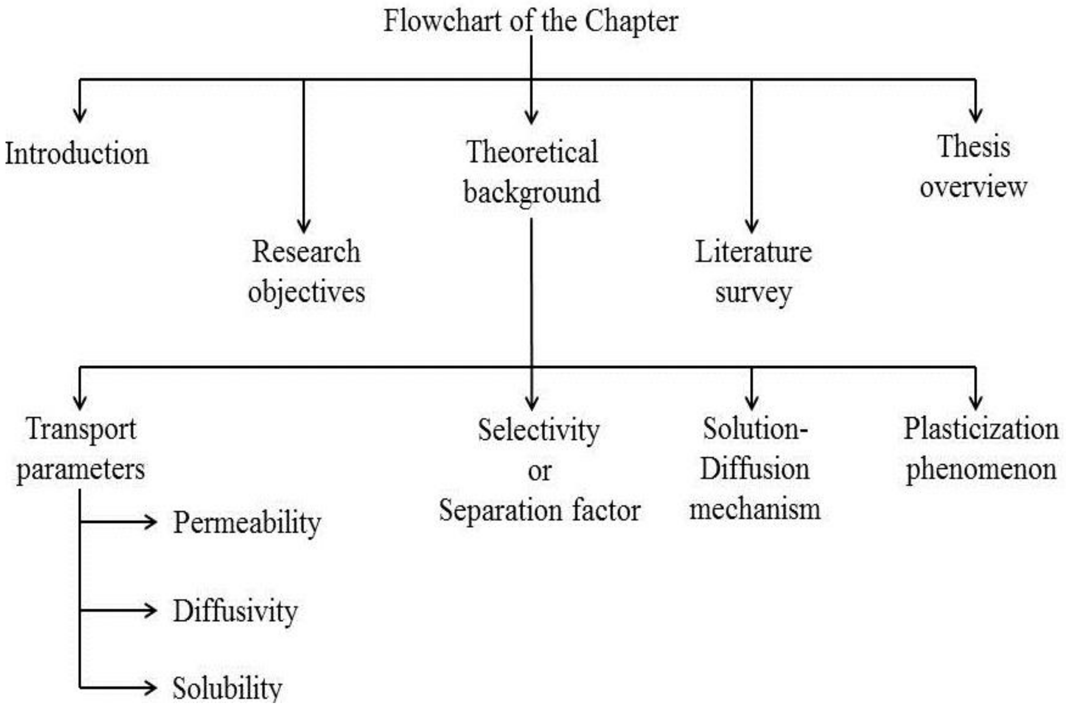
CHAPTER 1

INTRODUCTION

Chapter-1

Introduction

The proposed thesis is initiated with understanding the subject entitled "S*tudy of Gas Permeation for Polymer Blend & Composite Membranes*". In this title, the term "membrane" becomes the focal point of the presented subject. Therefore, the description can be initiated with understanding the term. In general terminology, membrane is a simple object such as filter which bypasses one component and restricts another, whereas in scientific terminology, membrane is a physically or chemically distinctive two phase system which consist group of phases between them. Due to differences in physical or chemical state of both the boundary phases, membrane can control the mass transport as per the applied force field [1]. Moving on the next term to be understood is the "gas permeation" means transportation of gas molecules with respect to applied force field. In the chemical industries, membrane based gas separation compete with other technologies such as adsorption, pressure swing adsorption and cryogenic distillation. But the membrane technology is more applicable compared to other separation processes on the basis of overall economy, safety point of view and due to environmental and technical aspects. In membrane fabrication, several organic and inorganic materials are used. Generally, polymeric materials are widely applicable in major gas separation processes such as hydrogen recovery, natural gas purification and air separation. Many new families of modifications in the membrane material have been developed to improve gas permeability and selectivity [2]. Therefore, the selection of membrane material for gas permeation process is an important task. As the polymeric materials are utilized for this study, to improve the membrane efficiency respected to the proposed application, several modifications can be applied to membrane materials for better performance. This chapter includes theoretical background, objective of the work, literature survey and finally the outline of the thesis. The flowchart of the chapter is given below.



1.1. Introduction

The wide spread interest in membrane technology which has been emerged in an extensive range of industrial applications including chemical, petrochemical, medical, pharmaceutical, water treatment, food packaging, dairy industry, electronic industry and textile industry. The existing applications of membrane technology includes: (1) reverse osmosis process for west water treatment and desalination of sea water, (2) biopharmaceutical separation by ultrafiltration, (3) nanofiltration for organic solvents, (3) tangential flow filtration for virus capture and clearance, (4) gas and vapour separation, (5) facilitated transport membranes for environmental and energy applications, (6) removal of large protein molecules from chees, milk and chasein whey, (7) sterilization of medical and pharmaceutical products by microfiltration. Even the membrane based separation and purification process have low energy consumption as well as cheaper in operating cost [3-7]. Moreover, the membrane processing is concerning huge potential towards

CO_2 separation compared to traditional processing such as absorption and adsorption [8].

