EXPERIMENTAL AND THEORETICAL INVESTIGATION ON MATERIALS, PREPARATION, PERFORMANCE AND STABILITY OF IMMOBILIZED LIQUID MEMBRANES FOR GAS SEPARATION

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
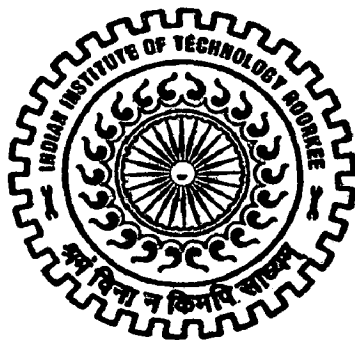*of*

MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Safety and Hazards Management)

By

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JUNE, 2007

CANDIDATE'S DECLARATION

I hereby declare that the work which is presented in the Dissertation entitled "Experimental and Theoretical Investigation on Materials, Preparation, Performance and Stability of Immobilized Liquid Membranes for Gas Separation" in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Chemical Engineering** with the specialization in **Industrial Safety and Hazards Management**" in the Department of Chemical engineering, Indian Institute of Technology Roorkee. This is an authentic report of my own work carried during the period from September 2006 to May 2007, under the supervision of **Dr. (Mrs.) Shashi,** Assistance professor, Department of Chemical engineering, Indian Institute of Technology Roorkee.

The matter embodied in this project work has not been submitted for the award of any other degree.

Date: 27th June, 2007

Place: IIT Roorkee

(Sachin Upadhyay)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.
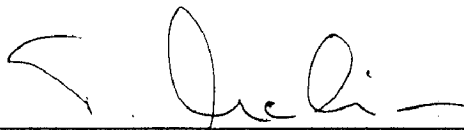
Dr. (Mrs.) Shashi
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I

Certificate

Mr. Sachin Upadhyay, born October 14th 1981 in Aligarh, India, stayed at RWTH Aachen University, Germany, within the IIT-Master-Sandwich-Program of the German Academic Exchange Service (DAAD). During his stay at the Institut für Verfahrenstechnik (IVT) from October 1st 2006 to April 30th 2007 he carried out experimental investigations in the field of membrane processes, preparing his thesis to obtain the degree of M. Tech. from the Department of Chemical Engineering of the Indian Institute of Technology Roorkee.

His tasks comprised an extensive literature review and the compilation of data on materials, performance, preparation and stability of immobilized liquid membranes (ILM) for gas separation. To prove an innovative insitu preparation method of flat-sheet ILM, he designed a dedicated membrane module. Using this module, he experimentally investigated two different ILM systems consisting of inorganic membrane-supports and an ionic liquid concerning their permeation performance, perm-selectivity and stability. He completed his work with a well written final report titled "Investigations on Materials, Performance, Preparation and Stability of Immobilized Liquid Membranes for Gas Separation".

As a result of his positive attitude towards scientific research, his willingness to work and his well written report, I would assess his performance with the grade "gut" = good, equivalent to A or 9 in the Indian grade-system).

Aachen, May 2nd 2007, Prof. Dr.-Ing. T. Melin
Chair of Chemical Reaction Engineering
Head of the Institut für Verfahrenstechnik (IVT)

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Abstract

The work at hand deals with Immobilized Liquid Membranes (ILM) for gas separation. In immobilized liquid membranes, the pores of a support are filled with a liquid. Polymeric supports and organic liquids are often used for preparation of supported liquid membrane. Immobilized liquid membranes can be used for ion-liquid separations, liquid-liquid separations and gas-gas separations. A review on immobilized liquid membrane for gas separation comprising literature of the last 15 year, has been performed in this work. The literature review is focusing on the kind of supports and liquids, which are used for the preparation of immobilized liquid membranes. The performance of these membranes has been given in terms of permeability, selectivity and stability.

A new membrane module has been designed and fabricated for insitu preparation of flat sheet immobilized liquid membranes. Novel immobilized liquid membranes have been developed with two different supports for the separation of propylene and propane gases. The results are shown in terms of permeabilities and selectivities of both gases for the respective membranes.

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1 Introduction

In this chapter the theory about membranes will be discussed concisely. Section 1.1 will be about basic definition of membranes and how they work. Classification of membranes will be discussed in section 1.2. The last section 1.4 will be about liquid membranes including operation concepts, types and properties of liquid membranes.

1.1 Membrane definition

In general, a membrane is a semipermeable barrier, letting pass desired species (cf. Figure 1.1) and restricting the transport of various chemical or biological species. Thus a feed is separated into two streams. The portion of feed which passes through the membrane is called permeate and the rejected stream is called retentate. This barrier can be solid or liquid.
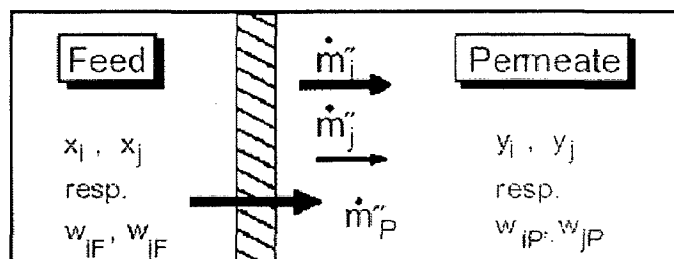
Figure 1.1: Basic membrane function [2]

A membrane may be neutral or may carry charges. The manner in which membranes restrict the transport of undesired species can be due to

- size difference,

- difference in diffusivities,

- electric charge,

- solubility.

Features, which distinguish membrane processes from other separation processes are, firstly, membrane processes are non equilibrium processes i.e. separation is continued as long as the driving force is present. The driving force can expressed as a difference in chemical potential. For gas separation, which are subject of this work at hand, this can be expressed in terms of difference of partial pressures or concentrations. Secondly, separation is achieved due to molecular recognition not due to absolute temperature, pressure etc.

Membranes are characterized in terms of permeability and selectivity. Permeability(Q) is nothing but the rate of flow of

$$Q = \frac{\dot{V}}{\Delta p \cdot A_m}$$

$$S = \frac{\frac{y_p}{x_p}}{\frac{y_f}{x_f}}$$

of any fluid per unit area at a given pressure difference or it can also be defined as, the ability of any fluid to pass through the membrane. Selectivity(S) is defined as the ratio of concentration in the permeate divided by that in the feed for two components or in other words, it is the ability to separate desired species from the feed. In this work, permselectivity has been used for checking the selectivity of a membrane components, which is nothing but the ideal selectivity of a membrane. It is defined as the ratio of permeability of one component to that of another. For the efficient membrane separation

$$S_{perm} = \frac{Q_j}{Q_i}$$

process, high permeability and high selectivity of membranes are required.

Membranes have various advantages, like in some cases higher separation value in comparison to other separation methods, easy installation, continuous as well as batch operations. Some species, which are difficult to separate by means of conventional separation methods can be separated by using membranes. Membranes also have some disadvantages, like high cost of membrane material, problems of fouling, cleaning and regeneration of membrane and their stability.

1.2 Classification of Membranes

Membranes can be classified into three main categories as shown in Figure 1.2. The very first category is on the basis of their origin as synthetic and biological membrane. Biological membranes are nothing else but cell membranes. Main functions of cell membranes are to keep the cell content together, allowing nutrient to pass in and most important to keep out many harmful substances. Cell membranes are about 5 nm thick and consist mainly of lipids and proteins. Proteins act as a carrier and provide channels for letting pass some desired constituents.

