Crude natural gas contains carbon dioxide (5–7 mol %), hydrogen sulfide (1500–2000 ppm) and water vapor as the major impurities, which cause corrosion of pipelines and thereby, lowering of the calorific value [1]. The present method to remove CO₂ and H₂S involves the absorption in amine solvents like monoethanolamine and diethanolamine [2]. However, this technique is energy-intensive and polluting due to solvent regeneration problems, large space requirements, high labor costs, besides corrosive nature of the solvents. Therefore, an economical, safe and eco-friendly alternative separation technology is the need of the day. In this context, gas separation using membranes could play a vital role in deacidification of natural gas, due to potential advantages such as low capital and operating costs, high recovery rates, simple and clean mode of operation [3]. A gas separation process can realize these advantages only through the development of a highly permeable and selective membrane, which is the principal objective of the present thesis.

VII.1. Research Summary

In this study, several polymeric membranes were synthesized, modified and tested for the separation of CO₂, the slowest permeating impurity from its mixture with methane (CH₄), which is rather fastest moving hydrocarbon. Membranes were characterized by scanning electron microscopy (SEM), Fourier transform infra-red spectroscopy (FTIR), X-ray diffractometry (X-RD), differential scanning calorimetry
(DSC) and tensile strength measurements to study the surface morphology, intermolecular interactions, crystallinity, thermal and mechanical stability, respectively. The most promising membrane was scaled up into a spiral wound module to make the process industrially viable. Mathematical modeling and computer simulation was attempted to design a commercial system capable of processing 100 m$^3$/h of crude natural gas.

Chapter I of the thesis deals with an exhaustive introduction to the research area under investigation. An overview of natural gas is provided, which includes its resources in India and typical gas mixture compositions, which have been subjected to membrane separations [4]. Properties and applications of natural gas and current methods for processing raw gas to pipeline quality is discussed [5]. The chapter also presents an overview of membrane separation processes with specific emphasis on theory of gas transport through polymeric barriers and various factors, which influence the separation characteristics [6].

The basic criteria for polymer selection such as chemical resistance, membrane polarity for preferential sorption, mechanical and thermal stability are investigated. The key factors for the membrane selection have been reported to be intrinsic membrane permselectivity, ability to resist plasticization, besides the feasibility to process the polymer into up-scalable asymmetric or thin film composite (TFC) morphologies. The current status of acid gas removal by membrane technology is also discussed. A thorough literature survey reveals that polyimides, especially 6FDA-based and cellulose acetate were the most commonly used membranes in natural gas processing, albeit some disadvantages such as plasticization by CO$_2$ gas at
higher pressures [7]. Since no company in India has the capability to fabricate gas-separating membranes and no imported plants have been installed for the separation of gaseous mixtures, there exists a tremendous scope and opportunity for developing membrane technology in India for natural gas purification, which forms the primary objective of the present thesis.

Chapter II provides detailed information on the types, properties and sources of the materials used and the methods adopted for synthesis and characterization of various polymer membranes for natural gas purification. Experimental protocols developed or adopted for membrane synthesis, membrane characterization, permeability measurement and gas sample analysis are described. Methods of calculation of important membrane properties such as flux, permeance, permeability coefficient and selectivity are presented.

General procedures for the preparation of dense (non-porous), asymmetric and thin film composite membranes are described with illustrations. Critical factors such as viscosity and composition of polymer solution, solvent volatility, solvent evaporation time membrane thickness and substrate porosity are discussed. The instruments and techniques used for the characterization of membranes by SEM, FTIR, X-RD, DSC, thermo-gravimetric analyses (TGA), nuclear magnetic resonance (NMR), tensile strength measurement using universal testing machine (UTM) and ion exchange capacity (IEC) measurements are described.

A detailed design of the stainless steel (SS316) permeability cell of 42 cm² effective area is provided along with the photographs of the cell and high-pressure (60 kg/cm²) gas separation unit. The high pressure feed side consisted of ¼" stainless
steel piping adjoined by nut and ferrule fittings, whereas nylon tubing constitute the low pressure permeate side. The continuous flow method, which employs an inert sweep gas (N₂) for sample collection was used for permeability measurements with the dense membranes. A soap bubble meter was provided on the permeate side for measurement of carrier gas flow rate.

For experiments with TFC membranes and spiral modules, which involved high permeate flow rates, a wet gas meter was used. The feed and permeate samples were analyzed by gas chromatography using Haysep ‘Q’ column and thermal conductivity detector. The principle gas chromatograph and description of the laboratory analytical facility are discussed with illustrations. Mathematical equations for the determination of permeability, selectivity and free volume fraction (FVF) [8] are presented at the end of Chapter II.