Membrane materials such as polymers are widely applicable to perform mass transport process as they are cost efficiently and environment friendly [9-11]. Furthermore, the applied upstairs to enhance performance of gas filtration and separation of gas species give rise to modifications in membrane technology. For effective gas separation application, polymers have been classified as their utility. Polymeric membrane for gas separation is generally non-porous and their gas permeability is described by solution-diffusion mechanism. Polymer materials such as polyimide, polysulfone and polycarbonate concern for structural variation providing considerable scopes. For separation process, membrane material should have some specific physical and chemical properties existing under the operating conditions. Polymeric materials having specific transport routs, choice of material can be fulfilled to achieve recovery of specific species and high purity separation. For gas separation, membrane transport follows trade-off relationship between permeability coefficient and separation factor. The plot of permeability versus selectivity for such materials fall below a limiting border line which is known as Robeson upper bound limit [12, 13]. The motivation of latest development going on new hybridized membrane materials is to surpass the Robeson upper bound with better selectivity performance as shown in **Figure 1.1** [13, 14]. Permeability and selectivity values ranges below the upper bound limit drawn in blue color. The majority membrane materials do not lie towards the attractive region which has been explained by Freeman especially for polymeric gas separation with respect to the basis of the trade-off relationship [15].

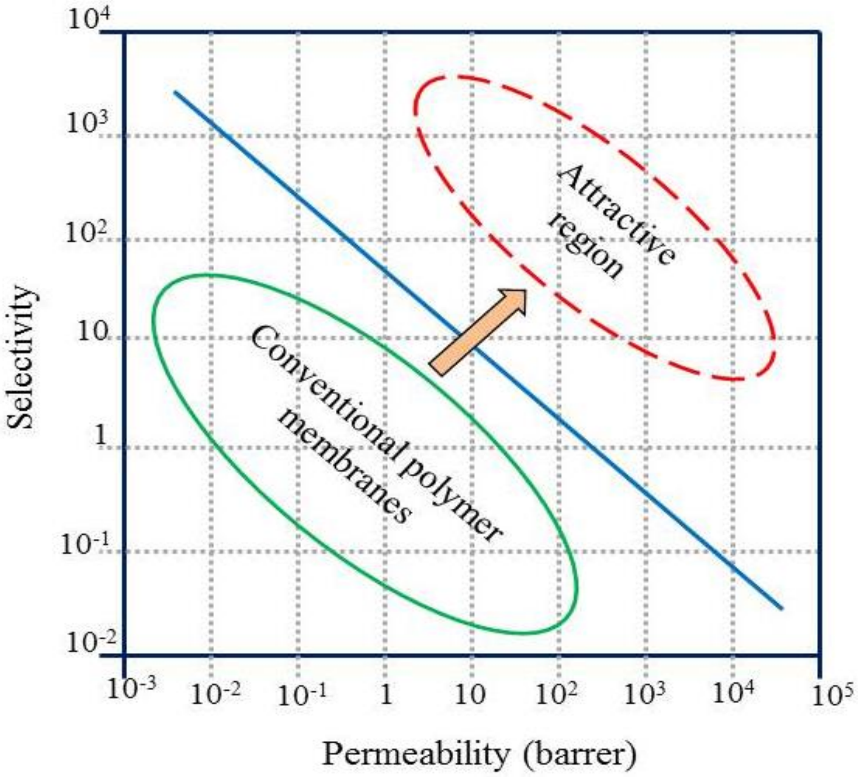


Figure 1.1 Robeson upper bound for gas separation membranes

1.2. Research objective

The overcharging goal leading to present study is to develop modified membranes that can improve transport parameters without loss in the trade-off separation factor. It was aimed to fulfill this research work with cost effective and well reliable techniques. As we talk about economical point of view, it is related to the cost of gas permeation testing equipment. The development of suitable system in our laboratory for analysis of synthesized membrane is one of the challengeable tasks in this work. Even the components to functionalize the equipment should be available in the nearby market. Overall, the selection of low cost and easily available materials can also reduce the research cost. Therefore, the choice of low cost membrane materials and chemicals is also a demanding task. Another objective to be implemented is the comfort membrane fabrication technique. The selection of synthesis process compatible with laboratory environment using available apparatus is also an important objective. Some specific objectives related to the research work are described below:

(a) To analyze gas transport parameters and selectivity of various gas pairs by metal coated polycarbonate membranes and their comparison with published work. The effect of gas leakage by the system and variation in gas permeation with respect to kinetic diameter of gases to be tested will be covered in this analysis.