In 1972, J. S. SINGER and G. NICHOLSON postulated the fluid mosaic model of
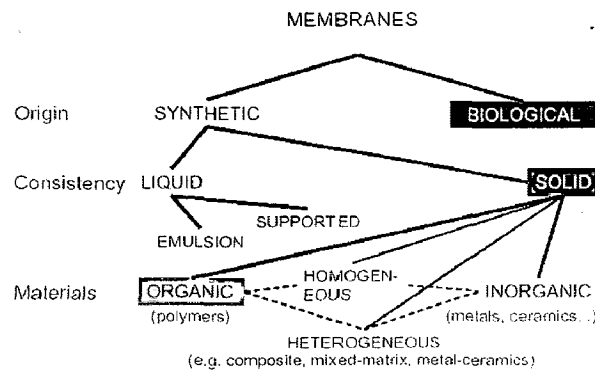
Figure 1.2: Classification of membranes [3]

membrane which is shown in Figure 1.3. It suggests that the lipids form a viscous, two-dimensional solvent into which proteins are inserted and integrated more or less deeply. The hydrophobic parts are in contact with the hydrophobic tails of the lipid molecules. In contrast to biological membranes, synthetic membranes represent artificially produced membranes. Synthetic membrane can be of solid or liquid form as to their consistency. Almost all of the industrial membrane separation processes employ solid membranes.
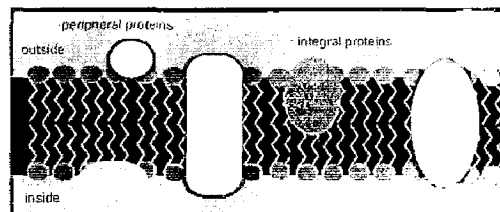
Figure 1.3: Fluid mosaic model of membrane [2]

The reason of lacking industrial application of liquid membranes is due to insufficient stability. This will be discussed precisely within this work.

Solid membranes can further be classified into two materialistic categories. First is organic membranes, which are made of organic materials like polymers. Properties of organic membranes can be divided into macromolecular and micromolecular being dependent on the processing and chemical composition respectively. By incorporating certain molecules inside the polymer matrix the properties of organic membranes can be influenced. Different organic membrane may fulfill different process requirements. On the other hand they have some disadvantages also like, they can not withstand high temperatures. They need cleaning time after time which is attributed to the loss of process flux value.

Inorganic membranes are another category of solid membranes. They are made of inorganic materials like ceramic, glass or metals. in comparison to organic membranes, advantages of inorganic membranes include, operability of these membranes at high temperatures e.g. metal membranes are stable at temperatures ranging from 500-800 $^\circ$C. Although, many ceramic membranes are usable at over 1000 $^\circ$C, often sealing materials impair the use at high temperature. They are also much more resistant to aggressive chemicals. Disadvantages in using inorganic membranes are high investment costs, difficult handling and material defects.

1.3 Application of membranes

Membranes have wide variety of separation applications. Membranes have been used for separations for very long time. Applications of membrane are dependent on the type of membrane used. Membrane applications are also divided on size of the separation species. Nowadays membranes are used in purification of various chemical but most often they are used for water purification. Microfiltration, ultrafiltration and nanofiltration membranes are used to purify water from dyes, pollutants and various chemicals. Reverse osmosis membrane can separate almost all type of impurities from water and gaining interest in industrial as well as domestic level. These all above membranes are preferably used to separate ions and salts from liquid.

There is a large variety of membranes which are used for gas separation. Gas separation is possible by using polymeric, ceramic, metal and liquid membranes. The latter can be used for both ion and gas separation . Supported liquid membrane is a class of liquid membrane which can be used to separate gases efficiently and will be discussed in Chapter 2 more precisely. They have been mainly investigated for separation of lighter hydrocarbon gases and separation of inorganic gases. Application of supported liquid

membrane is not possible yet on industrial level due to instabilities though they have shown their potential at laboratory scale.

1.4 Liquid Membranes

Liquid membranes represents a class of synthetic membrane resembling biological membranes to the most. As the name suggests, these are made up of liquids working according to the solution-diffusion mechanism. In some type of liquid membranes chemical agents or solvents called as carriers, for facilitating the transport, are applied and this will discussed in section 1.4.2 in much more detail. Liquid membrane can be used for ion liquid separation, liquid-liquid separation and gas-gas separation. Nowadays, they have also been investigated for gas-vapor separations. They are also used in biological and biochemical fields for separations because as said before they resemble biological membranes.

1.4.1 Classification of liquid membranes

Liquid membranes can be classified in to three basic forms. This classification is mainly dependent on the preparation of these membranes;

Bulk liquid membranes

Bulk liquid membranes (BLMs) represent the simplest type of liquid membrane being nothing else but diffusion cells.
BLMs can be prepared by several ways but the general concept always be the same. BLMs are made up of three parts, donor phase, acceptor phase and membrane liquid. The membrane liquid is a common part in BLMs and separated from donor and acceptor phase by means of a thick layer.
This thick layer can be an immiscible fluid or a solid impermeable barrier. The separation is then totally dependent on the solubility and the diffusivity of ions or molecules concerned. The membrane liquid contacts with diffused ions or molecules and effects the transfer between them. In some cases, stirring and carriers are employed to avoid the mixing donor and acceptor phase, which may be encountered due to slow diffusion and facilitate the transport respectively. The design of BLMs may vary from single diffusion cells to multiple diffusion cells. In Figure 1.4, a very general type of BLM can be seen.
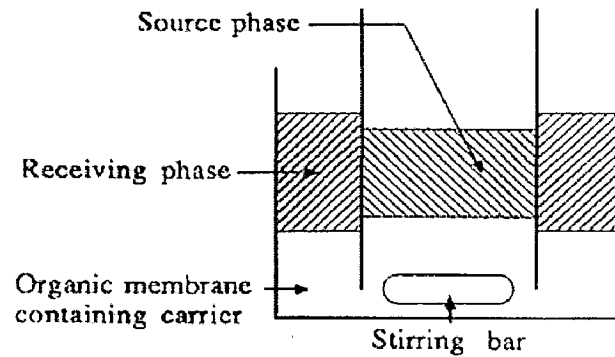
Figure 1.4: Bulk liquid membrane

The simple design and easy manipulation are the reason for their broad use in laboratory studies. These membranes can be used to find kinetics of the mass transfer process, for studying the reaction mechanism involved etc.. On the other hand, specific interface area limits the application of these membrane method to laboratory use.

Emulsion liquid membranes

Emulsion liquid membranes (ELMs) evolved in the late 1960s. These membranes have many common names like double emulsion membranes and surfactant liquid membranes. In these membranes, three-liquids i.e. the membrane liquid, the donor and the acceptor phase are stabilized by an emulsifier. The amount of emulsifier can be up to 5 percent of the membrane liquid. Preparation of emulsion is done by mixing the acceptor solution and the membrane phase. This emulsion solution is then contacted with donor liquid and forms emulsion globules as shown in Figure 1.5. These globules show a large interfacial area between donor and acceptor phases. Due to large interfacial area, mass transfer can be completed in small time. Finally, the emulsion is destructed to reuse membrane liquid. Donor and acceptor phase should be mildly hydrophobic to achieve stability of
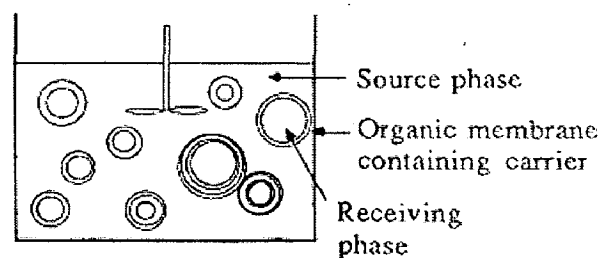
Figure 1.5: Emulsion liquid membrane

these membranes. Application of Emulsion liquid membranes are a three step process as described above and may be scaled up to a continuous process. Preparation and destruction of emulsion are fairly difficult tasks and limit this process. pH and ionic strength can affect the stability of the emulsion.

Supported liquid membranes

In most general sense, Supported Liquid Membranes (SLMs) have a porous support, pores of which are wetted by the membrane liquid. This support provides a mechanical strength to withstand large pressure differences. Though micro-porous polymeric membranes are used as supports, nanofiltration has also been investigated as supports and have shown good performance in comparison to micro-porous supports [6].In general, organic liquids are used as the membrane liquid. SLMs can be made in various combinations depending on the hydrophobicity or hydrophilicity of supports and liquids. Two possible combinations are, hydrophobic support and hydrophobic liquid or hydrophilic support and hydrophilic liquids. Wetting of the supports are done by different methods insitu and exsitu, which will be discussed in Chapter 2 in much detail. SLMs can be differentiated in terms of construction.

