATION WITH NOVEL SOLVENTS

4.1 Introduction

As discussed in Chapter 2, solvents industrially used for carbon dioxide separation from gas mixtures are frequently aqueous solutions of various amines. These amines include primary, secondary, tertiary and sterically hindered ones and/or mixtures of various amines. Even though they are currently used in industrial gas cleaning, most amines are volatile and toxic in nature; there is continuing loss with use. Due to more stringent air quality standards, the presence of these amines in the process/exhaust streams will pose a major problem. There is a need to identify new solvents/carriers which are non-toxic and non-volatile. In Chapter 2, polyamidoamine (PAMAM) dendrimer was identified as one such solvent/carrier with excellent facilitation for carbon dioxide. As part of the continuing efforts to identify such solvents, new solvents/carriers are explored in the present thesis for carbon dioxide separation from gas mixtures. One such solvent is glycerol carbonate which is likely to have a high solubility for CO_2 unlike glycerol.

There are several industrial processes for separating CO_2 based on physical/chemical solvents (Kohl and Riesenfeld, 1979). In order for the solvent based process to be practical, the solvents should have higher solubility for CO_2 than in water, must have extremely low vapor pressure, low viscosity and low or moderate hygroscopicity. Some of the solvents used are: methanol at low temperatures (Rectisol process), propylene carbonate (Fluor process), N-methyl-2-pyrrolidone (Purisol process), dimethyl ether of polyethylene glycol (Selexol process), tributylphosphate (Estasolvan process) and mixture of diisopropanolamine, sulfolane and water (Sulfinol process). Most of these solvents have higher solubility for H_2S than for CO_2 . Another common feature of these processes is that they are used in contactor-stripper mode, requiring two separate steps in CO_2 separation. None of these systems appear to have used glycerol carbonate for absorption or in a liquid membrane configuration. Glycerol carbonate is explored in the present study as a physical solvent in an immobilized liquid membrane configuration.

Common name	Glycerine carbonate		
Chemical formula	4-hydroxymethyl-1,3-dioxolan-2-one		
Chemical composition	C ₄ H ₆ O ₄		
Molecular weight	118		
Chemical structure			
Specific gravity	1.4		
Viscosity	44 cSt at 25 °C		
pH	6.5		
Boiling point	137-140 °C @ 0.5 mm Hg		
Solubility in water	1-10%		
Surface tension ^c	42 dynes/cm		
Toxicity	Non-toxic		

Table 4.1 Important characteristics of glycerol carbonate^{a,b}

a MSDS sheet, Huntsman Corporation, 1999

b Sigma-Aldrich Catalog, 2001

c Determined in a Kruss Interfacial Tensiometer at 20 °C. (Chapter 5)

Glycerol carbonate (also referred to as glycerine carbonate) is an experimental compound under trade name JEFFSOL[®] GLYCERINE CARBONATE (Huntsman, 1999). Some important characteristics of glycerol carbonate are provided in Table 4.1.

It should be noted that most of the alkaline carbonates (glycerol carbonate is one of them) are being developed as alternative "safe and environmentally friendly" solvents to conventional aromatic solvents. Glycerol carbonate satisfies most of the requirements for an ideal solvent for carbon dioxide separation. It is non-toxic and non-volatile (vapor pressure is reported to be very low). It will be of interest to study if glycerol carbonate can be an effective physical solvent for separation of carbon dioxide. It also would be of interest to study glycerol carbonate as an alternative solvent to either water or glycerol for dissolving various facilitating carriers such as sodium glycinate, sodium carbonate and dendrimers etc.

In the present thesis, glycerol carbonate in its pure form and in the presence of a few carriers have been studied in an immobilized liquid membrane configuration for separation of CO_2/N_2 mixtures. The main questions the present exploratory work attempts to address are:

- Can glycerol carbonate be used effectively as a solvent in its pure form for selective separation of carbon dioxide from gas mixtures?
- 2) Whether carbon dioxide concentration in the feed gas mixture (and hence carbon dioxide partial pressure difference across the membrane) has any effect on the carbon dioxide transport across glycerol carbonate-based liquid membranes?
- 3) Is the selectivity observed by glycerol carbonate dependent on the presence of moisture in the feed stream?
- 4) Does the thickness of the substrate (and that of the ILM) has any effect on the selectivity for and transport of carbon dioxide?

5) What are the effects of an addition of sodium glycinate and dendrimers on the separation behavior of the ILMs?

4.2 Experimental Details

Glycerol carbonate in its pure form was obtained from Huntsman Corporation (Huntsman Petrochemical Corporation, Houston, TX) as a research sample. It was used in all experiments without any further purification. 0.06M PAMAM dendrimer of generation zero in glycerol carbonate solution was prepared by dissolving pure dendrimer in glycerol carbonate. Preparation of liquid membranes having higher concentrations of dendrimer in glycerol carbonate was not attempted. Liquid membranes containing 0.1M sodium glycinate in glycerol carbonate was prepared by dissolving the required amount of sodium glycinate in glycerol carbonate and stirring it overnight. Higher concentrations of sodium glycinate (0.5M) tended to precipitate in the solution. Sodium carbonate could not be dissolved at all in glycerol carbonate.

The method of preparation of ILMs was similar to those for other ILMs studied in the present thesis and posed no significant problems. Wetting of both PVDF and hydrophilized Celgard films was almost instantaneous. Excess solution from the surfaces of the substrate was removed with kimwipes. All ILMs formed in this work were full ILMs filling the void region of the substrates completely. The experimental setup used in CO_2 separation studies with dendrimer liquid membrane was also used for the present work. All experiments employed dry helium as sweep gas while the feed gas was introduced after complete humidification. A few experiments were done with dry feed gas to study the effect of water vapor on the overall performance of glycerol carbonatebased liquid membranes. The calculation procedure for determining the permeance, the permeability of each gas species (CO₂ and N₂), and separation factor of the liquid membrane ($\alpha_{CO2/N2}$) and the parameters used earlier to describe the glycerol carbonate-based ILMs are same as those used for dendrimer liquid membranes.

4.3 Results and Discussion

4.3.1 Effect of Δp_{CO2} on the Performance of Pure Glycerol Carbonate ILM

Figure 4.1 and Table 4.2 present the performances of pure glycerol carbonate ILMs in a hydrophilic PVDF substrate of 100 μ m thickness having an average pore size of 0.1 μ m. The carbon dioxide partial pressure difference across the membrane was varied from 0.56 cm Hg to 28.1 cm Hg to observe any dependence of the ILM performance on Δp_{CO2} . The pure glycerol carbonate ILM was also exposed to dry feed gas to study the effect of moisture on the ILM performance. Figure 4.1 presents the variation of permeability of carbon dioxide, and the selectivity of the ILM for carbon dioxide over nitrogen against carbon dioxide partial pressure difference across the membrane.

Under humidified feed conditions, the carbon dioxide permeability ranged between 377 and 284 Barrers for the CO₂ partial pressure differences studied with no clear signs of significant facilitation at lower Δp_{CO2} s. The selectivity of the ILM ($\alpha_{CO2/N2}$) ranged between 86 and 105, depending on the nitrogen permeability. The $\alpha_{CO2/N2}$ and Q_{CO2} of glycerol carbonate ILM does not appear to be affected by Δp_{CO2} across the membrane, which is highly significant. Similarly, under dry feed gas conditions, the Q_{CO2} s were reduced to about one third of the humidified Q_{CO2} values. For the same Δp_{CO2} range, the Q_{CO2} values under dry feed gas conditions ranged from 77 to 109 Barrers with selectivities ranging from 88 to 127. The ILMs were found to be stable in the absence of water vapor in the feed gas mixture. Glycerol carbonate is partially miscible with water. In the presence of water in the feed gas, due to the sorption of water, the viscosity of glycerol carbonate ILM would be reduced, increasing the diffusion coefficients of both nitrogen and carbon dioxide in the liquid.

Δp_{CO2} ,	Feed	$(\mathbf{Q}_{\rm CO2}/t_{\rm m})_{\rm eff},$	$(Q_{N2}/t_{m)eff},$	Q _{CO2} , Barrer	Q _{N2} , Barrer	$\alpha_{\rm CO2/N2}$	
cm Hg	conuntion	Hg	Hg	Darrei	Darrei		
	(0.1 μm PVDF sub	ostrate; thickness	s 100 μm			
0.56	Humid	9.71E-07	1.84E-08	358	6.8	53	
2.14	Humid	1.02E-06	9.80E-09	377	3.6	105	
5.34	Humid	7.40E-07	7.70E-09	284	2.84	96	
28.1	Humid	8.73E-07	1.01E-08	322	3.74	86	
2.14	Dry	2.95E-07	2.33E-09	109	0.86	127	
5.34	Dry	2.10E-07	2.40E-09	77	0.88	88	
28.1	Dry	2.63E-07	2.99E-09	97	1.1	88	
	H	ydrophilized Cels	gard 2400; thickr	ness 25 μm			
0.55	humid	2.46E-06	4.47E-08	347	6.3	55	
2.32	humid	1.88E-06	4.20E-08	265	5.92	45	
28.10	humid	1.86E-06	3.08E-08	262	4.35	60	
28.1	dry	1.15E-06	2.47E-08	162	3.48	47	
2 PVDF substrates sandwiched; thickness 200 µm							
2.14	humid	3.77E-07	4.32E-09	278	3.2	87	
26.43	humid	3.00E-07	4.23E-09	221	3.12	71	

Table 4.2 Performance of pure glycerol carbonate ILMs in PVDF andhydrophilized Celgard substrates



Carbon dioxide partial pressure difference (Δp_{CO2}), cm Hg

Figure 4.1 Performance of pure glycerol carbonate ILM in PVDF substrate.

4.3.2 Effect of Feed Gas Relative Humidity

The behaviors of pure glycerol carbonate liquid membranes under both humidified and dry feed gas conditions indicate that the transport of both carbon dioxide and nitrogen are not substantially affected by the concentration of carbon dioxide in the feed gas mixture (and Δp_{CO2}). Any trend observed in the variation of $\alpha_{CO2/N2}$ with Δp_{CO2} is the result of the variation of Q_{N2} from experiment to experiment rather than any particular trend in variation of Q_{CO2} . The corresponding effective permeances of carbon dioxide and nitrogen for these conditions are provided in Table 4.2. This table indicates that glycerol carbonate in its pure form as the liquid membrane does not react with carbon dioxide reversibly as any facilitated transport carrier does and behaves like a physical solvent for carbon dioxide. The observed selectivity of glycerol carbonate for carbon dioxide over nitrogen could only be achieved due to considerably higher solubility of carbon dioxide as compared to that of N₂ in glycerol carbonate. The diffusion coefficients of CO₂ and N₂ are likely to be similar, due to their molecular sizes. This is a very significant observation.

Comparing with other solvents conventionally used, water has a $\alpha_{CO2/N2}$ of about 40 (Bhave and Sirkar, 1986) while pure glycerol without any sorbed moisture has a $\alpha_{CO2/N2}$ of only about 2 (Chen et al., 1999). Values of solubility of CO₂ and N₂ in either glycerol or glycerol carbonate are not available, making it difficult to compare the solubility behavior. It can be definitely inferred from Figure 4.1 that glycerol carbonate either has much higher solubility for carbon dioxide or much reduced solubility for nitrogen, resulting in higher selectivities; further such a behavior is not affected by the presence of water. Presence of water vapor in the feed gas (and in the liquid membrane) has the effect of increasing the permeabilities of both CO₂ and N₂ proportionally. Compared to this behavior, presence of water in glycerol ILM dominates its behavior by increasing Q_{CO2} significantly without a corresponding increase in nitrogen permeation

resulting in an increase in $\alpha_{CO2/N2}$ from 2 to 40 under humidified feed conditions (Chen et al., 1999). It appears that glycerol carbonate is an ideal CO₂-selective solvent.