(b) An investigation about plasticization of metal coated membrane by carbon dioxide gas.

(c) To study hydrogen transport through layered membrane and nanofillers doped in different filler content. The effect of the modifications made on selectivity with other gases should also be scrutinized.

(d) The development of blend and blend composite membranes with incorporation of nanofillers by solvent assists methodology. A key challenge in the synthesis of nanofiller MMM is the uniform dispersion within the polymer matrix.

(e) To study surface morphology, membrane strength and its thermal properties by complementary characterizations.

(f) To obtain permeability/selectivity values that can lie above or tend towards the Robeson upper bound.

(g) To conclude the entire research analysis and the future scopes which can be carry forward by the proposed work.

1.3. Theoretical background

1.3.1. Transport parameters

The penetrant mobility inside the membrane matrix is determined by its transport parameters such as diffusivity, solubility and permeability coefficient. The parameters depend on size of penetrant, membrane material, membrane thickness, exposed area, operating pressure and temperature.

(a) Permeability

Gas permeability coefficient of membrane is its intrinsic materialistic property. Permeability coefficient indicates the rate at which penetrant traverses across the membrane thickness given by equation **1.1**. It is the measure of amount of gas flux passing through unit area within unit film thickness in unit time interval.

$$P = l \cdot \frac{J}{\Delta P} \tag{1.1}$$

where, P is the permeability coefficient, ΔP is the pressure difference across the membrane and J is the amount of gas flux. Gas permeability is usually reported in unit barrer where 1 barrer = 10^{-10} cm^3(STP)·cm/ cm^2·s·cmHg. The unit of gas flux is cm^3(STP)/cm·s. Permeability coefficient is also defined as product of a kinetic parameter, diffusivity coefficient and a thermodynamic parameter, solubility coefficient [16] given by equation **1.2**.

$$P = D \cdot S \tag{1.2}$$

where, D is the diffusion coefficient and S is the solubility coefficient. Generally variations in diffusion coefficient are larger than the solubility coefficient which mainly dominates permeability coefficient. Permeability varies differently as per the operating pressure depending on the membrane material to be tested and nature of exposed gas. Up to 10 atm feed pressure, permeability coefficient of H_2, He, N_2 and O_2 is not affected in both glassy and rubbery polymeric membrane by pressure variations. Especially in the polycarbonate membrane permeability of such gasses remains constant within 3 atm to 10 atm pressure range [17]. Permeably of other gases in glassy polymer slower down with gain in pressure while in rubbery polymers it gains. Permeation rate increases for gases which exhibit swelling and plasticization after some pressure value. Low density and higher free volume promotes gas permeation. Higher crystallinity, cross linking and orientation of polymer chain segments reduces permeability coefficient [18].

Another parameter related to permeability is permeance which determines the steady state gas transport rate through the membrane.

Permeance is independent of membrane thickness. When permeance is multiplied with membrane thickness it becomes permeability [6, 19]. The unit permeance is applicable in packaging applications of the membrane.

(b) Diffusivity

Diffusivity indicates the transport rate of penetrant within membrane matrix. Diffusion of small gas molecules in the polymeric medium functionalizes both diffusant as well polymer. Diffusion coefficient is influenced by various factors such as: (1) Physical state and molecular size of penetrant, (2) Penetrant compatibility with polymer matrix, (3) Membrane morphology and (4) Interfacial energy of membrane structure [6, 20]. Diffusion through polymer membrane depends on the polymer free volume and its segmental mobility. The shape of diffusive gas molecule should not be ignored while discussing about diffusion coefficient as the spherical gas molecule diffuses faster compared to linear, elongated and flattened molecule. For gas molecules having weak interactions with polymer composition, diffusion coefficient is independent of gas concentration. For plasticized system and gasses influencing plasticization behavior do not possess constant diffusion coefficient. The diffusion of gas molecules in the glassy polymer membrane follows Fick's law of diffusion. According to this law gas flux passing through the membrane is directly proportional to concertation gradient:

$$J = -D \frac{dC}{dx} \qquad \textbf{1.3}$$

In equation **1.3**, dC/dx is the concentration gradient. The determination of diffusion coefficient can be performed by time lag interpretation. As the fed gas is applied at constant operating pressure to the membrane inside closed volume system, the gas permeates due to concentration gradient. The permeate gas is monitored towards downstream side as a function of time which is plotted in the **Figure 1.2**. The x-intercept of initial transient regime is considered as time lag denoted by Θ. The relation between time lag and diffusion coefficient is given in below equation **1.4**:

$$D = \frac{l^2}{6\Theta} \qquad \textbf{1.4}$$

where, *l* is the membrane thickness and unit of diffusion coefficient is cm^2/s.