The two kinds of SLM construction are shown in Figure 1.6. In Figure 1.6 (a), the open pores of support are soaked with membrane liquid and generally known as Immobilized Liquid Membranes(ILMs). In Figure 1.6 (b), the membrane liquid is supported on both
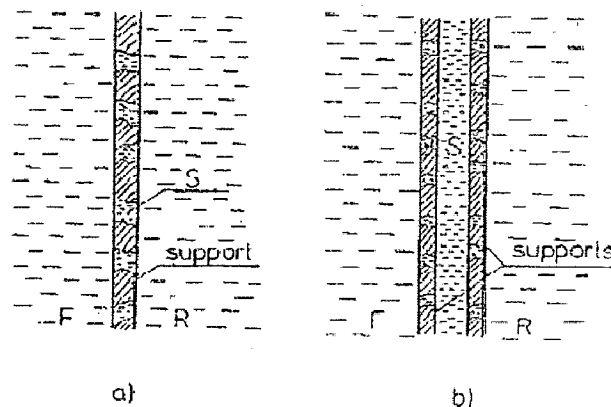
Figure 1.6: Liquid Membranes with support [1]

sides by support and commonly referred to SLM. Selection of the membrane liquid and the porous membrane is very important task to achieve stable solid-liquid interfaces. Supported liquid membranes have higher relative stability than other types of liquid membranes. Supported liquid membranes are thicker than other synthetic membranes.

Supported liquid membranes are discussed more precisely in Chapter 2. Supported liquid membranes can be used as following physical modules;

- Flat sheet supported liquid membranes,

- Hollow fiber supported liquid membranes(HFSLM),

- Spiral wound supported liquid membrane .

Flat sheet supported membranes are most simplistic in design from all of the designs given above. This makes them favorable for laboratory use. The design of the HFSLM is akin to a large electrical cable. High surface area and low thickness provide rapid transportation. Cleaning, pore fouling and high capital cost are some of the disadvantages of this module. Spiral wound supported liquid membranes are made up of several flat sheet membranes wrapped around a perforated tube, through which effluent streams out of the membrane. These membranes have less surface area and stability.

1.4.2 Mass transfer in liquid membranes

Mass transfer in liquid membranes is based on the solution-diffusion mechanism. This mechanism can be described by the following sub mechanisms,

Simple transfer mechanism

In a simple transfer (cf. Figure 1.7(a)), separation is achieved by solubility of feed molecules in the membrane liquid. Solubility results in a concentration gradient which is the cause of transfer of permeate specie from feed to acceptor phase. This mechanism limits due to lack of enough concentration after a period processing. To overcome this problem, a simple up hill transport (cf. Figure 1.7(b)) is described. In this mechanism, acceptor solution containing a reagent B irreversibly binds each permeate molecule and for making a complex AB, which is insoluble in the membrane liquid. This complex compound is then split and reuse the membrane liquid. This mechanism employs a third step other than the simple transfer, reaction.

Facilitated transfer mechanism

The transfer mechanism employs carriers to facilitate the transport of species from one phase to another. This mechanism does not require solubility of feed species in the membrane liquid. Figure 1.8 (a) shows a facilitated transport, in which membrane liquid
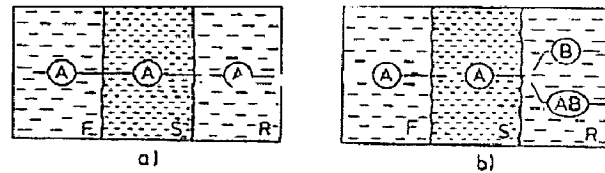
Figure 1.7: Simple transfer mechanism [1]

has active additives (x), which react selectively and reversibly with the permeate A by a reaction given below forming a complex AX)
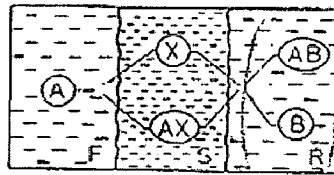
Figure 1.8: Facilitated transfer mechanism[1]

$$A + X \rightarrow AX$$
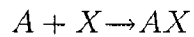
The complex is then split and permeate A binds irreversibly with some other reagent B forming a new compound (AB), which is insoluble in the membrane liquid. After splitting, the additive moves back to the feed-membrane interface due to the concentration gradient across the membrane and is free to bind again with A. The only small amounts of complexing additive are sufficient for the selective extraction and pre-concentration of various metal-ions from very dilute solution. This technique shows very selective separation behavior. Major application of facilitated transfer is in supported liquid membrane.

2 Literature Review

In this chapter a literature review on liquid membranes (LMs) of the last 15 years will be given dealing with gas and vapor seperations. In this review, the term liquid membrane comprises only Supported Liquid Membranes and Immobilized Liquid Membranes. Preparation, performance and the long term stabilities of LMs are the main concern of this review.

In the very first section 2.1, different combinations of supports and liquids will be discussed. In section 2.2, preparation of LMs will be discussed. The selection of supports and liquids will be discussed in section 2.3. At the end in section 2.4, performance of different LMs will be discussed.

2.1 Supports and liquids for liquid membranes

The Membrane is the heart of every membrane separation process and separation performance is mainly dependent on the properties of membrane. Properties of a membrane are dependent on its materials i.e. support and liquids in the case of LMs.

Supports do not only provide the mechanical stability but also enhance the stability for longer periods of application. A good support should have, small pore size, high porosity and be chemically inert. High thickness would be desired for bearing high operating pressures, but lowers the permeability. In Table 2.1-2.4 supports and liquids, used for different LMs, are given.

All the supports given in Table 2.1-2.4, are polymeric supports, with the exceptions, stainless steel woven wire mesh used by Pez etal and porous anodic alumina, which is an inorganic support, used by Baltus etal in 2005. Most of the polymeric supports used are microporous in nature, but Gan etal (2006) used mesoporous membrane instead of a micro porous membrane. As one can see from the Tables ??-2.2 Poly- vinyle-difluoride and poly propylene are the most commonly used support for the preparation of supported liquid membrane. Sometimes, a combination of two supports is also used to increasethe pressure strength of the membrane [12, 13, 15, 21].

Table 2.1: Materials, configurations and separation tasks of liquid membranes

Support	Configuration	Liquid	Carrier	Separation Species	Reference
Polypropylene (Celegard)	CLM^a	Water	CA, DEA, $NaHCO_3$	CO_2/O_2	[5]
Nanofiltration (Sterlitech)	ILM^b	$[C_4\text{-mim}][NTf_2]$ $[C_{10}\text{-mim}][NTf_2]$ $[N_{8881}][NTf_2]$ $[C_8P_y][NTf_2]$	None	H_2, O_2 CO, N_2	[6]
N/A	SILM	c.f [6]	None	H_2, CO N_2, CO_2	[7]
PVDF (Millipore)	ILM	DETA, DEA, DEYA, BEHA	N/A	CO_2/CH_4	[8]
Porous anodic Alumina (Whatman)	SLM^c	$[C_4\text{-mim}][NTf_2]$, $[C_8F_{13}][NTf_2]$	N/A	CO_2, N_2	[9]
Polypropylene (Celegard)	CLM	Water	20 wt DEA	CO_2/O_2	[10]
Polyether-Sulfone	ILM	[emim][Tf_2N], [emim][CF_3SO_3],	none	CO_2/CH_4 CO_2/N_2	[11]

a: Contained liquid membranes, b: Immobilized liquid membranes, c: Supported liquid membranes.

All of the supports given in Table 2.1 utilize three main configurations, ILMs, SLMs and CLMs. The latter is not used very often. The hollow Fiber module of CLMs have been presented by Bao etal (2006) and Bao etal (2005). Generally, SLMs and ILMs are employed as the main configurations. Both of these are employed with same principle but with different constructions, which we have discussed in chapter 1.

Liquids are the second and main constituent of a LM configuration. Liquids should have low viscosity, low volatility (specially for gas separations). Hydrophobicity or hydrophilicity of liquids are also accounted to match with hydrophilic or hydrophobic

Table 2.2: Materials, configurations and separation tasks of liquid membranes contd.