4.3.3 Effect of Liquid Membrane Thickness

Pure glycerol carbonate ILMs were studied in a 25 μ m hydrophilized Celgard substrate. The behavior is shown in Figure 4.2 and Table 4.2.



Carbon dioxide partial pressure difference (Δp_{CO2}), cm Hg

Figure 4.2 Performance of pure glycerol carbonate ILM in hydrophilized Celgard 2500 substrate.

For the range of carbon dioxide partial pressure differences studied between 0.55 and 28.1 cm Hg, there is no significant variation in carbon dioxide permeability. Q_{CO2} varied between 347 and 262 Barrers with the range of selectivity being 45 and 60. The somewhat lower selectivities observed in the case of Celgard substrates compared to PVDF substrates are expected. As noted in the chapter on dendrimer liquid membranes (Chapter 2), and elsewhere (Chen et al., 2000), the hydrophilization of Celgard substrates does not appear to be uniform and permanent. When the Celgard-based pure glycerol carbonate ILM was exposed to dry feed gas, the ILM was not stable over long time. Reintroduction of humidity on the feed side did not revive the ILM performance, indicating the possible loss of hydrophilicity of at least part of the substrate Celgard membrane. This behavior was also observed with dendrimer liquid membranes and in glycerol-based liquid membranes.

An important feature of any physical solvent for membrane-based carbon dioxide separation would be that its performance is not affected by carbon dioxide partial pressure and the thickness of the substrate. For a facilitated transport liquid membrane, higher thickness of the liquid membrane generally results in a higher value of $\alpha_{CO2/N2}$ and lower (Q_{CO2}/t_m). It has been already shown that carbon dioxide partial pressure does not affect the CO₂-selective behavior of pure glycerol carbonate full ILMs in both hydrophilic PVDF and hydrophilized Celgard substrates.

To verify that the thickness of the substrate (and that of the ILM) does not alter the performance of glycerol carbonate liquid membranes, two 100 μ m PVDF films filled with pure glycerol carbonate were placed one on top of the other to provide a total thickness of 200 μ m. Figure 4.3 compares the behavior of the three liquid membranes



Carbon dioxide partial pressure difference, cm Hg

Figure 4.3 Effect of substrate thickness on pure glycerol carbonate liquid membranes.

having thicknesses of 25 μ m (Celgard), 100 μ m (PVDF), and 200 μ m (2 PVDF membrane composite) for two different CO₂ partial pressures. The permeability of carbon dioxide and $\alpha_{CO2/N2}$ are plotted against the partial pressure difference of carbon dioxide for a humidified feed. The data are also presented in Table 4.2.

There does not appear to be any significant effect of liquid membrane thickness on Q_{CO2} for both Δp_{CO2} s studied. Variation in Q_{CO2} values seen are within the expected experimental variations. Similarly, $\alpha_{CO2/N2}$ values for 100 µm and 200 µm thick liquid membranes are quite similar for both Δp_{CO2} s studied. The selectivities observed in hydophilized Celgard are in reasonable agreement with those of PVDF substrates.

The reasons for this behavior of Celgard substrates are discussed earlier. The data indicate that the CO₂ permeability of glycerol carbonate membranes is essentially independent of substrate thickness and the selectivity can be retained, irrespective of the substrate thickness. In other words, if glycerol carbonate liquid membrane can be formed with thickness less than 25 microns, the Q_{CO2} and $\alpha_{CO2/N2}$ can be expected to be similar to that of 200 µm thick liquid membrane. However, as the permeability is the product of the true permeance and the membrane thickness, a reduction in liquid membrane thickness from 200 mm to say 10 micron, would increase the effective permeance of carbon dioxide by 20 times while maintaining the same selectivity. In essence, with glycerol carbonate, it would now be possible to form ultrathin liquid membranes with high permeances without compromising on its selectivity for carbon dioxide.

4.3.4 Effect of Addition of Carriers to Glycerol Carbonate

As seen above, pure glycerol carbonate liquid membranes provide a very good framework for preparing thinner liquid membranes for providing high CO_2 permeances. It would be of practical importance to see if the carbon dioxide permeances and selectivity can be enhanced further by adding facilitating carriers. A few carriers such as sodium carbonate, sodium glycinate and dendrimers were studied earlier by dissolving them in glycerol. The objective was to study the effect of these carriers by dissolving them in glycerol carbonate. However, sodium carbonate could not be dissolved in glycerol carbonate in any concentration whereas sodium glycinate was found to be sparingly soluble in glycerol carbonate. In the present thesis, a 0.1M sodium glycinate in glycerol carbonate solution was immobilized in a PVDF substrate. A 0.06M solution of PAMAM dendrimer of generation zero in glycerol carbonate could be easily prepared. Liquid membranes with higher concentrations of dendrimer in glycerol carbonate were not studied in the present thesis.

Figure 4.4 and Table 4.3 present the behavior of such glycerol carbonate-based ILMs under various carbon dioxide partial pressure differences. The effect of feed side relative humidity on these liquid membranes was also studied by subjecting the liquid membranes to dry feed gas conditions. Presence of small amounts of dendrimer or sodium glycinate in glycerol carbonate introduces the facilitation transport mechanism to carbon dioxide transport across the liquid membrane. For example, addition of 0.06M dendrimer to glycerol carbonate increases the carbon dioxide effective permeance by a factor of about 18 times for a Δp_{CO2} of 0.52 cm Hg. However, the average nitrogen permeance also increased marginally by a factor of 2, resulting in a $\alpha_{CO2/N2}$ of about 1005. Similarly at a Δp_{CO2} of about 5-6 cm Hg, there is an increase in the effective permeance is added to glycerol carbonate.


Figure 4.4 Performance of glycerol carbonate ILMs with various carriers in

PVDF substrate. Carriers: 0.06M PAMAM dendrimer; 0.1M sodium glycinate

$\begin{array}{c} \Delta \mathbf{p}_{\rm CO2},\\ \mathbf{cm} \ \mathbf{Hg} \end{array}$	Feed condition	$(Q_{CO2}/t_m)_{eff},$ cc/cm ² .s.cm	$(Q_{N2}/t_{m)eff},$ cc/cm ² .s.cm	Q _{CO2} , Barrer	Q _{N2} , Barrer	α _{CO2/N2}	
		Hg	Hg				
	0.061	M PAMAM dend	rimer-glycerol ca	rbonate II	LM		
0.52	Humid	1.78E-05	1.77E-08	6564	6.53	1005	
0.62	Humid	7.87E-06	1.74E-08	2900	6.4	453	
6.13	Humid	1.58E-06	1.53E-08	583	5.64	103	
26.43	Humid	6.52E-07	2.34E-08	240	8.62	29	
30.27	Humid	6.64E-07	2.27E-08	245	8.4	29	
0.62	Dry	-	1.74E-08		6.4		
30.27	Dry	9.30E-08	2.05E-08	34	7.56	4.5	
0.1M sodium glycinate-glycerol carbonate ILM							
0.52	Humid	5.30e-6	1.11e-8	1955	4.1	477	
1.64	humid	2.80E-06	2.82E-08	1031	10.38	99	
5.35	humid	1.76E-06	3.08E-08	647	11.3	57	
17.78	humid	1.27E-06	3.18E-08	469	11.7	40	
27.43	Humid	6.78e-7	1.73e-8	250	6.4	39	

Table 4.3 Performance of glycerol carbonate-based ILMs containing PAMAM dendrimer and sodium glycinate*.

* 100 μm PVDF substrate

However, at higher carbon dioxide partial pressure differences, there appears to be a slight decrease in carbon dioxide effective permeance for dendrimer-glycerol carbonate ILM. Combined with higher nitrogen permeances, the $\alpha_{CO2/N2}$ of such ILM was reduced to 29. This behavior is reproducible. Similar trend could be seen with sodium glycinate-glycerol carbonate ILM also (Chen et al., 2000). It is possible that the effective CO₂ permeance is lower at higher Δp_{CO2} s, due to saturation of dendrimer with CO₂ (carrier saturation) and salting out behavior (reduction in solubility in the presence of a salt). When the dendrimer-glycerol carbonate ILM was subjected to dry feed gas conditions, the CO_2 effective permeance reduced drastically by a factor of 9 compared to humidified feed gas condition. This observation lends credence to the following explanation.

It was observed earlier (Chapter 2) that dendrimer liquid requires a highly humid environment for effective facilitation. So, in the absence of feed side relative humidity, any reduction in CO_2 effective permeance in 0.06M dendrimer-glycerol carbonate ILM should mean a reduced solubility due to the presence of dendrimer and absence of any facilitation. However, the increase in nitrogen permeance in the presence of these carriers can not be explained. The transport behavior of nitrogen is reproducible for both these ILMs and seems constant for different experiments. It can be postulated that the presence of these carriers with their limited solubilities in glycerol carbonate is producing a heterogeneous phase mixture at microscopic level, resulting in potential corridors of increased nitrogen transport. At this point, any rigorous explanation of the observed behavior is not possible without studying these ILMs in greater detail in terms of their solution behavior.

4.4 Implications of These Results for CO₂ Separation

Glycerol carbonate, in its pure form, appears to be an ideal physical solvent for selective CO_2 separation. Its selectivity for CO_2 over N_2 is far superior than that of glycerol and almost two times that of water. The significance of glycerol carbonate is that its selectivity is not dependent on the presence of water vapor in either the feed side or the sweep side. From the exploratory experimental data collected during the present work,

glycerol carbonate liquid membranes were stable for more than a week of continuous operation. Further studies on the long-term stability of glycerol carbonate ILMs are necessary to confirm the promising trend observed in the present work.

Glycerol carbonate has a great potential in many current CO_2 separation applications. Liquid membranes are currently not used in most of the applications where CO_2 is encountered in low concentrations (e.g. atmosphere, space suit) or high concentrations (flue gas, biogas) the reasons mainly being the loss of solvent water and or the carrier. Glycerol has been shown earlier (Chen et al., 1999, 2000, 2001) and in the present thesis (in the context of olefin-paraffin separation) to offer a major improvement in providing stable ILMs. Glycerol carbonate could be the next generation solvent in the place of or in combination with glycerol in providing much higher selectivity for CO_2 even in the absence of moisture in the feed gas mixture.

In the case of CO₂ separation from flue gas mixture, CO₂ concentration in the flue gas is usually between 10-15%. Most of the membrane processes currently have CO₂ selectivities lower than 50 (Matsuyama et al., 1999). In PVA/PEI blend membranes, the CO₂ effective permeance at 30 cm Hg was about 2 GPU having a selectivity of about 50. In addition, these membranes show a dependence of carbon dioxide partial pressure on their permeance and selectivity. This would indicate a dependence on the membrane thickness as well (thickness of the membranes used in this study was 220 μ m). On the other hand, the pure glycerol carbonate liquid membranes in the present work did not show any effect of membrane thickness or carbon dioxide partial pressure on their CO₂ N₂ selectivity and CO₂ permeability. In this sense, if a 5 μ m substrate is immobilized with pure glycerol carbonate ILM, an effective CO₂ permeance of 60 GPU having

a CO_2/N_2 selectivity of 100 can be easily achieved. These values would place such a membrane within the realms of commercial success.