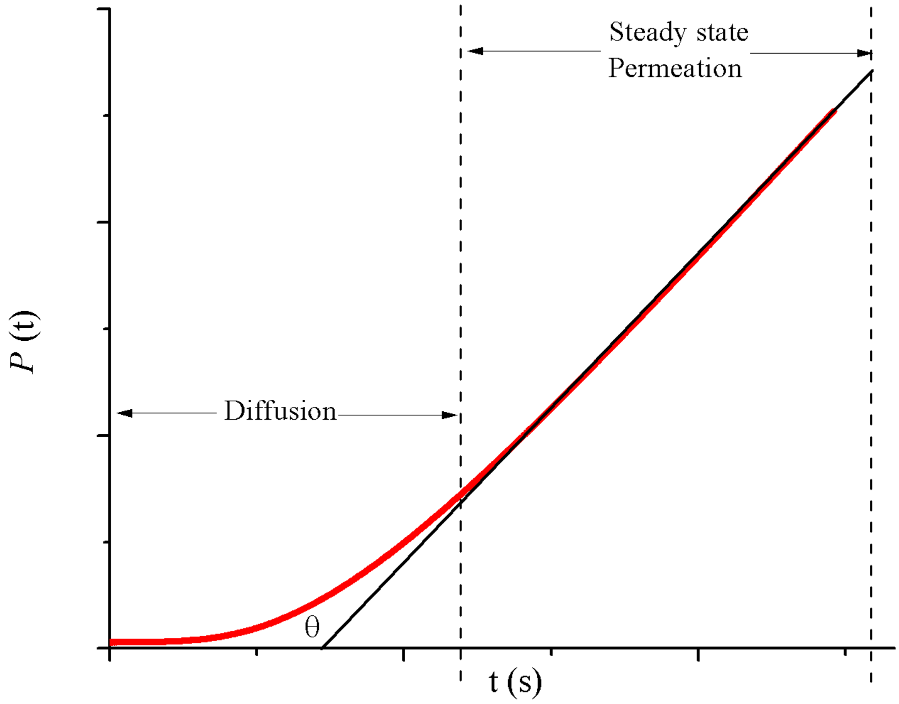


Figure 1.2 Time lag profile of gas permeation for glassy polymer membrane.

(c) Solubility

It is defined as the amount of gas molecules sorbed by the membrane. It is also called sorption coefficient which is thermodynamic parameter. The unit of solubility is $cm^3_{gas}(STP)/cm^3_{polymer} \cdot cmHg$. As it is related to specific interactions between penetrant and polymer, it is influenced by gas condensability, free volume distribution and distribution of electron density in the polymer matrix. Solubility increases as the interaction between a gas and polymer functional group becomes stronger. e.g. CO_2 being polar molecule, is much soluble in polymers having polar functional groups. Solubility coefficient can be determined by the permeability-diffusivity relation as per given in equation **1.5**:

$$S = \frac{P}{D} \qquad \textbf{1.5}$$

1.3.2. Solution-diffusion mechanism

The transport of gases through dense or non-porous polymer membrane obeys solution-diffusion mechanism. The model can be applied to study membrane performance such as in reverse osmosis, gas separation, pervaporation and dialysis [21]. In nonporous membrane system, solution-diffusion mechanism authorizes both solubility and mobility factors. Therefore, the separation based on this mechanism depends on solubility selectivity which favors most condensable gas molecule and selectivity by diffusion supports smallest gas molecule [22].