Support	Configuration	Liquid	Carrier	Separation Species	Reference
PTFE Supported on PVDF	ILM/SLM	TEG	$AgBF_4$ $AgNO_3$	C_2H_6 C_2H_8	[13]
c.f. [13]	SLM	TEG, TEG-MBEr, TEG-DME, TEG-DBE	None	CH_4 C_6H_6 $C_6H_5CH_3$ C_3H_6O	[15]
PVDF	ILM	Gycerol	$AgNO_3$	C_4H_8 C_4H_{10}	[16]
PVDF Celegard (2500)	ILM	GC, PAMAM	None	CO_2 N_2	[17]
Polypropylene Celegard (3401)	ILM	(d)	(e)	$H2S/CO_2$ $H2S/CH_4$	[18]
Polysulfone fibers	ILM	Gycine-Na Gycerol	None	CO_2 N_2	[19]
N/A	SLM	N/A	N/A	O_2/air	[20]

d: $[(CH_3)_4N]F.4H_2O$, e: $[(C_2H_5)_4N]CH_3CO_2.4H_2O$.

supports. Both organic and inorganic liquids are employed as a membrane liquid. But Pez etal (1992) and Laciak etal (1992) used some molten salts, which in molten state act as a membrane liquid. This process requires high temperature applications. Organic liquids are most often used as a membrane liquid.

Ionic liquids are also employed as a membrane liquid. A category of ionic liquids, which are used for the preparation of SLMs, called as Room Temperature Ionic Liquids (RTILs), [6, 9, 11, 12]. These are salts, which are liquid at room temperatures. They consist of an organic cation and an inorganic anion . The properties of RTILs include very low (almost negligible) volatility, high thermal stability and high ionic conductivity. A kind of RTIL has also been employed in this work.

Table 2.3: Materials, configurations and separation tasks of liquid membranes contd.

Support	Configuration	Liquid	Carrier	Separation Species	Reference
PTFE Supported PVDF	ILM/SLM	TEG DGA	None	CO_2 CH_4	[21]
PVDF Polypropylene Polyacrylonitrile Polysulfone	ILM	Glycerol	PAMAM dendrimer	CO_2 N_2	[22]
PVDF hydrophillic	ILM	Glycerol	Glycine-Na Na_2CO_3	CO_2 N_2	[23]
Porous $LiAlO_2$	ILM	Molten salts Li_2SO_4 K_2SO_4 Na_2SO_4	None		[24]
Cellulosic acetate nitrite	ILM	K_2SO_3	PEG,DBC K_2SO_3	CO_2	[25]
PVDF	ILM	Glycerol	Na_2CO_3	CO_2 N_2	[26]
PVDF	SLM	Deionized water	Water	SO_2	[27]

Inorganic liquid or sometimes only water is used as membrane liquid, [5, 10, 27].
Usually alkali liquids are used in the category of inorganic liquids, [24, 25, 27, 28]. Inorganic salts are usually employed for the separation of inorganic gases, because on combination they make some favorable matrix. For enhancing the rate of reaction and selectivity between the separation species and membrane liquids, carriers are used. These carriers are technically known as facilitator. Carriers selectively act as a catalyst in the reaction between separation species and membrane liquids. Carriers react with species selectively and make some complex, which is usually favorable to membrane liquid. After further reacting with membrane liquid, carriers are split from the complex and react reversibly with species again. Bao etal (2005) used diethyloamine for facilitating the CO_2 transport across the Hollow fiber CLM. Kovvali etal (2001) used dendrimer

polyamidoamine to facilitate the CO_2 transport from the mixture of CO_2/N_2. Teramoto et al (1999)

employed water as a carrier SO_2 transport.

SLMs can be used for separating both organic and inorganic gases. Most of the cited

Table 2.4: Materials, configurations and separation tasks of liquid membranes contd.

Support	Configuration	Liquid	Carrier	Separation Species	Reference
Cellulosic acetate nitrate	ILM	K_2CO_3 $KHCO_3$	None	CO_2 N_2	[28]
PVDF	SLM	DEA MEA	Water	CO_2 CH_4	[29]
Polypropylene PTMSP	ILM	(d)	(e)	CO_2,H_2 CH_4	[30]
Polypropylene Celegard-2500	ILM	Polyethylene glycol	DEA	CO_2 C_2H_6	[31]
Membrane filter (Gelman science)	SLM	(f)	PAM hydrochloride, EDA	CO_2 N_2	[32]
Polypropylene Celegard-2500	SLM	Polyethylene glycol	DEA DIPA	CO_2 CH_4	[33]
Stainless steel woven wire mesh	SLM	$LiNO_3$ $ZnCl_2$	Liquid acts as a carrier	NH_3 N_2,H_2	[35]
Stainless steel woven wire mesh	SLM	Anhydrous $LiNO_3$, $NaNO_3$	Liquid acts as a carrier	O_2 Dry Air	[36]

f: 1. 2-bromopropane, Ethylene glycol diglycidyl ether, CH_3OH,KOH, 2. HNO_3, Distilled water, NaOH, HCl, Ethylene diamine.

references reports separations of organic gases especially CO_2. As this was said earlier also, they have been investigated at laboratory scale only. Low molecular weight gases like carbon dioxide, propane, butane etc have their industrial importance and they are easily available in laboratories and have low potential risks. 22 out of 33 references employed CO_2 as a separation task. These CO_2 seaprations are mainly investigated

with N_2(9 out of 22) and others with O_2 and CH_4. Other separation tasks reported, are olefin-paraffin,[13, 15, 16], purification of oxygen,[20, 36, 6], and SO_2 separation,[27].

2.2 Preparation of supported liquid membranes

After selecting the supports and liquids of favorable choice, now next task is the preparation of SLMs. In the preparation of SLMs, support is wetted by the membrane liquid or liquid and carrier. This wetting of support is done by two main methods insitu and exsitu.

In the insitu method, online wetting is done i.e. support is first placed in the membrane chamber and then wetted by the membrane liquid. This method is not very common. Pez etal (1992) and Laciak etal (1992) have used this technique for wetting their supports by molten salts. The insitu method can be scaled up to continuous level, because wetting is done as the part of the process [5]. In gas separation, membrane liquid is lost due to evaporation. This problem can be solved by using this method.

The most common method of wetting the supports is exsitu. This is a discontinuous technique. In this technique, wetting is done outside of the membrane chamber. Wetting by this method is done by various ways, like impregnating, brushing, soaking etc. This technique may take minutes, hours and even days [8, 16, 29]. After wetting the supports, excess liquid should be wiped off. The Exsitu method cannot be scaled up to the continuous method.

Although, liquid layers on the supports are usually negligible in compare to support thicknesses, some liquids form thick layers on the supports [13, 15]. The thick layer may decrease the permeability values. A low selectivity combined with high permeability shows similar performance as high selectivity combined with low permeability.

LMs can be prepared as single layer or double layer. Single layer configurations employ one support and double layer configurations two support. The one more support is used to make LMs more stable at high pressures. In double layer LMs, top support is the one which is wetted by the liquid, bottom one is used as it is [12]. Sometimes, metallic supports are also used in place of polymeric support [28]. These techniques are often used in flat type SLMs. In this work, a flat type LM supported on a metallic mesh is prepared.

2.3 Selection of supports and Liquids

After having an idea about the supports and liquids, which are generally used for the LM preparation, selection of these materials is done. Though selections of these materials are made with respect to separation species, at research level different supports are tested to find the best match with the separation species. The selection of supports

Table 2.5: Properties of Supports

Thickness (μm)	Pore Size (μm)	Porosity [ϵ]	Tortuosity [τ]	Remarks	References
50	0.04	0.40	1		[5]
167+118	N/A	N/A	N/A	Additional Layer (118)	[6]
N/A	N/A	N/A	N/A		[7]
100	0.10	N/A	N/A		[8]
47	0.02	N/A	1		[9]
30	0.04	0.40	1		[10]
152	0.2	0.80	N/A		[11]
20-60	1	0.83	N/A	Two support Combination	[12]
45-65	1	0.83	N/A	Liquid layer accounted	[13]
12-85	1	0.83	N/A	Liquid layer accounted	[15]
100	0.10	0.70	2.58		[16]

is usually based on properties like its pore size, thickness, porosity and tortuosity. In Tables 2.5, 32 different sets of these values for the different supports are given. Some of the columns of the tables are not filled with values due to unavailability of respective information. Thickness is ranging from 20-450 μm with the exception of 2500 μm [30]. In reference [6], the author accounted experimentally calculated liquid layer thickness over the support. Yamanouchi etal (2004), Duan etal(2003) and Yamanouchi etal (2003) used combinations of two different supports and presented a range of thicknesses for LMs. The possible causes of presenting the ranges are formation of very thick layer on the membrane, vaporization of liquid layer time by time etc. .