Similarly, in situations where low concentrations of CO₂ are encountered, such as space walk, the glycerol carbonate membranes are ideally poised for greater attention. For example, addition of a small amount of dendrimer (0.06M) to pure glycerol carbonate results in ILM in 100 μ m PVDF substrate with an effective CO₂ permeance of 18 GPU and an $\alpha_{CO2/N2}$ of 1000. A thinner substrate, say 5 μ m thick and a modest increase in dendrimer concentration is bound to result in a stable liquid membrane with an effective CO₂ permeance of at least 100 GPU and an $\alpha_{CO2/N2}$ of 1000. To put this in perspective, the only other membrane with such a selectivity and CO₂ permeance was an aqueous based plasma grafted membrane impregnated with EDA (Matsuyama et al., 1994). The glycerol carbonate-based ILMs are expected to be environmentally friendly and inherently stable compared to the above liquid membranes.

At both ends of the spectrum of CO_2 separation, it appears that glycerol carbonate is likely to play a critical role in the commercialization of liquid membranebased processes for CO_2 separation.

4.5 Conclusions and Recommendations

From the above preliminary study on the utility of glycerol carbonate for carbon dioxide separation, the following conclusions and recommendations for future work can be drawn.

 Glycerol carbonate shows great promise as an attractive physical solvent for carbon dioxide separation. It is non-toxic and environmentally friendly.

- The performances of pure glycerol carbonate ILMs appear to be independent of carbon dioxide partial pressure difference and substrate thickness.
- 3) The CO₂-selective behavior of glycerol carbonate is not affected by the absence of moisture in the feed gas mixture. This makes glycerol carbonate an ideal solvent when RH values less than 100% or variation of feed side humidities are expected. Glycerol carbonate ensures that α_{CO2/N2} remains constant (around 80-100) for any value of feed side relative humidity.
- It is worth exploring the formation of ultra-thin liquid membranes using glycerol carbonate to achieve higher CO₂ permeances and a selectivity of about 80-100.
- 5) There is a need for studying the kinetic and physical parameters of glycerol carbonate with/without any carriers. The present study appears to be the first attempt in employing glycerol carbonate for any membrane gas separation application.

CHAPTER 5

THIN IMMOBILIZED LIQUID MEMBRANES

5.1 Introduction

Immobilized liquid membranes are formed by wetting a given substrate, either polymeric or inorganic, with the liquid solution of choice. Due to capillary action, the membrane liquid will fill the void region of the substrate. Once the liquid enters the porous region, it is immobilized in the pores through physical forces only. As there are usually no chemical forces present to bind the solvent or solute to the substrate, the liquid can disappear from the porous region via:

- evaporation of the solvent and/or carrier
- loss of the liquid membrane if trans-membrane pressure difference exceeds the critical bubble point pressure of the substrate.

Usually, the ILMs are operated below the critical bubble point pressure of the substrate, which is a function of its pore size. The immobilized liquid membranes discussed so far in the present thesis (Chapters 2, 3, 4) occupy the entire void fraction in a given substrate. They are referred to as "full ILMs". The substrates studied mainly were polymeric in nature.

The permeance of a gas species through a liquid membrane is a function of, amongst others, the thickness of the ILM. In facilitated transport liquid membranes, the relationship is nonlinear between the gas species permeances and thickness of the ILM. As the ILM thickness decreases, the effective permeance of all gas species increase with a reduction in the selectivity of the liquid membrane for the gas species of interest (e.g. CO_2 , 1-butene). As the thickness of the liquid membrane decreases, the diffusional path

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length for transport of all species, reacting and non-reacting gas species and their complexes, decreases. However, due to the kinetics of facilitated transport, the rate of increase in the fluxes of the reaction complexes decreases. In other words, the liquid membrane of large thickness will provide the highest possible selectivity and lowest possible permeance for the non-facilitated gas species. In a liquid film of small thickness, the rate limiting step in transport of reacting species-based complexes tend to be kinetics of the facilitation reaction. Theoretical analysis describing the effect of liquid membrane thickness is available in literature (Otto and Quinn, 1971; Guha et al., 1990), but direct experimental verification of this aspect of facilitated transport membranes is limited (Bhave and Sirkar, 1986; Chen et al., 2000). This was mainly due to the non-availability of thin substrates for immobilizing the liquid membranes.

In a non-facilitated liquid membrane, the relationship between the liquid membrane thickness and the permeances of gas species is linear. As the transport mechanism for all gas species is the same through the liquid membrane, whatever the effects of reduced thickness of the substrate are on the gas species of interest are, similar behavior will be observed for other gas species. In other words, the selectivity of the liquid membrane is independent of its thickness. However, few such physical solvents were studied in literature having selectivity for gases like carbon dioxide.

Most of the thin facilitated transport membranes studied in literature were prepared by grafting polymers (mainly gels) on hydrophobic substrates with carriers impregnated in them (Ho and Dalrymple, 1994; Matsuyama et al., 1996). Bhave and Sirkar (1986) studied formation of thin ILMs in a hydrophobic polypropylene substrate of 25 µm thickness by evaporating water partially. However, this technique is restricted to volatile solvents. As already noted, water as solvent makes the ILM unstable. This technique of partial evaporation of solvent can not be extended to non-volatile solvents. It is imperative that any technique of forming thin films should be applicable to the use of non-volatile solvents. Recently, a technique of partial immobilization of the liquid membrane in the pores of a hydrophilic PVDF substrate was attempted via controlling the time allowed for immobilization (Chen et al., 2000). Due to large pore size distribution and interconnected pores, the thin ILMs formed could not withstand reasonable transmembrane pressure differences to be practical. It should be pointed out that in these experiments, the feed gas mixture at a higher pressure was in contact with the liquid membrane on the side of the membrane used for penetration of the liquid.

In the present thesis, two novel techniques are proposed for forming thin ILMs. They are demonstrated by separating CO_2 from gas mixtures either with glycerol carbonate or glycerol-based ILMs. Broadly, the two techniques can be described as:

- 1) formation of an ILM in a thin section of the substrate membrane, and
- formation of a support layer on top of a substrate membrane on which the liquid membrane can be immobilized.

The overall goal in adopting these two techniques in the context of the present thesis is to demonstrate the possibility of improving the carbon dioxide permeances via these techniques and to identify the key parameters that are involved.

5.2 Formation of an ILM in a Thin Section of the Substrate Membrane

Any liquid filling the pores of a substrate can be displaced by a second fluid when the transmembrane pressure difference across the original liquid-in-pores is larger than

a critical pressure called the critical displacement pressure. This is also referred to as the bubble point. The critical displacement pressure is a function of the pore size, surface tension of the membrane liquid (when being displaced by air) and the contact angle between the liquid and substrate. The relationship between these variables and the critical displacement pressure is described by Young-Laplace equation as

$$\Delta p_{cr} = \frac{4\gamma\cos\theta}{d} \tag{5.1}$$

where γ is surface tension of the membrane liquid, θ is the contact angle between the liquid and the substrate and d is the diameter of the pore from which the liquid is displaced. Note "pore size" usually refers to pore radius, r.

For glycerol carbonate ($\gamma = 42$ dynes/cm, Table 4.1) which has very good wetting characteristics ($\theta \sim 0$) for the hydrophilic substrates studied here, it would take a transmembrane pressure of about 245 psi (1.69 MPa) to displace the liquid from a pore diameter of 0.1 µm. Whereas it would take about 367 psi (2.53 MPa) to displace a liquid with similar wettability but a surface tension of about 63 dynes/cm (e.g. glycerol) from the same pore. In general, the smaller is the pore diameter, the greater is the critical displacement pressure. The Young-Laplace equation described here is applicable for straight-through cylindrical pores. For a qualitative analysis of the present technique, the equation is assumed to be applicable for the substrates considered in the present thesis. Even though there is considerable pore size distribution in hydrophilic PVDF membrane, there is no perceived asymmetry in the dimensions of pores along the substrate thickness.

However, the Young-Laplace equation does not take any such asymmetry of the pore into consideration. Even if the pore size on one side of the substrate is different from

the pore size on the other side of the membrane, the above equation is valid. If the pores present in the substrate are asymmetric, it implies that the liquid from the larger pore size regions can be displaced by applying a certain transmembrane pressure difference, while the liquid from the smaller pore size regions (called "skin region") will not be displaced. In other words, by applying a transmembrane pressure slightly above the critical displacement pressure for pores of a certain size, it is possible to displace all the liquid from such pores except in a thin region (skin region) of the substrate membrane whose pore sizes are smaller. This concept is schematically shown in Figure 5.1.

The main difference between the ILMs formed with this technique and some of the thin ILMs studied in literature (Bhave and Sirkar, 1986; Chen et al., 2000) is that the present technique utilizes the asymmetry of the pores in a given asymmetric or composite substrate. In other words, the present technique is applicable to asymmetric substrate membranes and not to symmetric substrate membranes. However, the perceived advantage of the present technique is that it can lead to stable and thin ILMs in a small section of the substrate and is easily applicable to non-volatile solvents.



Figure 5.1 Schematic of thin ILM formation via displacement of pore liquid

Figure 5.2 presents the relationship between the critical displacement pressure and the diameter of the pore from which the liquid will be displaced under that pressure.

The pore diameter at the critical pressure is shown on a logarithmic scale. Two representative liquids, one having a surface tension of 42 dynes/cm and one having a surface tension of 63 dynes/cm are considered as the liquid membranes to be displaced



Figure 5.2 Relationship between the critical displacement pressure for an ILM and pore diameter.

from the larger pores of an asymmetric microporous substrate. While the higher surface tension considered in this analysis is that of pure glycerol, the lower value is that of glycerol carbonate. The surface tension of glycerol carbonate was experimentally determined to be 42 dynes/cm using an interfacial tensiometer by De Nuoy ring method (Model K8, Kruss, Burlington, MA). For convenience, the ILMs are referred to as glycerol ILMs and glycerol carbonate ILMs.

The objective of the above analysis is to demonstrate the potential of the proposed technique rather than attempting to predict the behavior of such a thin ILM formed. It should be mentioned that most membranes, either polymeric or ceramic, do have a pore size distribution both along and across the substrate membrane.

When a small value of excess pressure is applied across the full ILM, the liquid from the largest pore region will be displaced. For example, it can be seen from Figure 5.2 that when a pressure of, say 20 psig is applied, glycerol carbonate ILM will be pushed out of pores or porous region having diameters greater than 1.22 µm, whereas pure glycerol ILM will be displaced only from pores or porous region having diameters larger than 1.83 μ m. Similarly, it would be difficult to displace pure glycerol ILM from a pore of 0.18 µm diameter when a transmembrane pressure of 200 psig (typical maximum allowed pressure for the housing of ALCOA ceramic membrane used here) is applied from shell side. However, when similar pressure is applied to polysulfone membrane having a pore diameter of 0.1 μ m, glycerol carbonate can be hypothetically completely displaced from the pores when a pressure of about 240 psig is applied. It should be noted that the above analysis assumes no pore size distribution in the microporous substrate. As with any polymeric membrane (except track-etched membranes), pore size distribution can be expected. The displacement pressures discussed above would in essence reflect the largest pore size in a given substrate.