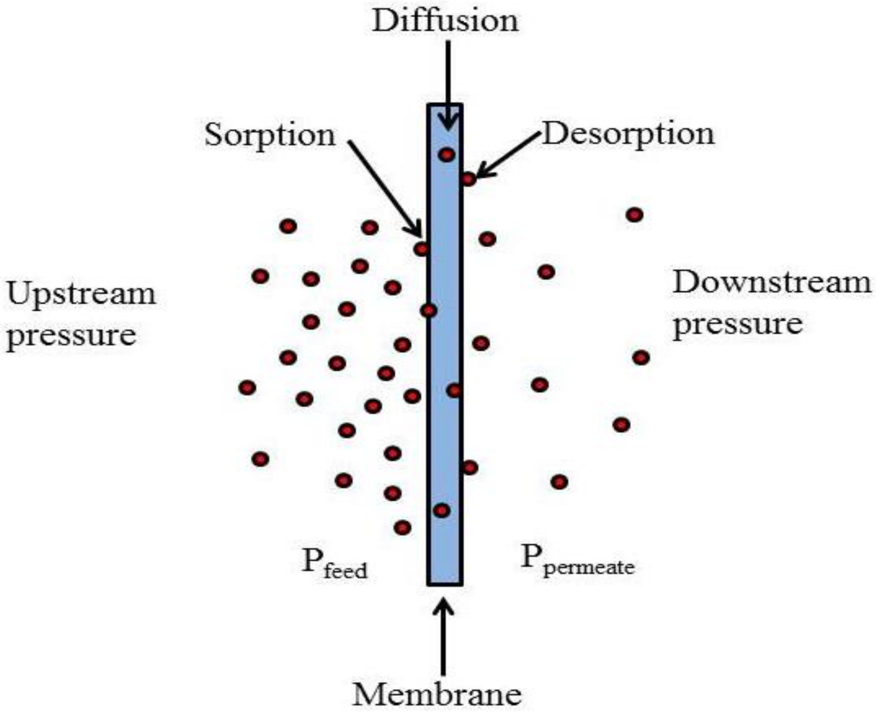


Figure 1.3 Schematic of solution-diffusion model

Figure 1.3 shows the transport of small gas molecules by dense membrane is described by solution-diffusion mechanism classified in to three steps mentioned below:

(a) *Sorption*: Gas molecules dissolve in upstream side of membrane under the driving force of pressure difference. Thus gas molecules are absorbed by the membrane surface where the feed gas is exposed normal to the membrane surface.

(b) *Diffusion*: Gas molecules are diffused through the membrane matrix under concentration gradient developed by pressure difference between the membrane surfaces.

(c) *Desorption*: Desorption of gas molecules occurs towards downstream side of the membrane as it is placed in a closed volume system under constant feed pressure.

The diffusion process is much slower than the gas absorption and desorption at the membrane surfaces. Therefore, solution-diffusion model assumes rapid occurrence of equilibrium conditions between molecules within gas phase and molecules selective on membrane surface [23].

1.3.3. Selectivity or Separation factor

Membrane is molecular scale filter which permeate one component at particular feed pressure and resist another component according to the penetrant size. Selectivity or separation factor is defined as the membrane ability to separate different species of binary gas mixture as shown in the **Figure 1.4**.

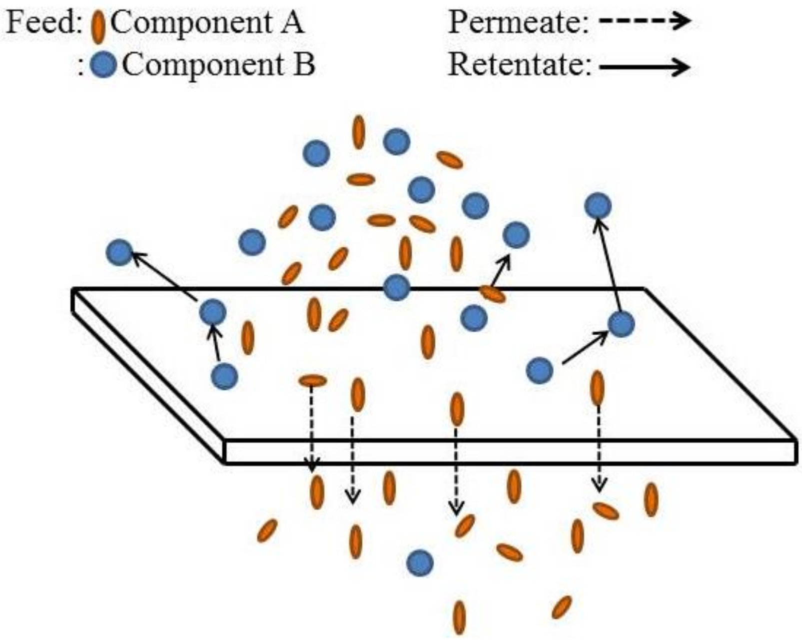


Figure 1.4 Schematic diagram of membrane based separation process

It is the ratio of permeability coefficients of two gasses as given in the below equation **1.6**:

$$\alpha_{AB} = \frac{P_A}{P_B} \qquad \textbf{1.6}$$

Where, α = Separation factor, P_A = Permeability of gas A, P_B = Permeability of gas B. The above equation is applicable when the downstream pressure is negligible as compared to upstream gas pressure. In glassy polymer membrane the permeation rate is very slow which indicates the gas pressure towards permeating side is very small relative to operating side of the membrane. The above equation is also true for diffusivity selectivity and solubility selectivity. Factoring the permeability term in the form of diffusivity and solubility the above equation can be written as:

$$\alpha_{AB} = \left[\frac{D_A}{D_B}\right] \cdot \left[\frac{S_A}{S_B}\right] \qquad \textbf{1.7}$$

where, D and S are diffusivity and solubility respectively for A and B gas components [24].