The pore size of the support plays an important role in transport of species through the LMs. The pore sizes also play an important role in stability of LMs determining the critical displacement pressure of LMs . The pore sizes given in Tables 2.5-2.7 are in the range of 0.02 to 1 μm. The stainless steel support, which is used by Pez and Laciak

Table 2.6: Properties of Supports

Thickness (μm)	Pore Size (μm)	Porosity [ϵ]	Tortuosity [τ]	Remarks	References
100, 25	0.10	N/A	N/A	Comparison of two supports	[17]
25	N/A	0.5	1.25		[18]
225	0.1	0.75	N/A		[19]
N/A	N/A	N/A	N/A	A review	[20]
35	1	0.83	N/A		[21]
F-1^a:100	0.10	0.70	2.58	4 different	[22]
F-2:25	0.08	0.45	2.54	supports and	
H-1^b:50	70000	N/A	N/A	two different	
H-2:40	0.10	0.30-0.40	N/A	configurations	
100	0.10	0.70	2.58		[23]
N/A	N/A	N/A	N/A		[24]
457.5	0.80	0.82	3.05		[25]
100	0.10	0.70	2.58		[26]
100	N/A	0.63	2.61		[27]
150	0.8	N/A	N/A		[28]
100	0.1	0.70	N/A		[29]

a: Flat support, b: Hollow fiber, N/A: Information not available

etal (1992), has a range of pore size 4-13 μm. Generally, microporous supports are used for LMs preparation, but nowadays mesoporous supports are also being investigated for LMs preparation, [10].

Next, the porosity is defined as the area which is open for flow of any fluid in the range of 0-1. For the making of LMs, the support needs to be highly porous. The membrane liquid reside in the pores of a support, where all the reactions occur. In Table 2.5, the given porosities are ranging from 0.4-0.83 with exception of 0.3 in reference [22].

Table 2.7: Properties of Supports contd.

Thickness (μm)	Pore Size (μm)	Porosity [ϵ]	Tortuosity [τ]	Remarks	References
2500	0.05×0.125	0.5	1.25	Pore dimensions are given	[30]
25	0.075×0.25	0.45	1.75		[31]
320,200	N/A	N/A	N/A	Two different supports	[32]
25	0.04	0.45	2.1, 2.2	τ is given for two carriers	[33]
380	4-13	N/A	N/A	Stainless steel mesh	[35]
200	4-13	N/A	N/A	Stainless steel mesh	[36]

The path length of the pore of a membrane is usually somewhat curve or tortuous. To define this property of a membrane, tortuosity(τ) is used

$$\tau = \frac{L}{C}$$

where L is the straight length of the curve and C is the distance between the ends of it. In Table 2.5, different values of tortuosity are given. The tortuosity value ranges from 1-2.54 with the exception of 3.05 in reference [25]. Tortuosity is a property of a support but some application of carriers affect it [33].

2.4 Performance of liquid membranes based on experimental results

The performance of liquid membranes is expressed in terms of their permeability and selectivity of the desired species. These properties are very dependent on the long term stability of the membrane. Problems generally occurring in application of liquid membranes are breaking of membranes, vaporization of liquid from the surface of the support etc. So, for the good performance of the liquid membrane, stability of membrane is necessary.

Table 2.8: Performance of supported liquid membranes

Permeability $l/m^2.s.bar$	Selectivity	Stability	Remarks	References
C: $3.6\text{-}1.54*10^{-2}$	C/O: 98.8-152	50 days	long term stability may concern	[5]
H: $21.02\text{-}0.4*10^3$ CM: $24.25\text{-}0.16*10^3$	H/CM: 4.3	Up to 7 bar	Several stability tests are given	[6]
N: $38.8\text{-}0.43*10^6$	N/CM: 93(max)	Up to 9 bar	Nanofiltration supports shows better stability	[7]
C: $13.6\text{-}1.6*10^3$ M: 67-0.8	C/M: 1000(max)	N/A		[8]
C: $3.27\text{-}1.2*10^3$ M: 25-16	C/N: 125-72	N/A		[9]
C: $0.32\text{-}0.072*10^6$	C/O: 115	5 days		[10]
C: $2.6\text{-}1.9*10^4$ N: 918-180 C: $1.6\text{-}0.56*10^3$	C/N:105-28 C/M:34-15	N/A		[11]
C: $3*10^3$	C/M:20	N/A		[12]

a: PVDF, b: PVDF+Celegard 2500(double layer)

The Tables 2.8-2.10 are all about the performance of different liquid membranes in terms of permeability, selectivity and long term stability. The Permeability and the selectivity values, which can be seen in Tables 2.8-2.10, are given in a range of maximum to minimum.

The range of permeabilities for desired species given in Table 2.8, is 38.30×10^6 to 10^3 $l/m^2 \cdot s \cdot bar$ with the exception of very low permeability of the order of 10^{-2} reported by Bao etal(2006) for CO_2. For undesired species this range is $21 \times 10^3\text{-}16$ $l/m^2 \cdot s \cdot bar$. The selection of desired and undesired species is totally based on the interest of a author. The maximum N_2 permeability i.e. 38.30×10^6 is shown by an ionic liquid supported by a mesoporous membrane [7]. The range of CO_2 permeability, which is the most common

Table 2.9: Performance of supported liquid membranes contd.

E: 41.54-6.31*10^3 A: 0.33-0.29*10^3	E/A: 25-150	N/A		[13]
AC: 5.4*10^6	B/AC:54	N/A		[15]
BE: 24.83*10^3 BA: 12.03*10^3	BE/BA: 320-250	3 weeks		[16]
C^a: 2.75*10^3 C ^{b}: 1*10^3	C/N: 110-50	N/A		[17]
HS: 8.8-2.07*10^3 C: 18-0.32*10^3	HS/C: 8.2-6.4 HS/M: 140-34	N/A		[18]
C: 90-71.86*10^3 N: 37.8-27	C/N: 2800-2000	Up to 30 hrs		[19]
N/A	25-60 depending on operating pressure	Stable	stabilized by encapsulation	[20]
C: 3.09-0.78*10^3 M: 115.72-30.85	DGA-C/M: 100 TEG-C/M: 40	Up to 160 hrs		[21]
F-1-C: 8.64-.81*10^3 F-2-C: 7.7*10^3 H-1-C: 35.1*10^3 H-2:C: 26.2*10^3	C/N:163400-760 C/N:3900 C/N:1300 C/N:1350	Up to 0.7 atm Up to 1.6 atm N/A N/A	Four differents supports and two different configurations	[22]
C: 72-26.6*10^3 N: 16-8.64	C/N: 7000-2000	N/A		[23]

among all the cited literature, is 90×10^3-0.32×10^3 $1/m^2 \cdot s \cdot bar$.

Next, the selectivity, which is given in Table 2.8-2.10, are varied from 4.3-10,000 in two groups, one with 4.3-760 and other with 1000-10,000 with the exception of very high selectivity 163400 for CO_2/N_2 separation by Kovali etal (2001). These selectivities are the range for all the LMs given in the Tables 2.8-2.10. The comparison of selectivity is difficult because not all the LMs have employed the same separation tasks e.g. CO_2/CH_4 and CO_2/N_2. The influence of carriers on performance can also be seen i.e, by the use of carrier enhanced selectivities have been reported (e.g. [22, 23]).

The major problem of using LMs are their stability. Although, LMs are advantageous in terms of their performances, they lack in commercial use. Very few authors have

Table 2.10: Performance of supported liquid membranes contd.