The present analysis indicates two major aspects of non-aqueous solvent based ILMs for gas separation, particularly for carbon dioxide separation. It would be easy to form thinner ILMs with glycerol carbonate than with glycerol for the same maximum pressure allowed by practical constraints. At the same time, thinner ILMs formed with glycerol can withstand higher transmembrane pressure differences than those formed with glycerol carbonate. These two features will have great significance in designing ILM systems to suit particular applications.

5.2.1 Experimental Details

The hollow fiber substrates studied in the present thesis, particularly polysulfone hollow fibers, are asymmetric in nature. The present technique of partial displacement is demonstrated using two types of substrates: polysulfone (0.05 μ m average pore size with the skin on the inside diameter) and an ALCOA tubular ceramic membrane (US Filter, Lowell, MA) having the skin on the inside diameter. The details of polysulfone hollow fibers are provided in Chapter 2 (Table 2.4). Details of the ceramic module are provided in Table 5.1. It should be pointed out that while polysulfone fiber modules were fabricated for these experiments, a stainless steel casing was already available for the ceramic substrate (Cha, 1994). The ceramic module is a composite having multiple layers formed with γ -Al₂O₃ on a very thick (1500 μ m) α -Al₂O₃ substrate. Due to the multiple steps involved in the membrane making, the porosity of each particular layer is different. In polymeric asymmetric membranes, the asymmetry can be obtained by having a composite layer on a porous substrate (e.g. MPF series nanofiltration membranes of Koch Membranes, Wilmington, MA) or during the membrane making itself (e.g. phase inversion membranes for reverse osmosis). Depending on the procedure, the porosity and pore structure of the given membrane will change along its thickness.

Two types of liquid membranes were employed to form thin ILMs in the present thesis. Pure glycerol carbonate was studied in both polysulfone and ceramic membranes. Glycerol carbonate, as discussed earlier (Chapter 4), is a physical solvent selective for carbon dioxide. The variation in the CO_2 permeances can be expected to be linear with the inverse of the thickness of the liquid membrane. A 2.25M sodium glycinate-glycerol liquid membrane was studied in the ceramic membrane to observe the effect of reduced thickness of the ILM on CO_2 permeance for a facilitated transport membrane.

	Layer	Material	Pore diameter (µm)	Porosity (%)	Thickness (µm)
Membrane	1	γ-Al ₂ O ₃	0.005	50	5
	2		0.2	35	30
	3		0.8	40	50
Support		α -Al ₂ O ₃	10-15	40-45	1500

Table 5.1 Specifications of ALCOA ceramic membrane^a

a Cha (1994).

The first step in the thin ILM formation was similar to that of formation of a full ILM. The liquid membrane was introduced from the shell side of the substrate membranes (polysulfone and ceramic membrane) by completely filling the shell side for at least a few hours. This step was taken to ensure that all the pores of the substrate were filled with the liquid membrane. The shell side was drained by removing the excess liquid and nitrogen was passed for at least 30 minutes at high flow rates on both shell and

tube sides to purge any excess liquid. Experiments done with these modules yielded the CO₂ permeances characteristic of full ILMs.

As smaller pore sizes are expected in the skin region of the substrate fibers, a specific pressure was applied from the shell side for at least one hour to displace the liquid membrane from the large pore region of the substrate. This procedure was repeated by increasing the pressure in specific increments after obtaining data with the thinner ILMs formed with this technique at a lower pressure.

5.2.2 Results and Discussion

Figure 5.3 and Table 5.2 present the experimental results on thin ILMs formed in the ALCOA ceramic module. ILMs were formed with both pure glycerol carbonate and 2.25M sodium glycinate-glycerol solutions. In Figure 5.3, the effective permeances of carbon dioxide and nitrogen are plotted against the pressure applied to displace the ILM in the larger pores.

5.2.2.1 Glycerol carbonate thin ILMs in the ceramic membrane. The ideal approach for demonstrating the technique of partial displacement of the pore liquid is to use a physical solvent which will provide almost linear behavior for permeance with the pressure applied to displace the liquid form the pores. For a pure glycerol carbonate ILM filling the entire porous region of the ceramic module, the carbon dioxide effective permeance was about $7.74 \times 10^{-8} \text{ cc/cm}^2$.s.cm Hg for a feed gas mixture containing 24.7% CO₂. Such a low value of carbon dioxide effective permeance is not unexpected as the total thickness of the full ILM in the ceramic membrane was about 1585 µm, almost 16 times that of a PVDF membrane used in most of the present thesis. However, there

appears to be some minor defects in the membrane, allowing a small fraction of nitrogen, resulting in a loss of selectivity. Similar nitrogen permeance was observed when 2.25M sodium glycinate-glycerol ILM was studied in the same module. As mentioned earlier, the ALCOA ceramic module used in the present work was used earlier (Cha, 1994) and it is possible that the module or the gaskets separating the shell and tube sides developed defects with time. The main focus in rest of the discussion will be on the effective permeance of carbon dioxide.

Table 5.2 Effect of applied pressure for forming thin ILMs in various modules viapartial displacement of pore liquid

ILM	Pressure applied,	(Q _{CO2} /t _m) _{eff} , cc./cm ² .s.cm Hg	$(Q_{N2}/t_m)_{eff},$ cc./cm ² .s.cm Hg	Selectivity, $\alpha_{\rm CO2/N2}$			
	Pure glycerol car	bonate II M in AI	COA ceramic modu	ıle ^a			
Full		7.74×10^{-8}	9.09×10^{-9}	85			
1 411	77	7.71×10^{-7}	1.95×10^{-8}	38			
	110	1.44×10^{-6}	2.70×10^{-8}	53			
	150	2.26×10^{-6}	3.32×10^{-8}	68			
2	.25M sodium glvc	inate-glycerol in A	LCOA ceramic mo	dule ^a			
Full	0	6.17 x 10 ⁻⁹	9.15 x 10 ⁻⁹	1			
	10	1.17 x 10 ⁻⁷	8.99 x 10 ⁻⁹	13			
	23	7.66 x 10 ⁻⁷	6.95 x 10 ⁻⁹	110			
	35	1.40 x 10 ⁻⁶	2.47 x 10 ⁻⁸	57			
	45	1.57 x10 ⁻⁶	2.89 x 10 ⁻⁸	54			
	62	1.24 x 10 ⁻⁶	2.67 x 10 ⁻⁸	46			
	95	9.87 x 10 ⁻⁷	1.87 x 10 ⁻⁸	53			
	150	9.86 x 10 ⁻⁷	1.82 x 10 ⁻⁸	54			
Pure glycerol carbonate ILM in polysulfone module ^a							
Full	0	4.04 x 10 ⁻⁶	4.48 x 10 ⁻⁸	90			
	10.5	5.32 x 10 ⁻⁶	6.52 x 10 ⁻⁸	82			
	20	6.83 x 10 ⁻⁶	$1.04 \ge 10^{-7}$	66			
	30	5.17 x 10 ⁻⁶	7.08 x 10 ⁻⁸	73			
	36	7.01 x 10 ⁻⁶	9.28 x 10 ⁻⁸	76			

a Module log mean area 59.5 cm^2 .

b module log mean area 49.95 cm^2 .



Figure 5.3 Thin ILMs formed via partial displacement of pore liquid in ALCOA ceramic module. ILMs: pure glycerol carbonate, feed: 24.7% CO_2 -N₂ at 6 psig; 2.25M sodium glycinate-glycerol, feed: 25.4% CO_2 -N₂ at 6.5 psig. Feed humidified, on shell side.

When about 77 psig pressure was applied from the shell side, the effective permeance of carbon dioxide increased by an order of magnitude, indicating that the resulting ILM was in fact much thinner than the full ILM. When about 110 psig pressure was applied on the shell side, the ILM had an effective carbon dioxide permeance of 1.44×10^{-6} cc/cm².s.cm Hg (1.44 GPU), 20 times that of full ILM. Further application of pressure at 150 psig, increased the carbon dioxide permeance even more to about 2.26 GPU. The ILM formed under such pressure was studied continuously for about a week with no signs of any changes in either selectivity or the carbon dioxide permeances. It should be mentioned that the selectivity achieved during the latter part of the experiments was about 68, close to what was observed in PVDF flat membranes. This confirms that the module has some defects resulting in higher nitrogen fluxes in the initial stages which were plugged under higher pressures.

5.2.2.2 Sodium glycinate-glycerol ILMs in the ceramic membrane. When a facilitated transport liquid membrane was employed in producing thin ILMs using the partial displacement technique, the behavior was similar to that of glycerol carbonate. Because of higher viscosities associated with sodium glycinate-glycerol systems (Chen et al., 2000) and the large thickness of the ceramic module, the effective carbon dioxide permeance for a full ILM of 2.25M sodium glycinate-glycerol solution was about 6.17 x 10^{-9} cc/cm².s.cm Hg. This value was increased drastically by about 19 times to about 1.17 x 10^{-7} cc/cm².s.cm Hg when the shell side was pressurized at 10 psig to displace the liquid from the large pores in the support region. Subsequent increases in the applied pressures for displacement between 35 and 150 psig increased the CO₂ effective permeance to a maximum about 1.57 x 10^{-6} cc/cm².s.cm Hg and a stable $\alpha_{CO2/N2}$ value of around 50 for a 24.7% CO₂ in the feed gas mixture at 6 psig feed gas pressure. The slight decrease in the effective permeances of carbon dioxide and nitrogen could be partly due

to carrier saturation and/or higher water flux across the ILM due to its smaller thickness. It was shown that glycinate-glycerol ILMs transmit higher amount of water across them (Chen et al., 2000). This would result in reduced feed outlet RH and resultant increase in the ILM viscosity. There are theoretical studies (Otto and Quinn, 1971; Guha et al., 1993; Matsuyama et al., 1999) indicating a decrease in aqueous-based ILM selectivity with reduced thickness. However, the behavior of glycerol as a solvent is different from that of water and this aspect needs to be studied further to draw more definite conclusions.

5.2.2.3 Pure glycerol carbonate ILMs in polysulfone hollow fibers. Pure glycerol carbonate ILM was studied in polysulfone fibers to observe the effects of reduced thickness on the ILM performance. Figure 5.4 and Table 5.2 present such data obtained by increasing the applied pressure on the shell side of polysulfone module successively in small increments. As can be seen, the trend of increasing carbon dioxide permenaces with increased applied pressure is unambiguous. As can be expected from pure glycerol carbonate ILMs, the selectivity of the liquid membrane for CO₂ over N₂ remained essentially constant for the pressure range studied, while the carbon dioxide effective permeance increased by almost 2 times.

When pressures higher than 36 psig were applied, the fiber-epoxy interface developed stresses, breaking a few fibers. The same behavior was observed with another polysulfone module prepared for these experiments, indicating systemic stresses. It should be pointed out that hydrophilized polysulfone fibers are known to be fragile.



Figure 5.4 Thin ILMs formed via partial displacement of pore liquid in polysulfone hollow fiber membranes. ILM: pure glycerol carbonate. Feed: 0.53% CO₂-N₂ mixture at 6 psig; humidified; flowing on shell side.

An attempt was made to explore the above technique in flat membranes using hydrophilic nanofiltration membranes (MPF 44, Koch Membranes Inc., Wilmington, MA) with pressure applied from the substrate side. Due to the nature of the membrane preparation (possibly lamination of a composite film on top of the substrate), it was observed that due to delamination, the membrane/coating was buckled under pressure and developed defects.