1.3.4 Plasticization phenomenon

The term plasticization is referred as the reduction of stiffness in the polymer chain and promotes its mobility. Plasticization of membrane at higher feed pressure depends on the penetrant concentration. Due to high penetrant concentration, free volume increases which facilitate molecular motion inside the membrane matrix promoting permeability. Generally, the gain in the polymer chain mobility promotes diffusion coefficient. In glassy polymer membrane, as the feed pressure is increased, permeability coefficient decreases for CO_2 and organic vapors [25]. The effect of plasticization on permeability and selectivity is explained by **Figure 1.5**.

(a) *Effect of plasticization on permeability*: It reaches up to a minimum value as per gain in pressure and starts increases beyond this minimum permeability for further increase in upstream pressure as shown in **Figure 1.5**. This operating pressure at the minimum permeability is called plasticization pressure denoted by P_p and the membrane is completely plasticized at this pressure value. The diffusion of slower gas molecule is more affected by faster gas molecules due to plasticization which overall increases permeability of slower gas molecules.

(b) *Effect of plasticization on selectivity*: In the binary gas mixture, selectivity reduces with gain in pressure although it consist plasticizing and non-plasticizing gas molecules [26]. The plasticization phenomenon also follows the trade-off nature for the glassy polymeric system.

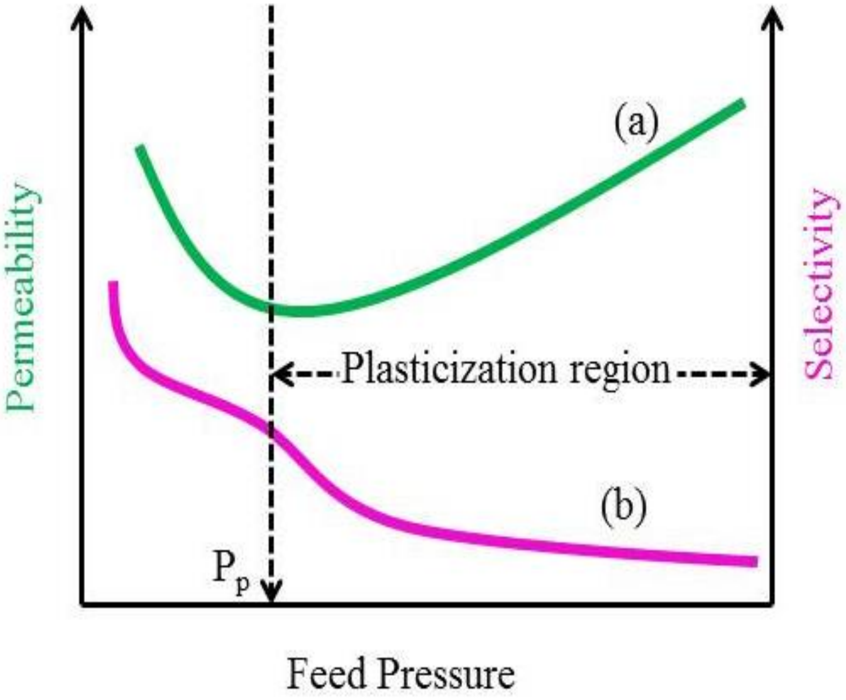


Figure 1.5 Permeability and selectivity versus feed pressure for plasticization effect

1.4. Literature survey

In the past few decades, different hybridizations are taken in to account such as irradiation, grafting, electron beam bombardment, etching, cross linking etc. to improve membrane performance [27-30]. The resultant composite membrane shows drastic change in polymer free volume as well in membrane morphology. Permeability coefficient and separation factor are effective parameters to determine better membrane performance. Therefore, modified membrane structure may overcome trade-off relationship between permeability and selectivity. It is expected to result in better separation performance for such alteration in membrane structure that selectivity may cross or tend to the Robeson upper bound limit. Polymer modification can also be obtained by layer deposition, blending, composite and mixed matrix formation. A huge potential reward can be offered by this alteration not only in the gas transport applications but also in rest of the industrial applications [28, 31, 32]. The operations performed in the separation process are: recovery of H_2 from N_2 gas mixture, CO_2 removal from air, H_2 separation from CO_2, enrichment of nitrogen, acid gas treatment, refinery gas purification etc. [2, 11]. Several factors, such as properties of gas penetrant, membrane material, its morphology as well its structure and operating conditions influence flow of gas flux across the membrane [33]. Usually, membranes are prepared from polymer or inorganic materials. Both are having several advantages and disadvantages. Polymer material is hard in glassy state and soften as well flexible in rubbery state. While inorganic materials are susceptible towards microbial attack and resistive to higher temperature, pressure and fouling effect. Some of the polymers are plasticized under CO_2 explosion which lead to lower the separation factor. The inorganic materials do not show such an issue. The mixed matrix membrane (MMM) composed of organic and inorganic material combines improved permeability, selectivity, flexibility, mechanical strength and thermal strength. Moreover, the resultant composition also reduces capital cost [34].