S: 1-3.5*10^{-7}	N/A	N/A	Permeability is in kmol.m^{-2}.s^{-1}	[24]
N/A	N/A	N/A		[25]
C: 81-6.75*10^3	C/N: 3440-100	UP to 10 days		[26]
S: 27-1.8*10^3	S/N: 10^5-10^3	N/A		[27]
N/A	N/A	N/A		[28]
c: 162-13.5*10^3 d: 243-54 e: 189.5-0.0189*10^3 f: 270-81	g:2000-100 h: 2000-100	N/A		[29]
C: 20-21*10^6	C/H: 360	N/A		[30]
C: 115.2-14.4	C/E: 130-10	N/A		[31]
i-C: 1.4-0.5*10^{-9} j-C: 0.6-0.4*10^{-9} k-C: 1.8*10^{-9}	N/A	N/A	Flux values are in mol.cm^{-2}.s^{-1}	[32]
l-C: 7.9-3.8*10^3 m-C: 7.9-3.8*10^3	l:45-33 m:29-25	N/A		[33]
Am: 497.3-156*10^3	Am/N: 1000	N/A		[35]
n-O: 27.81-3.24*10^3 o-O: 15-0.793*10^3	n-O/N:20-170 o-O/N:4-79	temperature dependent	discontinuties had been seen	[36]

presented the stability of LMs used. The highest stability which can be seen among all reported LMs in Tables 2.8-2.10, is 50 days of continuous application [5]. Rooney etal (2006) have tested the LM for different stability influencing properties. Stability of any LMs are depend on absence of chemical bonding of carrier and liquids, evaporation of liquids or carriers, lower pressure tolerance etc. Support, liquid and carriers, all play a similar role in stability of LMs. Some of the efforts, which have been done in the field of instability of LMs, use of nanofiltration membrane [7], use of encapsulation technique [20].

3 Experimental

In this chapter, all the aspects of experimentation will be discussed. The description of liquid membrane module setup will be given in section 3.1. The information about the membrane liquid and the supports will be given in section 3.2. In section 3.3 the experimental setup for the permeability measurement is described. The experimentation method of supported liquid membrane preparation and permeability measurement will also be discussed in this section.

3.1 Supported liquid membrane module

In this work a novel membrane module for insitu preparation of flat sheet supported liquid membrane has been developed. For the case of manufacturing and the non-corrosive materials used in experiments, the module is made of aluminium. This module consists of four parts, which can be seen in Figure 3.1. The Figure 3.1 (a) shows the top part. To

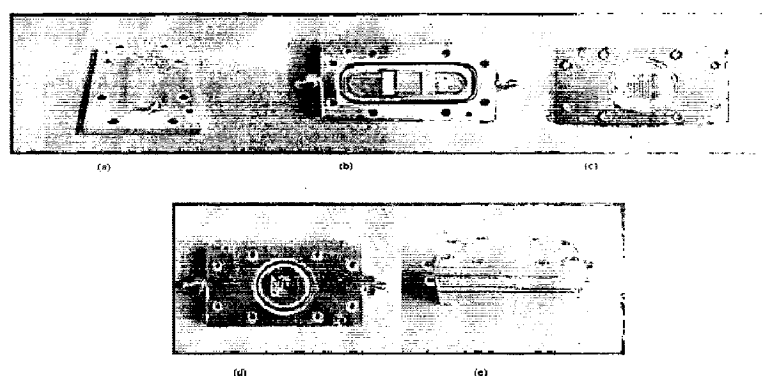Figure 3.1: Experimental module of supported liquid membrane

minimize the channel volume of the feed side, the top part Figure 3.1 (a), shows an extra oval projection. This extra projection is made due to following reasons:(i) it decreases the residence time, (ii) less requirement of liquid for LM preparation (iii) better analysis of gases in gas chromatography (GC). The Figure 3.1 (b) shows the second part, which

is the most important part of this membrane module. This part has flow ramps, which prevent the stay of liquid on the membrane after preparation. Excess liquid would increase the actual membrane thickness, which may decrease in permeability. The second part covers the membrane plate which is shown by Figure 3.1 (c). The wire mesh given in this part provides mechanical strength for the support and easily exchangeable for different membranes. The Figure 3.1 (d) represents the bottom part of this module. It has a small volume chamber, which provides good sweep conditions, less residence time and better analysis of gases in a GC. fluid and transfer it easily. For easy compaerison of different LM configurations , the open membrane area in the module is shaped to a square of 2×2 cm. Figure 3.1 (e) shows the assembly of all four parts.

3.2 Supports and liquid for SLM preparation

For the preparation of supported liquid membranes, two types of support are used in this work. The First is supplied by the Whatman and the second is supplied by the FluXXion. The specification of both flat-sheet supports are given in Table ?? and are quite comparable except the thickness. All the parameter shows difference of factor 1 or 2 after one decimal place, while thickness shows a factor of 60. The membrane liquid used in this work is 1-n-Butyl-3Methylimidazolium Bis(Tri-fluoro-methyl-sulfonyl)imide ([bmim][Tf$_2$N] or [BMIM][BTA], which is an ionic liquid.

3.3 Setup for permeability measurement of SLM

The experimental setup, which is shown in Figure 3.2, is used for preparation of liquid membranes and permeability measurements of propane and propene gas. Valves V$_{101}$, V$_{201}$ and V$_{301}$ are located at the gas supply cylinder and regulate the flow of N$_2$, C$_3$H$_6$ and C$_3$H$_8$ respectively. The valve V$_{203}$ allows one gas at a time to enter the membrane module. The fine dosing valve V$_{311}$ controls the immediate supply of pressure of the gas stream and protects the breakage of support membrane due to sudden pressure maxima. The Pressure indicator (PI/P04)indicates the pressure values just before the membrane module. This device is necessary because the support membranes used in this work are very pressure sensitive. The Valve V$_{401}$ allows either the feed gas or the membrane liquid to enter the module. The membrane feed pump, conveys the membrane liquid up to the membrane chamber for wetting the support. For the flow measurement a bubble flow detector is used in this work.
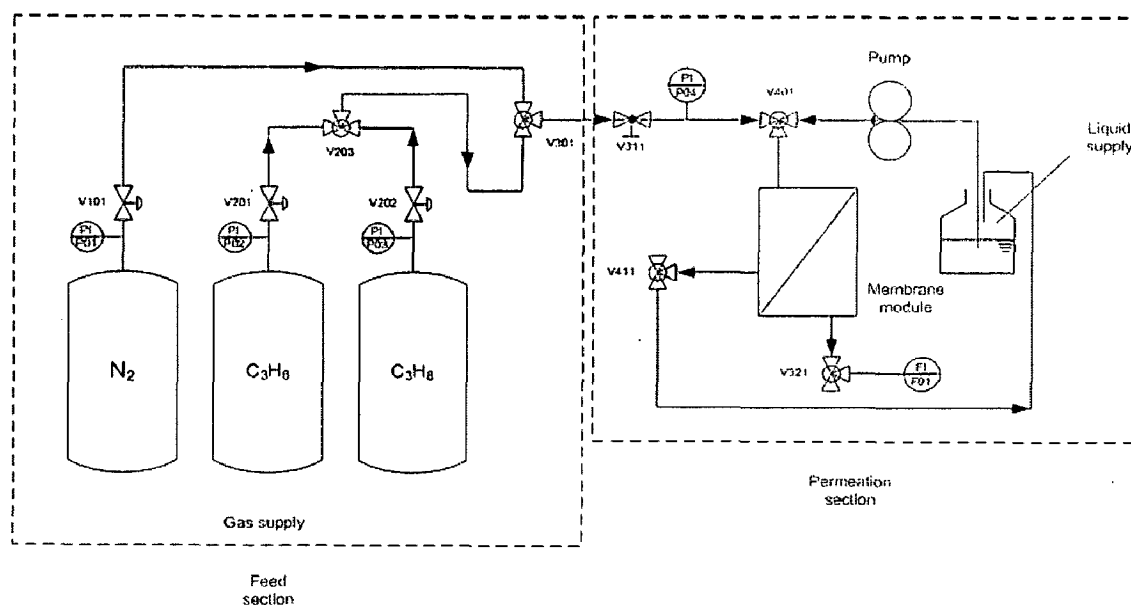
Figure 3.2: Setup of SLM preparation and permeability measurement

3.3.1 Preparation of Supported liquid membrane

The method of preparation of liquid membrane divided into three following steps,

1. **Wetting of support membrane**: After placing the support into the the module, the module is then installed to the main setup. A 50 ml volume of [BMIM][BTA] is put into a round flask and evacuated for at least 1 hr to release the dissolved gases from it. Now, the flask is connected to the pump. The [BMIM][BTA] is then pumped into the membrane chamber via a hose pump for 1 min and then allowed for 1 more min for wetting the support. This time may vary for different membranes, like in this work, for wetting the Whatman membrane, 1 min of wetting time and 1 min of retention was employed whereas Fluxion membrane 5 min of wetting time was employed.