5.3 Formation of a Support Layer for the Immobilized Liquid Membrane

If an ILM is located in a thin support film on top of a substrate matrix, it can be expected that the thickness of the ILM is very small compared to that of a full ILM, and equal to that of the thin support film. The practical utility of the thin ILM formed will essentially depend on the support film formed. The support film should have the following characteristics for a successful thin ILM:

- it should offer as little resistance to the transport of gas species as possible by having as open a structure as possible;
- it should be able to withstand reasonable transmembrane pressures;
- it should be possible to form on any type of substrate matrix, either flat films or hollow fiber modules without much difficulty.

As mentioned earlier, thin films (or support matrices) were formed on hydrophobic substrates in literature for facilitated transport membranes for gas separation (Ho and Dalrymple, 1994; Matsuyama et al., 1996; Quinn et al., 1997) by adopting various techniques. Most of these thin ILMs have thicknesses ranging from 2.9 μ m to 50 μ m. In the present thesis, a novel way to form such thin porous films by interfacially polymerizing the support film on a porous substrate matrix was explored.

Interfacial polymerization occurs between a water soluble reactant A and an organic soluble reactant B at the aqueous-organic interface (Cadotte et al., 1981). The polymeric films formed through interfacial polymerization generally are very thin in micron range and have been primarily used as reverse osmosis and nanofiltration membranes. Formation of interfacially polymerized thin films on substrates for supported

liquid membranes has been a recent activity (Clement and Hossain, 1997; Wang et al.,1998; Kemperman et al., 1998), directed toward improving their stability for metal recovery from an aqueous feed into an aqueous strip. The present work appears to be the first attempt in using the interfacially polymerized films for immobilizing liquid membranes in them. A schematic of a thin ILM on a support layer is shown in Figure 5.5.



Support film Formed via Interfacial polymerization

Microporous substrate

Figure 5.5 Schematic of the thin ILM on a support layer formed via interfacial polymerization

The formation of thin films on substrates, either flat films or hollow fibers, depends on the reaction system selected for the film formation. This includes the selection of the reactants and the organic solvents, the concentrations of the reactants, the duration of the reaction, the pre- and post- treatment of the thin film and/or the ILM. Some of the parameters that are important in the thin ILM performance are: initial carrier concentration on the performance of the ILM for a facilitated transport system, the ability of the thin film ILMs to withstand transmembrane pressures, selectivities and fluxes of the gas species, particularly at higher partial pressure ranges of carbon dioxide.

5.3.1 Experimental Details

For demonstration of the technique, hydrophobic Celgard flat films were used for forming the support layer. There are many reaction systems possible for interfacial polymerization. The objectives of the present thesis are, however, restricted to demonstrating the concept and its applicability in the context of ILMs for gas separation. An aqueous phase containing hexane diamine in concentrations up to 4% and an organic phase of xylene containing sebacyl chloride up to concentrations of 4% were chosen to form the support layer on hydrophobic Celgard films. Details of the support layer formation and the possible variations in the techniques are provided in Appendix B.

5.3.2 Results and Discussion on Thin ILMs Formed via Interfacial Polymerization

5.3.2.1 Glycerol carbonate ILMs. As discussed in the earlier section on thin ILMs formed via partial displacement of pore liquid, a suitable way to demonstrate the implications of forming thin ILMs via interfacial polymerization would be to employ pure glycerol carbonate as the ILM. As discussed in Chapter 4, glycerol carbonate provides the ideal situation. The resultant effective permeances of CO_2 and N_2 are not significantly affected by the carbon dioxide partial pressure. Also, exposure to dry feed gas does not affect the selectivity of pure glycerol carbonate.

Table 5.3 presents the data on the thin ILMs formed via interfacial polymerization. These ILMs were exposed to both humidified and dry feed gas mixtures. For comparison, full ILM data obtained in a hydrophilized Celgard 2500 substrate were also presented. The thin ILMs were formed under three different reactant concentrations.

ILM	Feed pressure,	Δp _{CO2} , cm Hg	$(Q_{CO2}/t_m)_{eff},$ cc/cm ² .s.cm Hg	$(Q_{N2}/t_m)_{eff},$ cc/cm ² .s.cm	α _{CO2/N2}	
	psig	Humidi	fied feed gas	IIg	<u> </u>	
					· · · · · · · · · · · · · · · · · · ·	
Celgard 2500 full ILM	6.7	28.1	1.86e-6	3.08e-8	60	
Thin ILM ^a	6.7	28.1	4.24e-6	1.37e-7	31	
Thin ILM ^b	6.7	28.1	3.29e-6	1.21e-7	27	
Thin ILM ^c	9	30.27	1.44e-5	4.97e-7	29	
Thin ILM ^d	9	30.27	1.21e-5	3.99e-7	30	
Dry feed gas						
Thin ILM ^a	6.7	28.1	2.27e-6	8.10e-8	30	
Thin ILM ^c	9	30.27	7.32e-6	3.11e-7	24	
Thin ILM ^d	9	30.27	7.27e-6	3.08e-7	24	
Thin ILM ^d	9	0.63	5.54e-6	2.51e-7	22	

Table 5.3 Thin ILMs of pure glycerol carbonate via interfacial polymerization

a support layer formed with 4% hexane diamine aqueous solution and 4% sebacyl chloride in xylene solution.

b support layer formed with 4% hexane diamine aqueous solution containing 10% glycerol and 4% sebacyl chloride in xylene solution.

c support layer formed with 2% hexane diamine aqueous solution and 2% sebacyl chloride in xylene solution.

d support layer formed with 1% hexane diamine aqueous solution and 1% sebacyl chloride in xylene solution.

By immobilizing the liquid membrane on a thin support layer formed with 4% each of reactants on a hydrophobic Celgard substrate, the effective CO_2 permeance was increased by more than 2 times that of the full ILM. Dilution of the reactant concentrations for forming the support layer was supposed to reduce the possible thickness of the support layer. This rationale was supported with the ILM formed on a support layer formed with reactants with 2% concentration each. The effective CO_2 permeance was increased to 1.44 x 10⁻⁵ cc/cm2.s.cm Hg, almost 8 times that of the full ILM. Further reduction in reactant concentrations does not appear to improve the ILM

performance beyond this value. As was seen earlier with the hollow fiber substrates, the nitrogen permeance in all these thin ILMs was relatively higher, resulting in $\alpha_{CO2/N2}$ s of around 30. This is possibly due to two reasons. The first reason is due to the very fine pore structure formed in the support layer, the immobilization of the liquid membrane in the support layer may not be complete. This would provide channels for additional nitrogen transport resulting in a reduction in selectivity. The second reason could be that the support layer inherently may have higher permeances for both the gases. This would have the net effect of diluting the selective behavior of glycerol carbonate with non-selective behavior of the support layer. This situation would be analogous to that observed with dendrimer-glycerol ILMs studied in Chapter 2. In that particular ILM, an increase in glycerol concentration in the ILM diluted the selective behavior of the dendrimer liquid.

Of equal significance in the case of thin ILMs formed via interfacial polymerization was their ability to withstand dry gas mixtures. One of the problems associated with hydrophilized Celgard 2500 membranes (Celgard LLC, Charlotte, NC) in the present work and elsewhere (Chen et al., 2000) was their poor performance in the presence of dry feed gases. After their exposure to dry feed gases, their performance could not be recovered for dendrimer ILMs in hydrophilized Celgard substrate.

The present ILMs were able to withstand dry feed conditions and yielded lower CO_2 effective permeances than when exposed to humidified feed gas. Some of the ILMs in the present study were tested in cycles of humid-dry-humid feed gas mixtures without any apparent loss of performance.

The trend seen with thin ILMs via interfacial polymerization is encouraging. The CO_2 effective permeance was increased by at least 8 times with this approach, indicating that with a proper optimization of parameters, it is possible to obtain very high CO_2 effective permeances without compromising on the CO_2/N_2 selectivity.

There is one important difference in the properties of Celgard substrate (hydrophobic Celgard or hydrophilized Celgard) and the interfacially formed support layer on top of hydrophobic Celgard. The Celgard substrate has a porosity of about 40% and a tortuosity of 2.54. The porosity and thickness of the support layer formed could not be determined in the present study. As the film was formed via polymerization, it can be expected that the porosity of the support layer would be considerably lower than that of Celgard film. In that sense, the results obtained with such less porous thin films are highly encouraging. If the porosity of the support layers could be improved, the CO_2 permeances could be even higher, bringing them close to what is commercially practical.

5.3.2.2 Thin ILMs with sodium carbonate in glycerol solution. Table 5.4 presents the data for thin ILMs formed with 1M sodium carbonate in glycerol on the support layer formed via interfacial polymerization. It also presents the data obtained with full ILMs in the hydrophilized Celgard 2500 substrate.

One of the requirements of a suitable support layer is that it should not offer any resistance to gas transport. This requirement was verified with the support layer formed with 4% hexane diamine aqueous solution and 2% sebacyl chloride in xylene solution. Without immobilizing any liquid membrane on it, the thin support layer yielded very high gas permeances, at least by two orders of magnitude. When 1M sodium carbonate ILM

was formed on the support layer, the bulk transport of both nitrogen and carbon dioxide was prevented.

$\Delta p_{\rm CO2},$	Feed Pressure,	$(Q_{CO2}/t_m)_{eff},$	$(Q_{N2}/t_m)_{eff},$	$\alpha_{\rm CO2/N2}$			
cm Hg	psig	cc/cm ² .s.cm Hg	cc/cm ² .s.cm Hg				
Hydrophiliz	Hydrophilized Celgard 2500 full ILM						
0.52	6	8.47e-6	1.48e-8	572			
0.75	15	5.36e-6	1.24e-8	432			
1.01	25	3.38e-6	1.09e-8	305			
Support lay	Support layer ^a on hydrophobic Celgard 2400 with no ILM						
0.55	5	6.16e-3	8.31e-4	7			
Thin ILM on support layer							
1.93	5	9.80e-6	2.53e-7	39			
2.43	10	9.6e-6	2.44e-7	39			
2.94	15	8.12e-6	2.84e-7	29			
1.91 ^b	5	1.34e-5	1.12e-7	119			

Table 5.4 Full and thin ILMs of 1M sodium car	rbonate in	glycerol
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a support layer formed with 4% hexane diamine aqueous solution and 2% sebacyl chloride in xylene solution. Aqueous solution applied at 5 psig pressure for 1 min.
 b support layer heat treated at 40 °C for 1 hour.

The effective carbon dioxide permeances in the thin ILMs in general are higher than those for full ILMs. Compared to full ILM performance for 1M sodium carbonate on a hydrophilized Celgard 2500 substrate, the thin ILMs provide higher permeances for carbon dioxide by approximately a factor of 7 (by extrapolation of full ILM data) while nitrogen permeance increased by a factor of 25, resulting in lower selectivities. Even though this trend is expected for thin ILMs, the selectivity could be improved by wetting the support layer for longer times and if necessary, applying pressure to make sure the ILM is occupying the entire support layer.

However, due to large nitrogen transport, the selectivities obtained with these ILMs were much lower. The reasons could be the same as those described for glycerol carbonate thin ILMs. The support layer either has unwetted areas or it has relatively higher transport for both gases. When the support film was heat treated at 40 °C for 1 hour, the nitrogen effective permeance was reduced by more than one half. This resulted in the selectivity of the ILM increasing to about 119. Heat treatment of any porous polymer film results in densification of the polymer network. In the present case, the heat treatment could be densifying the support layer, essentially closing the very small porous regions which were the main corridors for nitrogen transport.