The latest technologies have developed membrane matrix composed of inorganic filler within organic frame which serves future applications of mixed matrix membrane. Loading of nanoparticles in the polymer nanocomposite (PNC) membrane promotes gas transport properties and also influences separation factor up to some extent [35, 36]. Described by Idris et al., the inorganic filler is preferred in nanorange that can effectively contribute to respected field applications. The dispersion of SiO_2

nanoparticles in to the host polymer matrix qualify the intermolecular chain packaging of PC membrane resulting in the morphological change along with polymer structures. PNC membrane with silica content can improve thermal and mechanical properties as suggested by Idris et al. [37]. CO_2 permeability was enhanced with maintaining CO_2/N_2 and CO_2/CH_4 selectivity by nanosilica loading in brominated poly (2,6-diphynyl-1,4-phenylene oxide) nanocomposite membrane compared to pure polymer membrane as reported by Cong et al. [38]. In free volume increase mechanism, polymer-chain packing is disturbed by addition of nanofiller in the polymer material tending to promote FFV. Specific nanovoids developed in the membrane matrix enhance the diffusion pathway of penetrant resulting gain in permeation. Zeolite imidazolate framework (ZIF) incorporated in to polystyrene plays vital role to improve CO_2/N_2 selectivity at high pressure. The modification does not affect CO_2 plasticization and its permeation at higher operating pressure [39].

Among number of modification techniques reported in the literature, polymer blending is simplest approach to fabricate high performance membranes. The selection of compatible materials for blending can improve properties of resultant material which is not found in the individual [40]. The blend membrane matrix composed of torlon and carboxylate polymers of intrinsic microscopy (cPMI-1) increases gas permeation and its anti-plasticization quality promotes separation of O_2/N_2, CO_2/CH_4, CO_2/N_2 and H_2/N_2 gas pairs. Therefore, its separation exists closer to Robeson’s upper bound value [41]. Separation factor is optimized by PSF/PES blend membrane for CO_2 gas from CO_2/CH_4 gas mixture [42]. Separation of H_2 from CO_2 and N_2 is promoted by blending of matrimide and PBI due to high polymer chain packing density. Thus, the segmental mobility is demoted which allows smaller kinetic diameter gas molecules to bypass and restrict the larger molecules [43].

Surface modification accomplishes barrier properties by thin film deposition which can be achieved by metal coating to promote separation factor. Coating of inorganic layer over polymer membrane is also a better option for surface modification of the membrane. In case of layered polymer membrane, the coating reduces permeability promoting separation factor or it may gain permeability as a result of defecting coating layer. Ti coating on polycarbonate membrane reduces the permeability of H_2 and CO_2 and simultaneously increases the selectivity of H_2 [44, 45]. Zhongde Dai et al. published his work on multilayer polymeric membranes amending separation of H_2/CO_2, CO_2/N_2 and CO_2/CH_4 gas pairs. The layer deposition promotes not only separation factor but also improves an important selective criteria such as high permeability [46]. The mechanical and thermal stability are remarkably improved in polymer/layered silicate membrane compared to conventional composite membranes. Lower silicate content is required relative to conventionally filled membrane composition and such membranes are lighter in weight. Due to lower weight, the membrane can be applicable in automotive and food packaging industry [47].