2. **Removal of membrane liquid**: The removal of extra membrane liquid is then carried out by using N_2 gas. N_2 gas was used for this purpose, because it is an inert gas and dissolves to little extend in [BMIM][BTA]. The time of cleaning is 1 min for the Whatman membrane and 3 min for the FluXXion membrane. Initially, 1 min was also used for the FluXXion membrane but on checking some liquid was found on the membrane. During the cleaning operation, the gas pressure must not

exceed the maximum bubble point pressure of the supports. If the gas pressure exceeds this pressure, there may be a chance of breaking the LM.

3. **Check for wetted membrane**: After the cleaning operation, a checking of the membrane is done to see whether the membrane has been completely wetted or if it has some vacant pore sites. For checking, N_2 gas is again used because the permeability of N_2 gas is much smaller compared to other gases used. The permeability is checked for wetted and non-wetted support. If the wetted permeability is as high as the un-wetted membrane, this gives an indication of possibility that support may be broken or partially wetted.

After completion of these three preparation steps, supported liquid membrane is ready to use for permeability tests.

3.3.2 Permeability measurement

For the measurement of permeability, the volumetric flow rate of gas across the membrane is needed. The volumetric flow rate ($\dot{V}$) is then combine together with transmembrane pressure difference (Δp) and membrane area (A_m) to calculate permeability.

$$Q = \frac{\dot{V}}{\Delta p \cdot A_m}$$

The following precautions have to be taken in to account before starting the experiments,

1. Due to low thickness and sophisticated nature of these membranes, much care should be taken in placing of membranes inside the module.

2. The gas pressure should not reach the bubble pressure(P_B) of the membranes.

$$P_B = \frac{4 \cdot \sigma \cos \theta}{d_p}$$

3. The valve V_{311} must be opened slowly.

4. Before taking measurements with a new gas, the module must be flushed to ensure the correct readings.

5. Wear hand gloves and eye glasses during experiments, which prevent you from membrane liquid, in case of leakage or spillage.

The following procedure is applied to measure the gas flow rate:

- Connect the desired gas cylinder to the main line say for propane gas, open the valve V_{202} and adjust desired pressure maxima.

- Now, open the valve V_{203}, V_{301} and V_{401} to flush the membrane module with propane gas.

- Adjust the fine dosing valve now, to a desired flow rate.

- Close the valve V_{411} and allow the buildup of rea desired feed pressure.

- Measure the flow readings from the bubble flow detector FI/F01.

- Repeat the procedure for different pressures.

4 Results and Discussions

In this chapter, the results obtained from the experiments will be given. The permeability experiments have been performed in two sets. One set of experiments are performed with the Whatman membrane and second set of experiments are performed with the FluXXion membrane, which are being described in section 4.1 and section 4.2 respectively. The experiments were done for permeability and perm-selectivity measurement of propane and propene gases. All the experiments are carried out at constant temperature.

4.1 Experiments on Whatman membrane

In this section 4.1, performance of whatman supported liquid membrane for the propane and the propene gas is discussed. The experiments were carried out with the $[BMIM]^+[BTA]^-$ ionic liquid supported on a whatman membrane. Before starting the experiments, support has been wetted with ionic liquid and then tested for complete wetting by procedure given in Chapter 3. A pressure range of 1-5 bar has been applied due to the pressure tolerance given by the manufacturer.

In Table ?? experiments, which are carried out for the propane and the propene gas at two different pressures, can be seen. In both the experiments roughly the same pressure intervals have been applied to assume good comparability between them. The procedure of carrying out the experiments is given in section 3.3.2. The gas flow was not detected until it reached certain value i.e. 2.2 bar in this case The molar flow rates, which are given in Table 4.1, are calculated by modified ideal gas law;

$$p \cdot \dot{V} = \dot{n} \cdot R \cdot T$$

Where, p is the pressure difference, $\dot{V}$ is the volumetric flow rate of respective gas, R is the universal gas constant, T is the operating temperature i.e. room temperature. The experimental permeability values are calculated by the formula given below;

$$Q = \frac{\dot{V}}{A \cdot \Delta p}$$

27

Table 4.1: Experimental results of propane gas for the Whatman SLM

Gas	Pressure (bar)	Volumetric flow rate $\times 10^4$ (cm^3/sec)	Molar flow rate$\times 10^{11}$ (mole/sec)	Permeability (l/m^2.h.bar)
Propane				
	2.2	3.75	3.33	2.28
	3.5	19.16	27	6.9
Propene				
	2.4	8.33	8.05	5.34
	3.6	56	82.22	19.4

where, Q is the permeability, A is the membrane area, Δp is the pressure difference between feed side to permeate side.

Figure 4.1 shows a permeability comparison of propane and propene gas. Propene shows results show higher permeability than propane gas at the constant pressure and resulting a difference of about 60 percent. The selectivity with respect to propene gas can also be
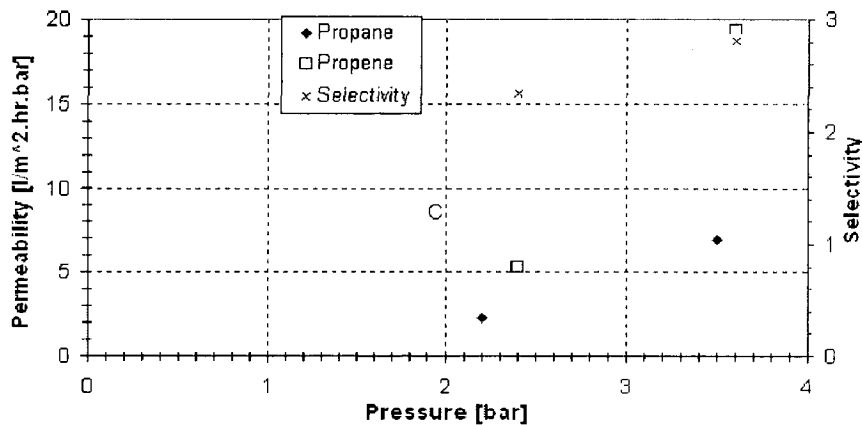

Figure 4.1: Permeability and selectivity of propane and propene gas for the Whatman LM

seen in Figure 4.1 and clearly shows this combination of liquid and support is selective for the propene gas though the selectivities are not very high.