5.3.2.3 Dendrimer-based thin film ILMs on PVDF substrate. PAMAM dendrimer has amine functional groups on its surface. It is logical to assume that these amine groups would function in a similar way as the amine groups in hexane diamine in terms of their ability to form polymers. If polymeric thin films could be formed in a <u>controlled manner</u> with PAMAM dendrimer as the aqueous reactant, the resulting polymer film would have remaining free amine groups, presumably as primary amines. This could be a novel way of making functional polymeric membranes for carbon dioxide or other separations. To verify this concept, one such film was formed on a microporous PVDF substrate. Again, the objective was to study the feasibility of such a concept of functional membrane formation.

Table 5.5 presents the data for one such membrane formed and compares it with the full dendrimer ILM. The thin ILM was formed by soaking the PVDF substrate in 4% sebacyl chloride in xylenes for a few minutes; the substrate was drained of any excess organic solution on the surface; the substrate was placed carefully on top of the generation zero pure PAMAM dendrimer solution at room conditions for 2 minutes for the reaction between the dendrimer and sebacyl chloride to occur. After the reaction, vacuum was applied to the membrane+ the dendrimer solution for 1 hour to remove any xylene remaining in the pores of the substrate. The excess dendrimer solution from the surface was wiped thoroughly using kimwipes. The occurrence of the polymerization reaction between the dendrimer and sebacyl chloride was also verified independently in a small sample vial.

ILM $\Delta \mathbf{p}_{\rm CO2}$,		(Q/t) _{eff,CO2}	$(Q/t)_{eff,CO2}$ $(Q/t)_{eff,N2}$	
	cm Hg	cc/cm ² .s.cm Hg	cc/cm ² .s.cm Hg	
Full ^a	5.09	1.06 e-6	5.07e-10	2300
Full ^a	7.68	7.8e-7	5.07e-10	1700
Thin ^{b,c}	5.09	1.36e-6	142.0e-10	100

Table 5.5 Comparative performance of full and thin dendrimer based ILMs.

a) Data interpolated for the CO₂ partial pressures and feed pressure was 3 psig.

b) Thin ILM formed by reacting pure dendrimer liquid with 4% sebacyl chloride in xylene solution

c) Feed pressure was 5.25 psig.

There was marginal improvement in the carbon dioxide permeance with the thin ILMs but a considerable increase in the permeance of nitrogen. This could be due to possible incomplete wetting in a very small area of the membrane contributing to the large nitrogen permeances. The dendrimer solution used for forming thin ILMs was very shallow, possibly leading to this situation. The experiment was run for about 24 hrs without any increase in nitrogen permeance even at the feed pressure of 15 psig. But the carbon dioxide permeance decreased below that of full ILM. This needs to be further investigated.

5.4 Conclusions and Recommendations

The present thesis demonstrated the feasibility of two novel techniques in forming thinner ILMs. One technique was to employ an existing asymmetric membrane and forming the ILM in a thin section of the substrate. The other technique was to form a new support layer on top of a given substrate and immobilizing the liquid membrane on it. The preliminary investigations on both these techniques conducted in the present thesis showed promise on their technical feasibility and potential. From the above work, the following conclusions can be drawn and a few recommendations can be made.

- Thinner ILMs formed with pure glycerol carbonate liquid improved the carbon dioxide effective permeances. Thin ILMs formed via partial displacement technique improved CO₂ effective permeance by about 2 times in the case of polysulfone fibers to about 30 times in the case of ceramic membrane.
- 2) Higher pressures could not be applied in polysulfone based ILMs to form even thinner ILMs due to the fragile nature of hydrophilized polysulfone fibers. With more stable fibers, it should be possible to form thinner and stable ILMs which would give higher CO₂ permeances.
- CO₂ permeance was increased by about two orders of magnitude when thinner ILMs were formed via partial displacement technique in ceramic membranes.
- 4) The nitrogen permeances in general at initial applied pressures were higher than what would be expected compromising the CO_2/N_2 selectivity. However, this aspect is more related to the structure of the substrate rather than the technique.
- Improvement in CO₂ effective permeance of about 8 times was observed with thin ILMs formed via interfacial polymerization technique.

- 6) The thin ILMs formed via interfacial polymerization technique were stable even under dry feed gas conditions.
- 7) Formation of thin films incorporating dendrimers was feasible.
- Methods of immobilizing liquid membranes in both these techniques need to be improved. This would reduce the nitrogen permeation through the liquid membrane, resulting in higher CO₂/N₂ selectivities.
- There is great potential in both techniques for improving the ILM performance to make the ILM based gas separation commercially viable.

CHAPTER 6

THEORETICAL UNDESTANDING OF THE OBSERVED BEHAVIOR OF NON-AQUEOUS ILMS

6.1 Introduction

In terms of the various phenomena that occur during the transport of gases, both reacting and nonreacting, the non-aqueous immobilized liquid membranes present a different scenario compared to any aqueous-based ILMs. The ILMs studied in the present work differ from the other aqueous-based ILMs in many ways. The content of water in the ILM, which is considered essential for CO₂ facilitation reactions, is limited and a variable both in dendrimer and glycerol-based ILMs. The same is true for glycerol carbonatebased ILMs as well. The sweep stream is always a dry gas in the present work. This is a marked difference between the current ILMs and aqueous-based ILMs. The reaction kinetics and physical parameters for the aqueous-based liquid membrane systems are fairly well studied. However, literature data on glycerol-based systems are very limited. It should be borne in mind that the field of dendrimers has been developing only in the past two decades. Further, similar parameters are non-existent for dendrimer-based facilitated transport-diffusion systems and for glycerol-based systems. The present work is the first published application of dendrimers as facilitated transport carriers for carbon dioxide. Similarly, the present thesis appears to be the first attempt in using glycerol carbonate for any gas separation application.

6.2 Unique Features of the Present Experimental Setup

Most of the work in the present thesis and the recent work on glycerol-based ILMs (Chen et al., 1999, 2000) have been performed with flat membrane substrates. In the test cells

used for flat membranes, gas stream inlets and outlets were located in each half-cell with two holes each for the inlet and outlet. This would result in a gas stream, either on the feed side or the sweep side, impinging on the membrane perpendicularly, flowing parallel to the membrane, and then leaving perpendicularly. The feed gas mixture entering the cell is either completely humidified or partially humidified, while the sweep gas entering the cell is always dry. There would be a decrease in the feed side relative humidity from the inlet to outlet because of the permeation of water vapor. As a result, there would be an increase in the sweep side RH at the outlet. These variations of RHs along the feed side and sweep side produce RH gradients in the non-aqueous ILMs which would vary both along and across the ILM.

The variation of water content in the ILM due to RH gradients has considerable effect on the parameters for gas transport:

- The solubilities of gas species, both reacting and nonreacting, change with the water content in the ILM. RH gradients along and across the ILM essentially create solubility gradients along and across the ILM for all gas species. There is limited amount of data available in literature on the variation of the solubility of CO₂ with water content in glycerol. As mentioned earlier, dendrimer and glycerol carbonate -based gas separation is a recent activity and no data exist on solubility of gases in these liquids.
- The diffusivities of gas species, both reacting and non-reacting, change with water content in the ILM. This is mainly due to the change in viscosity of the liquid membrane with water content in it.

6.3 Objectives of the Present Theoretical Interpretation of ILMs

In the present thesis, an attempt has been made to predict the transport rates of nitrogen and carbon dioxide through the glycerol-based ILMs. The exercise has been undertaken primarily to determine the uncertainties involved in the theoretical estimation of transport rates of reacting and non-reacting species through the glycerol-based ILMs. In essence, the present exercise is applicable to olefin-paraffin separation using silver nitrate-glycerol ILMs, glycerol carbonate-based ILMs for carbon dioxide separation, and dendrimerbased ILMs. The uncertainties involved in all these specific applications are same, even though their relative magnitudes could differ.

Permeabilities of nitrogen and carbon dioxide at different RHs through "pure glycerol ILM" where no carrier (sodium glycinate, sodium carbonate, dendrimer, silver nitrate) was present were calculated to establish the baseline behavior of these ILMs. The calculations were based on diffusion coefficients and solubilities of nitrogen and carbon dioxide in glycerol taking into account its water content at different RHs. In this thesis (Chapter 2) and in literature (Chen et al., 1999), the equilibrium water uptake by glycerol for a range of RHs was obtained.

6.4 Estimation of Parameters and Discussion

The values of all parameters for calculations were obtained from the literature or estimated at 25 °C. The diffusion coefficients of nitrogen and carbon dioxide in water were taken as 3.05×10^{-5} and 1.92×10^{-5} cm²/s respectively (Calderbank, 1959). Diffusion coefficients of carbon dioxide in glycerol-water mixtures were obtained from literature (Calderbank, 1959; Krulen et al., 1993) for water content ranging from 12.5%
to 46%. The ratio of diffusion coefficients of nitrogen and carbon dioxide was assumed to be constant for the glycerol-water mixture for the range studied and taken to be equal to that of pure water at 25 °C. Based on this assumption, diffusion coefficients of nitrogen in glycerol-water mixtures were estimated. Solubilities of carbon dioxide and nitrogen in glycerol-water mixtures without any carrier present were estimated based on the approach suggested in the literature (Rischbieter and Schumpe, 1996) and were extrapolated to the glycerol-water mixture range of interest created by the relevant RH environment. The solubility of CO_2 , also available in glycerol-water mixtures (Krulen et al., 1993), was about 10.6% higher than reported by Schumpe (1993). The solubilities and diffusion coefficients thus obtained were interpolated to predict their values at the RHs of interest. The RHs considered were in the range for which the equilibrium water content was available. A sample calculation is shown in Appendix C.

Table 6.1 presents the values of the parameters (solubility, diffusivity, permeability) for both nitrogen and carbon dioxide obtained via this approach. It also presents the experimentally obtained permeabilities of carbon dioxide and nitrogen through pure glycerol ILMs under 100% feed inlet RH conditions (Chen et al., 1999). The average feed side RHs were calculated as (feed inlet RH+feed outlet RH)/2. As can be seen, the general behavior of the pure glycerol-based ILMs can be reasonably predicted from these estimates.

The experimental permeabilities of CO_2 and N_2 compare well with the calculated values, given the fact that the experimental RHs reported are averaged feed side values. The diffusion coefficient and the solubility of the gases change drastically as the RH increases. For example, the predicted value of the permeability increases by about 80%

for a change in RH from 81.7% to 84.5%. For the same change in RH, the predicted permeability of carbon dioxide increases by about 56%. It was not possible to compare the permeabilities at different RH conditions for pure glycerol ILMs.