As hydrogen energy has become major energy source since last few decades, its extraction from hydrocarbons, water, natural gases and coal has become the need of hours. In recent scenario, clean energy resources are considered to use for pollution free environment. Therefore, hydrogen is the most applicable fuel as water is produced as by-product by its combustion. Production of hydrogen gas from hydrocarbon also produces CO_2, the most responsible gas for greenhouse effect. Therefore, its separation is necessary from hydrogen. Material compatibility with penetrant gas also affects its separation from the gas mixture and palladium is most selective material as it attracts H_2 molecule. The composite material formed by Pd membrane with other membrane compositions performs better for hydrogen separation from the mixed gas states [22, 48]. Material composition for fair hydrogen gas filtration should be semi permeable rigid enough that can separate small species of gas molecules. Certain metallic membranes supports flow of hydrogen affinity but refuse to permeate other gases. The most compatible material for hydrogen diffusion is palladium which exhibits better selectivity compared to other membrane compositions and possesses good mechanical strength at higher temperature [22, 49, 50]. Palladium membrane is considered as extremely selective for hydrogen gas but due to few drawbacks it is doped or composites with other compositions. Gas permeation applications are limited for pure Pd membranes due to its irreversible damage by sulphide formation and its high coast. At low temperature the exposed H_2 molecules in to Pd are locked inside the lattice causing stress in the membrane matrix. In addition, if Pd membrane is subjected at 450 ºC by carbon compounds, deactivation occurs and below 300 ºC temperature, hydride formation takes place as exposed by H_2 gas. Pd alloyed with Pt performs better to overcome these difficulties [51]. CNTs compositing with Pd nanoparticles perform better improvement of H_2 sensing [52]. Kadirgan et al. scrutinized Pt compatibility with other metals in alloying for modification of legend structure of Pt in week effect of CO absorption on Pt surface. Hydrogen oxidation is more effectively proceed on Pt surface for fuel cell applications. Additionally, separation of hydrogen can be improved by the alloy structure. Due to the compatibility of hydrogen gas molecules with Pd which provides vacant site to dissociate from the surface improving desorption from downstream side of the membrane [53]. The issue can be remedied by alloying Pd with other metallic materials such as silver or platinum. Doping material can improve interaction of penetrant and host membrane material protecting lattice structure. As the gases interact with metal surface forms charge transfer improving solubility of gas molecules within the member [28, 54]. The performance of fuel cell can be improved by Pt-Pd alloy due to resultant FCC structure acting as electrode material [55]. The earth climate has been change due to most remarkable factor responsible for global warming due to increase of CO_2 in the atmosphere. It is identified as major environmental issue in present era. This anthropological effect can’t be completely stopped but it can be mitigated up to some extend by capturing of CO_2 from fuel gases. Powel has investigated CO_2/N_2 separation by polyimide/polyethylene oxide membranes developed for carbon dioxide capture [56].

The material selection as host membrane composition is a challengeable task to obtain improvement in permeation with its trade off selectivity parameter. Although, the thesis focusses the gas permeation application but other properties such as mechanical behavior and thermal stability are also taken in to consideration. The polymer material used here is bisphenol-A polycarbonate (PC) which serves better physical as well chemical properties to its respected applications. It also provides better dimensional stability, thermal stability, mechanical strength, optical transparency and toughness. The key future to select this material is its cheaper cost which makes its bulky applications in the industrial field. PC supports the dispersion of filler composition that can modify its functional properties improving its applications for gas permeation and separation performance [37, 57].

1.5. Thesis overview

The proposed work focusses the effect of membrane modification on transport parameters and provides depth of analytic study by respective characterization techniques. The thesis background and objectives associated with the subject have been explained in this **Chapter 1.**

Chapter 2 offers the whole experimental work including membrane fabrication, gas permeation experiments and other analytic characterization. Different modifications applied during membrane synthesis process are described in this chapter. Furthermore, gas permeation tests such as constant pressure/variable volume and constant volume/variable pressure systems are also included. The chapter also provides mechanism and accuracy of constant pressure/variable volume system developed in our laboratory during this research work. The details of system information and other characterization techniques are also provided in this chapter.

Chapter 3 focusses the transport behaviour of various gases across the metal coated membrane which has been studied and compared with that of standard polycarbonate membrane. Moreover, the effect of system leakage and kinetic diameter of various gases to be tested is studied in this chapter. Gas separation study was also performed by mathematical calculation. Analysis of carbon dioxide plasticization effect by layered polycarbonate membrane has also been covered.

In **Chapter 4**, the transport behavior of H_2 across the different metal coated and nanocomposite membrane has been studied with some applied characterization techniques. The comparison of metal coating and nanofiller mixed matrix membranes (MMMs) is given by measurement of gas flux and permeation values. The mechanism and hypothesis applied are described with required references. Moreover, the effect of pressure on H_2 transport is studied in this chapter including selectivity. The effect of filler content on hydrogen permeability has also been analyzed in this chapter.

The role of blending and blend composite membrane is describe in the **Chapter 5.** This chapter also includes selectivity of performed gas pairs and comparison of resultant outcomes by various membrane samples. Oxygen transmission rate was also studied in this chapter applicable in the packaging industry. Additional characterization techniques applied on blend and blend composite membrane was studied and compared with resultant data of neat membrane with reported data.

Conclusion and the future scope of the proposed research work have been explained in the **Chapter 6.** It also includes the whole resultant summary of the thesis concluding necessary comments.

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