Figure 4.2 shows a graphical representation of the propane gas permeabilities between this work and the work, which has been done by Koaster [4]. Koester has used the same
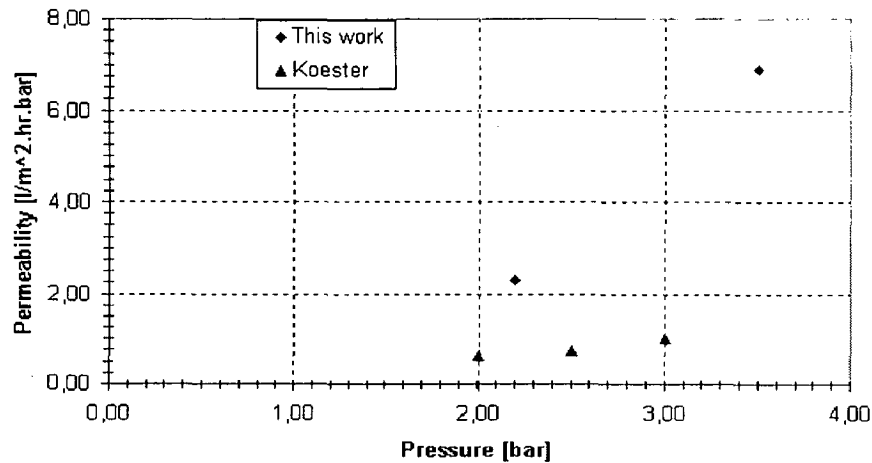
Figure 4.2: Comparison of propane permeability results with Koester's [4]

Whatman membrane and assumed no liquid layer on top of the support. The values corresponds to Koester's are comparable to some extent. The values, which are taken for comparison, are almost at the same pressure differences. Figure 4.3 shows the similar
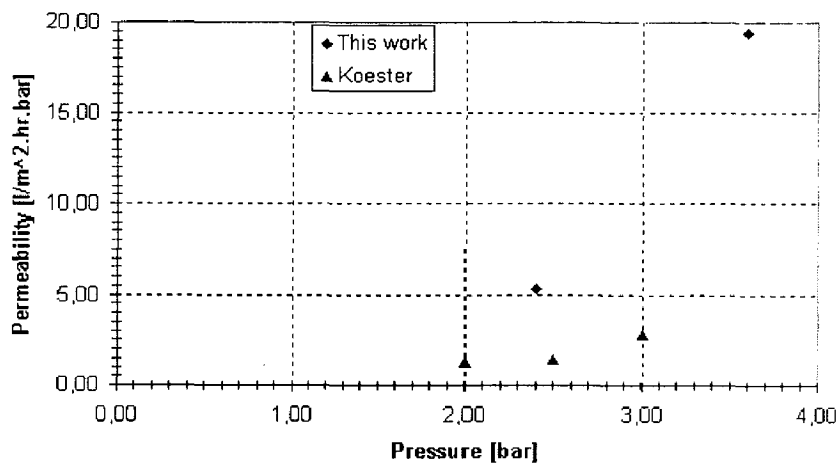
Figure 4.3: Comparison of propene permeability results with Koester's [4]

comparison but for the propene gas. The same trend is also been found in this case but the difference in this case is even higher. Koester's value for the gases are comparable to this work's values up to 3 bar whereas at 3.5 bar are out of range.

In Koester's work, there is no liquid layer, but in this work liquid layer is presented but the reason og getting higher values of permeability and selectivity is has not been found and could be the objective of a continuation work to this work. It may also possible that in this work, pores of the supports are not totally filled i.e.the overall thickness of

the membrane is decreased. In this work, the area, which is open for the flow of the gases, is regarded as the membrane area. But the possibility of leakage from the sides of the open area walls to the membrane might be there. The trend from all measurements which is coming out from Koester's work, is like a bubble point pressure curve, which dictates that after reaching the disjoining pressure pores are no longer being filled by the liquid. Due to time limitation, more observation has not been taken in this work for a clear trend. But it might be said that, in our case bubble point pressure has been reached and some pores may be get opened.

4.2 Experiments on FluXXion membrane

In this section experiments, which were performed on the FluXXion supported liquid membrane, will be presented. The experiments was performed for one gas pressure only, for both of the gases. Temperature is assumed to be constant during the experiments. The FluXXion support is more sensitive than the Whatman support, so the more care was taken while doing the experiments with it.

The results of the performed experiments, which have been performed on Fluxxion membrane, are given in Table 4.2. The procedure as given in Chapter 3 has also been adopted in this case. At almost the same operating pressure propene has got higher value by, a factor of 2 in volumetric flow rate or molar flow rate and a factor of 3 approx in permeability.

Table 4.2: Experimental results of propene gas for the FluXXion LM

Gas	Pressure (bar)	Volumetric flow rate $\times 10^4$ (cm^3/sec)	Molar flow rate $\times 10^{11}$ (mole/sec)	Permeability (1/m^2·h·bar)
Propane				
	1.26	3,17	16.1	11.15
Propene				
	1.18	6.33	30.6	31.65

Figure 4.4 shows a permeability comparison of the propane and the propene gases. The Figure 4.4 shows a obvious trend between the propane and propene gases, which can be seen for Whatman performance also, that the permeability of propene is higher than that of propane. On comparison, it has been found that the selectivity of the propene/propane
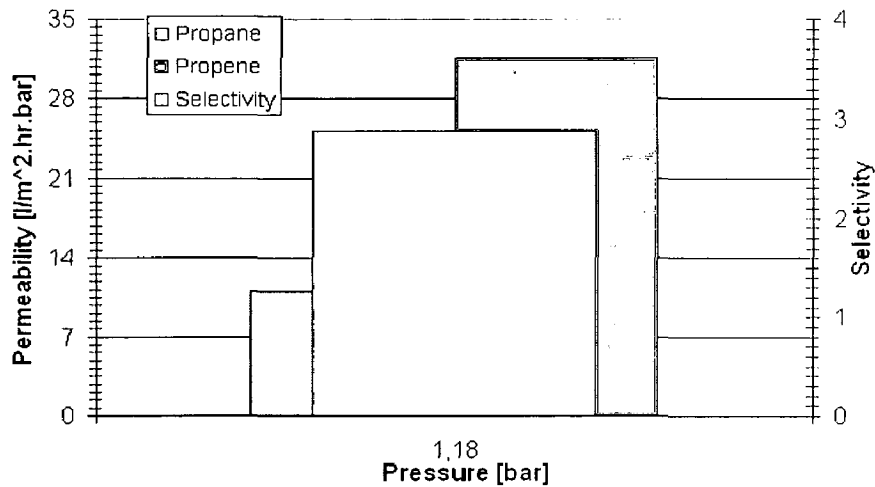
Figure 4.4: Permeability and selectivity of propane and propene gas for the FluXXion LM

gas using the FluXXion LM is slightly higher than the Whatman membrane. Due to low pressure tolerance of the FluXXion membrane, more observation has not been performed. But if the similar may follow as in the case of Whatman i.e. permeability increase with increase in pressure difference, so at the same pressure, the FluXXion would have higher permeability ans selectivity values than the Whatman membrane.

Symbols

A	Propane	C_3H_8
C	Carbon dioxide	CO_2
E	Propene	C_3H_6
H	Hydrogen	H_2
M	Methane	CH_4
O	Oxygen	O_2
S	Sulfur dioxide	SO_2
Am	Ammonia	NH_3
BA	Butane	C_4H_{10}
BE	Butene	C_4H_8
CM	Carbon monoxide	CO
HS	Hydrogen sulfide	H_2S
Q	Permeability	$[l/m^2 \cdot hr \cdot bar]$
S_P	Permselectivity	$[-]$
Δp	Pressure difference	$[bar]$
A_m	Membrane area	$[m^2]$
σ	Surface tension	$[N/m]$
$\dot{V}$	Volumetric Flow rate	$[cm^3/sec]$

Abbreviations

Abbreviation	Meaning
CA	Carbonic anhydrase
GC	Glycerol carbonate
DEA	Di-ethanol-Amine
MEA	Mono-ethanol-Amine
TEG	Tri-ethylene-glycol
$BEHA$	Bis(2-ethyleexyl)-amine
$DETA$	Di-ethylene-tri-amine
$PAMAM$	Poly(amidoamine)
$PVDF$	Poly-vinyl-difluoride
$[BTA]$	Bis(trifluoromethyl)sulfonylamide
$[Bmim]$	1-butyl-3-methylimidazolium
$[Emim]$	Ethyle-methylimidazolium
$[Pmim]$	1-propyl-3-methyleimidazolium

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A Appendix I

Abbreviations in Table 2.10

a	PVDF
b	PVDF+celegard 2500(double layer)
c	MEA-CO_2
d	MEA-CH_4
e	DEA-CO_2
f	DEA-CH_4
g	MEA-C/M
h	DEA-C/M
i	Primarily cross linked membrane
j	Secondary cross linked membrane
k	Ion-exchange support
l	DEA
m	DIPA
n	$LiNO_3$
o	$NaNO_3$

B Appendix II

Properties of supports used in this work

Support	Porosity (ε)	Pore size $[\mu m]$	Tortuosity (τ)	Thickness $[\mu m]$	Membrane area $[cm^2]$
Whatman	0.4	0.1	1	60	4
FluXXion	0.2	0.35	1	1	4