RH, %	Wt. fraction of water	$D_{N2} x$ 10 ⁶ (a)*	$S_{N2} \ge 10^{5(b)*}$	$Q_{N2} \times 10^{11}$	D _{CO2} x 10 ⁷ (c)*	S _{CO2} x 10 ³ (d)*	Q _{CO2} x 10 ⁹
Predicted	1	- k	·	L		4	-L
48.5	0.157	1.37	1.06	1.45	8.64	3.66	3.16
57.6	0.187	1.54	1.63	2.52	9.72	3.83	3.73
61.4	0.209	1.74	2.06	3.60	11.0	3.96	4.35
63.0	0.221	1.87	2.28	4.28	11.8	4.03	4.75
68.6	0.246	2.20	2.75	6.05	13.8	4.18	5.77
75.2	0.331	3.88	4.38	17.0	24.4	4.67	11.4
81.7	0.366	4.82	5.05	24.4	30.4	4.88	14.8
84.5	0.432	6.99	6.30	44.0	44.0	5.26	23.1
Experim	iental ^(e)						
77.5 ^(f)				28.5			11.0
82.5 ^(f)				38.0			

Table 6.1 Comparison of experimental and predicted behavior inpure glycerol ILMs

- * D_i (diffusivity) in cm²/s; S_i (solubility) in cc(gas)/cm³.cm Hg; Q_i (permeability) in cc(gas).cm/cm².s.cm Hg
- (a) Estimated based on D_{CO2} from Krulen et al. (1993).
- (b) Calculated based on Henry's law constants form Rischbieter and Schumpe (1996).
- (c) From Krulen et al. (1993).
- (d) Calculated based on Henry's law constants from Rischbieter and Schumpe (1996).
- (e) Experimental values from Chen et al. (1999).
- (f) Average value of feed inlet and outlet relative humidities.

For any theoretical or semi-theoretical determination of the effect of carrier on the transport of gases through glycerol-based or glycerol carbonate-based ILMs, one requires the rate constants for the facilitation reaction, change of viscosity and hence diffusion coefficients, and some method to calculate the reduction in solubilities due to the addition

of carriers. Further, the water content varies both across the membrane and along the membrane; this affects the diffusivity and solubility drastically. For the remainder of the analysis, the diffusion coefficients are assumed to be independent of the carrier concentration: this could be a major limitation of this analysis. Because the reaction rate constants are not available for any of the carrier systems studied, the analysis is confined to predicting the nitrogen permeability.

The theory of salting-out of gas species due to the addition of salts is based on aqueous solutions. There are no theoretical or empirical predictions available to calculate the lowering of solubilities with the addition of carriers. This is true even when the carrier is used in its pure liquid form as in pure dendrimer liquid membranes. The parameters available for aqueous salt solutions may not be adequate to describe the phenomena occuring in glycerol-water-salt or glycerol-carbonate-water-salt systems. The salting-out of nitrogen due to addition of 1M sodium carbonate was calculated using the method developed by Schumpe (1993). It was assumed for simplicity that all carbonate ions are converted to bicarbonate ions and only bicarbonate ions contribute to the salting-out of nitrogen. According to these calculations, a 1M sodium carbonate solution would reduce the solubility of nitrogen to 33% of its value in pure water. Experimentally it was observed that the reduction in the permeability of nitrogen was only 13% from its value in pure glycerol ILM (Chen et al., 1999). This could be due to either salting-out or reduction in the diffusion coefficient. In either case, the reduction in nitrogen permeability is much less than what would be predicted by the theory based on aqueous solutions. Similarly, it does not appear that glycine sodium salt would reduce the nitrogen permeability significantly with an increase in its concentration in glycerol.

Therefore, there is a need for fundamental understanding of these aspects in these novel ILMs.



Figure 6.1 Comparison of experimental and predicted behavior of N_2 permeability for glycerol-based ILMs (\bullet : pure glycerol- predicted; \blacksquare : 1M sodium carbonateglycerol- experimental (Chen et al., 1999); \blacktriangle : 2.25M sodium glycinate-glycerolexperimental (Chen et al., 2000))

For a comparison, the predicted N_2 permeabilities are plotted in Figure 6.1 along with experimental results for 1M Na₂CO₃-glycerol ILM (Chen et al., 1999) and 2.25M sodium glycinate-glycerol ILM (Chen et al., 200)) with varying feed side RHs. In both sets of experiments, two test cells were used, resulting in a greater reduction in RH at the feed outlet. The calculated values for pure glycerol ILM always underpredicted the experimental results for both sodium carbonate and glycine sodium salt carries. The agreement at higher RHs is much better. The theoretical predictions were, however, able to provide a first-order estimate of the permeation behavior of the non-reacting species, nitrogen.

As discussed earlier, the effects of the addition of carrier in the novel solvents like glycerol or glycerol carbonate on the solubility and diffusivity of gas species need to be understood better for any realistic theoretical or empirical estimation of the transport rates through these ILMs. A more defined gas flow geometry may help in obtaining a more accurate description of the RH profile to which the ILM is exposed.

6.5 Conclusions and Recommendations for Future Work

Modeling of ILMs with non-aqueous solvents and/or carriers is complicated due to the uncertainties involved in the parameters involved. As applications grow using solvents/carriers such as glycerol, glycerol carbonate, and dendrimers, there will be a need for obtaining fundamental physical and chemical parameters for gas transport in these liquids. The purpose of the present exercise is to demonstrate the uncertainties involved in modeling glycerol-based ILM behavior. It also highlights the parameters that need to be determined for non-aqueous systems, such as solubility, diffusivity of gas species in the solvents and the reaction kinetics of various facilitated transport systems in non-aqueous environments. The geometry of the membrane module plays a significant role in the concentration and relative humidity gradients along and across the membrane. The features of the experimental setup used in the present thesis are not oriented toward obtaining fundamental data such as relative humidity variation along the membrane length, effects of test cell geometry and hydrodynamics on the ILM performance. These data are important for a detailed modeling of the non-aqueous ILMs.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

Separation of gas mixtures is a major activity in chemical industry. Gas separation using facilitating transport membranes has received considerable attention over the years. Immobilized liquid membranes, an important class of facilitated transport membranes, are not yet commercially viable despite their many advantages. One of the main reasons for this is their instability. There is potential for commercialization of ILMs if their stability can be improved. Recent research addressed the issue of stability of ILMs by replacing water as the solvent successfully with glycerol (Chen et al., 1999,2000, 2001).

The present thesis had two main objectives:

- Development of stable immobilized liquid membranes via novel solvents and carriers.
- 2) Improvement of the permeances of preferred species (e.g. CO₂, 1-butene) through the ILMs via novel techniques.

7.1 Development of Stable ILM via Novel Solvents and Carriers

In the present thesis, stable ILMs were formed via three approaches. The first approach of forming a stable ILM using a carrier which does not require a solvent was demonstrated with PAMAM dendrimers of generation zero for separation of CO_2 from N_2 , O_2 etc. The ILMs formed with the dendrimer liquid were found to be stable and highly selective for carbon dioxide over nitrogen under highly humidified feed conditions. This behavior was attributed to almost complete rejection of nitrogen in the presence of highly charged environment in the liquid membrane in the presence of high humidification on the feed

side. The addition of a small amount of glycerol to the dendrimer liquid (25%) was found to substantially increase the range of feed relative humidity (compared to that of pure dendrimer ILM) over which the essential molecular gating ability and permeances of pure dendrimer ILM were retained. In terms of CO_2 -N₂ selectivity, the performance of dendrimer-based ILMs is superior to most membrane configurations studied in the open literature. The permeances of CO_2 through these membranes immobilized in thick supports were reasonable. However, there is a need to improve the CO_2 permeances for the dendrimer-based ILMs to be competitive. Thinner supports or thinner ILMs are obvious directions of future work.

The second approach of forming stable ILMs using glycerol as the solvent in place of water was demonstrated with the example of selective separation of 1-butene (olefin) over n-butane (paraffin). Silver nitrate was used as the facilitating carrier dissolved in glycerol. Glycerol was found to be a suitable solvent for silver nitrate and was effective for the olefin-paraffin separation. The ILMs studied in the present thesis gave stable performance under different humidity conditions and transmembrane pressure differences. The selectivity of the ILMs for 1-butene over n-butane was as high as 1000 and was comparable to the highest selectivities reported in literature for similar olefin-paraffin systems. There is need for understanding the behavior of silver nitrate in glycerol solution for proper design and implementation of the present ILM technology in industrial practice. The viscous behavior of silver nitrate-glycerol solutions at high AgNO₃ concentrations was considerably different from what was observed with glycerol-based solutions used earlier for carbon dioxide separation (Chen et al., 1999, 2000).

The third approach of using a physical solvent which does not require the presence of water for facilitation was demonstrated with glycerol carbonate for carbon dioxide separation. Glycerol carbonate showed great promise as an attractive solvent for carbon dioxide. With respect to the membrane selectivity for CO₂ over N₂, the performance of glycerol carbonate ILMs appear to be independent of carbon dioxide partial pressures, the feed relative humidity or the ILM thickness. The value of $\alpha_{CO2/N2}$ remains essentially constant (around 80-100) over a very wide range of these variables. The CO_2 permeances, however, increase in the presence of feed relative humidity. Glycerol carbonate offers opportunities for forming thin ILMs with thicknesses in the range of a few microns without sacrificing its CO₂/N₂ selectivity while increasing the CO₂ permeances. Addition of carriers, such as, PAMAM dendrimer, sodium glycinate etc. appear to improve the selectivity and CO_2 permeances of glycerol carbonate-based ILMs for low CO₂ partial pressure differences. As glycerol carbonate is a novel physical solvent, there is a need for understanding its kinetic and physical parameters with/without any carriers for any membrane gas separation application. Specifically, the solubility and diffusion coefficients of CO₂ need to be determined. The role of any other solvent in glycerol carbonate is also of interest.

7.2 Improvement of Permeances through the Present ILMs

All solvents/carriers used to form stable ILMs in the present thesis have high viscosity and almost zero volatility. As a consequence, the ILMs formed were stable and resulted in high selectivities for the species of interest, carbon dioxide or 1-butene. However, for the same reason, the fluxes of these species through the present ILMs were lower. For any of the approaches studied in the present thesis to be commercially viable, the permeances have to be increased. Often, the limiting factor is the thickness of the substrate used. There is a need for suitable hydrophilic substrates with thicknesses lower than those studied here. However, development of such substrates is difficult and it is uncertain if the membrane manufacturing community will address this issue in the near future. The present thesis proposed and demonstrated two novel techniques for forming thin ILMs.

One approach was to place the liquid membrane in a small section of an asymmetric substrate via partial displacement of the pore liquid by applying pressure from the non-skin side of the substrate. The other approach was to form a finely porous thin support layer on top of commercially available membrane material via interfacial polymerization. The liquid membrane in turn can be immobilized in this support layer. Both these novel techniques have unique advantages in terms of the ease of operation and range of applicability. The present thesis demonstrated the principal concept of improving the CO₂ fluxes via both these techniques successfully. The liquid membrane immobilized in interfacially polymerized support layer increased the CO₂ permeance by 8 times. The ILMs were stable under different pressure and relative humidity conditions. The thin ILMs formed in a section of the substrate via partial displacement improved the CO_2 permeance anywhere from 2 to 25 times, depending on the substrate used. Both the techniques of forming thin ILMs are inherently practical, easy and commercially viable. There is a need however, to optimize various parameters that are involved in forming these thin films. One would like to know how thin an ILM can be formed under practical conditions and how stable will such an ILM be.

APPENDIX A

SAMPLE CALCULATIONS FOR THE ILM PERMFORMANCE

A sample calculation for the determination of pure dendrimer ILM performance in a hollow fiber module is shown here. The data point refers to Figure 2.14 (page 61)

ILM: Pure PAMAM dendrimer, generation zero

Membrane: Hollow fiber module

Fiber details:

	Fiber:	Hydrophilized polysulfone	
	Pore diameter:	0.1 µm	
	Outside diameter (d _{out}):	360 µm	
	Inside diameter (d _{in}) :	280 µm	
Modu	le details:		
	Number of fibers:	20	
	Length of module:	18 cm	
	Area based on d _{in} (A _{in}):	$=\pi * 280*10^{-4} 18*20$	$= 31.6 \text{ cm}^2$
	Area based on d _{out} (A _{out}):	$= \pi * 360*10^{-4}*18*20 = 40.7$	cm ²
	Log-mean area (A _{lm}):	= $(A_{out}-A_{in}) / \ln(A_{out}/A_{in})$	
		$= (40.7-31.6) / \ln(40.7/31.6)$	
	$\mathbf{A_{lm}}$	$= 35.96 \text{ cm}^2$	

Feed gas conditions:

Feed flow:	Countercurrent
Feed gas composition:	2.2% CO ₂ - balance N_2
CO_2 mole fraction in feed ($x_{f,CO2}$):	0.022

Feed pressure(P _f):	5 psig
Feed flow rate (V _f):	29.7 cc/min
Feed temperature:	20.6 °C
Feed inlet relative humidity (RH _{in}):	100%
Feed outlet relative humidity (RH _{out}) :	76.9%

Sweep gas conditions:

Sweep gas:	Dry helium
Flow rate (V _p):	6.38 cc/min
Pressure:	atmospheric

Permeate side analysis:

CO_2 mole fraction in the permeate ($x_{p,CO2}$)	= Average peak area * GC slope
	$=43,170 * 7.621 * 10^{-8}$
	$= 3.29 * 10^{-3}$
N ₂ mole fraction in the permeate	= Average peak area * GC slope
	$= 3297 * 8.797 * 10^{-8}$
	$= 2.9 * 10^{-4}$

Partial pressure difference of carbon dioxide across the ILM (Δp_{CO2}):

Δp_{CO2} at the feed inlet end ($\Delta p_{CO2,f}$):	$= ((14.7 + P_f) * x_{f,CO2} - 14.7 * 0) * 76/14.7$
	= ((14.7+5)*0.022-0)*76/14.7
	= 2.241 cm Hg
Δp_{CO2} at the feed outlet end ($\Delta p_{CO2,p}$):	= $((14.7+P_f)*x_{f,CO2}-14.7*x_{p,CO2})*76/14.7$
	=((14.7+5)*0.022-14.7*3.29*10 ⁻³)*76/14.7
	= 1.991 cm Hg

Logarithmic mean partial pressure difference for CO₂ across the ILM:

 $\Delta p_{CO2,lm}$:

$$= (\Delta p_{CO2,f} \Delta p_{CO2,p}) / \ln(\Delta p_{CO2,f} / \Delta p_{CO2,p})$$
$$= (2.241 - 1.991) / \ln (2.241 / 1.991)$$
$$= 2.11 \text{ cm Hg}$$

CO₂ effective permeance across the ILM

$$(Q_{CO2}/t_m)_{eff,lm} = V_p * x_p/(A_{lm} * \Delta p_{CO2,lm})$$

= (6.38/60)*3.29*10⁻³/(35.96*2.11)
= 4.6 *10⁻⁶ cc/cm².s.cm Hg
= 4.6 GPU

A similar calculation for nitrogen in the permeate stream would result in $(Q_{N2}/t_m)_{eff,lm}$

$$(Q_{N2}/t_m)_{eff,lm} = 8.61 \times 10^{-9} \text{ cc/cm}^2.\text{s.cm Hg}$$

$$\alpha_{\text{CO2/N2}} = (Q_{\text{CO2}}/t_m)_{\text{eff,lm}} / (Q_{\text{N2}}/t_m)_{\text{eff,lm}}$$
$$= 4.6 * 10^{-6} / 8.61 * 10^{-9}$$
$$= 536$$

Water flux across the membrane

$$y_{H2O}^{s}$$
 at 20 °C (from Perry et al., 1984) = 1.82 cm Hg
Total feed side pressure, P_{tot} = (14.7+P_f)*76/14.7
= (14.7+5)*76/14.7

= 102 cm Hg

Water flux

- = $V_f * y_{H2O}^s (RH_{in}-RH_{out})/(A_{lm} * P_{tot})$
- = 29.7 * 1.82*(100%-76.9%)
 - /(35.96* 102)
- $=3.4 \times 10^{-3} \text{ cc/cm}^2.\text{min}$

APPENDIX B

SUPPORT LAYER FORMATION VIA INTERFACIAL POLYMERIZATION FOR ILMS

Polymeric films formed via interfacial polymerization have been in commercial use in various membrane processes. The composite membranes formed by interfacially polymerizing on top of substrates (polymeric, woven cloth) are routinely used in reverse osmosis (RO), nanofiltration (NF) and gas separation (Petersen, 1993). These are called thin film composites (TFC) to indicate the nature of the membrane formation. Given the stringent requirements of performance on these membranes, namely, solute rejection, fouling resistance, chlorine resistance etc., the polymer thin film is usually a dense network. This is required to ensure 99%+ solute rejection characteristic required in sea water desalination by RO and other applications.

Polymers made via interfacial polymerization are mainly polyamides, polyimides, polyurethanes. Of these polymers, polyamides have been widely used for their chemical and mechanical properties. Polyamides are made by reacting a poly-amine (di-, tri-, poly-) in aqueous phase with a poly- acid (di-, tri-, poly-) in an organic phase. The principal polymerization reaction to produce a polyamide can be written as:

$$-NH_2 + -COOH = -CONH + H_2O$$
(B-1)

Or, if a poly-chloride is used,

$$-NH_2(A) + -COCl(B) = -CONH + HCl$$
(B-2)

A typical example of a polyamide made like this is Nylon 6-10. It is made from a diamine (hexane diamine) in aqueous solution reacting with sebacyl chloride in organic phase. There are excellent resources available describing the principles and practice of interfacial polymerization (Morgan, 1965; Cadotte et al., 1981; Petersen, 1993). There has been recent activity in extending the concept of interfacially polymerized thin film composites for applications other than the conventional membrane applications. Recently, the TFCs were formed for improving the stability of supported liquid membranes (Kemperman et al., 1996; 1998; Wang et al., 1998; Wijers et al., 1998). All these studies focused on forming thin films either on one side or both sides to improve the stability of supported liquid membranes for metal recovery. Both the streams in contact with the coating in these cases were aqueous. Inherently, supported liquid membranes are unstable. It appears that the approach of thin film composite SLM does not solve the main issues involved in the SLM instability.

There were no studies where the interfacially polymerized thin films were used not as protective barriers, but as support layers for any specific application. A major objective of the present thesis is to demonstrate the utility of interfacially polymerized thin films for immobilizing liquid membranes on them. With this approach, the ILMs thus formed would have thicknesses comparable to that of the support layer. It is well documented that the thin films formed via interfacial polymerization are extremely thin, as low as a micron or less.

As mentioned earlier, the aqueous solution usually contains the amine, and the organic solution contains the dichloride. In the present work, hexane diamine and sebacyl chloride are used as aqueous and organic reactants respectively. Xylene was used as the organic solvent. The main steps involved in forming a thin ILM on a support layer formed on top of a hydrophobic surface are:

- surface treatment to promote adhesion of the substrate and the support layer

- wetting the substrate with organic solution and draining the surface to remove excess organic solution
- contacting the treated surface with the aqueous solution for a prescribed duration
- any post treatment of the formed thin support layer
- immobilization of the liquid solution on to the support layer through wetting.

Hydrophobic Celgard 2400 flat membranes were used as the substrate. One side of Celgard films was treated with freshly prepared chromic acid solution at room temperature for 1 minute to prepare the surface. The resulting Celgard film was soaked in the organic solution containing sebacyl chloride for 5 minutes. After wetting with organic solution, the substrate was drained to remove excess solution. This step usually would take about one minute. The Substrate was placed on top of the aqueous solution containing hexane diamine carefully. Care was taken not to stir the solution as it would affect the continuity of the film formation. The reaction was allowed to continue for 2 minutes. The film was washed in excess water to quench the reaction completely. The resulting composite membrane was placed on top of the liquid membrane solution overnight. Excess liquid solution was wiped thoroughly to remove excess liquid membrane solution.

APPENDIX C

PREDICTION OF Q_{N2} IN PURE GLYCEROL ILMS

Sample calculation for the prediction of Q_{N2} in pure glycerol ILMs (for Table 6.1 and Figure 6.1) consists of predicting the diffusion coefficient and the solubility.

Prediction of diffusion coefficient of carbon dioxide and nitrogen in pure glycerol:

Diffusion coefficients of carbon dioxide in water-glycerol mixtures are available in literature (Calderbank, 1959; Krulen et al., 1993) for water weight fraction ranging from 0.125 to 0.905. In the present thesis, the diffusion coefficients of carbon dioxide (D_{CO2}) in glycerol-water mixture were considered only for water weight fraction between 0.125 and 0.46. The literature data on D_{CO2} were fitted as a polynomial curve of second order. The regression obtained was:

$$D_{CO2} = 3.78x10^{-5}y^2 - 9.400x10^{-6}y + 1.408x10^{-6}$$
 (C-1)

with a R^2 of 0.977. Here y is the water weight fraction in glycerol-water mixture. As diffusion coefficients of nitrogen (D_{N2}) in glycerol-water mixtures are not available in literature, the ratio of D_{N2}/D_{CO2} in pure water (Calderbank, 1959) is assumed to be the same in glycerol-water mixtures also. With this assumption, D_{N2} can be calculated from:

$$D_{N2} = 6.005x10^{-5}y^2 - 1.493x10^{-5}y + 2.237x10^{-6} \qquad (C-2)$$

For example, for a water weight fraction of 0.187 (corresponding to 57.6% relative humidity), from equations C-1 and C-2,

$$D_{CO2} = 9.72 \times 10^{-7} \text{ cm}^2/\text{s}$$
$$D_{N2} = 1.54 \times 10^{-6} \text{ cm}^2/\text{s}$$

Calculation of solubility of nitrogen and carbon dioxide in glycerol-water mixtures: Solubility of nitrogen and carbon dioxide in glycerol-water mixtures are available in literature (Rischbieter and Schumpe, 1996) for water weight fraction in the range of 0.39-0.98. The solubility data for nitrogen (S_{N2}) and carbon dioxide (S_{CO2}) in glycerol-water mixtures for the water weight fraction range of 0.39-0.91 were fitted with a linear regression. The resulting correlations were:

$$S_{CO2} = 5.81x10^{-3} y + 2.74x10^{-3}$$
 (C-3)

$$S_{N2} = 1.91 \times 10^{-4} y - 1.93 \times 10^{-5}$$
 (C-4)

The regression coefficients were 0.99 for both correlations. Using these correlations, one can estimate the solubility of carbon dioxide and nitrogen in glycerol-water mixtures at various water fractions. For example, for a water weight fraction of 0.187, these values are:

$$S_{CO2} = 3.83 \times 10^{-3} \text{ cc(gas)/cm}^3.\text{cm Hg}$$

 $S_{N2} = 1.64 \times 10^{-5} \text{ cc(gas)/cm}^3.\text{cm Hg}$

The permeability of nitrogen or carbon dioxide is the product of its solubility and diffusion coefficient through the glycerol-water mixture. Hence, the respective permeabilities through pure glycerol ILMs can therefore be calculated at various relative humidity (water fraction) values. From the above calculated values, at a relative humidity of 57.6% (water weight fraction of 0.187), these are:

$$Q_{N2} = 2.52 \times 10^{-11} \text{ cc(gas).cm/cm}^2.\text{s.cm Hg}$$

 $Q_{CO2} = 3.73 \times 10^{-9} \text{ cc(gas).cm/cm}^2.\text{s.cm Hg}$

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