Literature reveals that cellulose-based membranes and polyimides have been the most successful materials for natural gas deacidification [9]. Chapter III describes studies on cellulose acetate (CA), cellulose triacetate (CTA) and three types of polyimides, viz., Matrimid, P84 and Kapton polyimide. Dense membranes of CA and CTA were prepared using acetone and dioxane solvents, respectively and characterized by FTIR, X-RD and TGA. For a binary feed mixture of 5% CO₂ and 95% CH₄, the CA gave a permeability of 7.1 Barrers with a selectivity of 17.7, whereas CTA exhibited a comparable permeability of 6.8 Barrers with a much lower selectivity of 7.7 for CO₂ gas at the feed pressure of 40 kg/cm².

Results obtained for Natural gas mixture containing 1.86 % CO₂ are similar to those reported for 2 % CO₂ binary feed, which indicated that studies with binary
mixtures could generate reliable data for correlating membrane performance to multicomponent natural gas mixtures. Permeability and selectivity of membranes were lower for mixtures compared to single gases due to coupling effect between the permeating species. For preparing asymmetric cellulose acetate membrane CA (ACA), a mixed solvent system consisting of 20 % wt. CA in 55 % acetone + 25 % formamide mixture was used. The resultant membranes were annealed in hot water bath at 95°C to eliminate any defects. SEM pictures showed the formation of a defect-free skin layer. ACA membranes gave higher fluxes than their dense counterparts, but exhibited lower selectivities. CA membrane could not be scaled up in TFC form due to cracking of the ultraporous polyethersulfone substrate by acetone solvent.

Kapton polyimide was prepared by imidization of 12 % (w/v) polyamic acid solution cast from dimethyl acetamide solvent, and heated in an oven at 160°C for 3 hours, followed by raising the temperature to 210°C for 6 h, which gave 80 % imidization. P84 membrane was prepared from a 10 % (w/v) polymer solution in a mixed solvent system consisting of 80 % dioxane + 20 % dimethyl formamide mixture. Matrimid was prepared using a mixture tetrahydrofuran and 1,4-dioxane. Over the feed CO₂ concentration of 5 mol % to 2 %, Kapton polyimide exhibited the highest average selectivity of 50.8 followed by P84 with 20.0 and Matrimid with 4.1 at a pressure of 40 kg/cm². The permeabilities were obtained in the reverse order with Matrimid showing the highest CO₂ permeability of 20.8 Barrers, whereas P84 exhibited 4.4 Barrers and Kapton polyimide had only 1.5 Barrers. Kapton exhibited swelling-induced plasticization with increasing feed CO₂ concentration [10].
Effect of operating parameters on the separation performance of three types of polyimides is also reported. Only Matrimid could be scaled-up into a hollow fiber module of 0.3 m² effective area, which gave better results with a continuous feed gas flow, but its limitation was maximum operating at the pressure of 20 kg/cm². The effect of flow pattern was evaluated for binary feed mixture (2–20 % CO₂ in CH₄) by comparing the performance of the flat sheet Matrimid in dead-end mode with its hollow fiber counterpart in a cross flow mode. The selectivity of hollow fiber module (8.1–33.5) was much higher than that of flat sheet membrane (2.2–12.6), which suggests that the concentration polarization of CH₄ molecules near the membrane surface is minimized due to the continuous movement of feed molecules. The pure H₂S permeability was 2.2 times greater than that of pure CO₂ through the matrimid hollow fiber membrane, which may be attributed to higher polarity and smaller molecular size (higher diffusivity) of H₂S gas.

Chapter IV deals with the modifications made to three aromatic polymers, viz., poly(phenylene oxide) (PPO), polycarbonate (PC) and polysulfone (PSF). Sulfonation was the major route of modification chosen to improve the permeation characteristics of these polymers. PPO and PSF membranes were sulfonated using chlorosulfonic acid and PC was reacted with acetyl sulfate. FTIR studies showed an attachment of sulfonic acid groups at the para-position of benzene ring in the respective polymers [11]. The aromatic segment of proton ¹H NMR spectra was diminished due to the replacement of aromatic protons with sulfonic acid groups. X-RD and DSC studies were also carried out to determine the effect of sulfonation on the degree of crystallinity and glass transition temperature (T_g), respectively.
Upon sulfonation, the polymers showed a decrease in permeability with increasing selectivity due to increasing chain packing density, which caused a much greater steric hindrance for the diffusing gaseous species [12]. For example, pristine PPO gave a pure CO$_2$ permeability of 43.7 Barrers at an ideal selectivity of 12.1, whereas PPO sulfonated to 20% exhibited a permeability of 18.4 Barrers at a selectivity of 27.2.

The experimental results are supported by estimation of free volume fraction ($FVF$) through group contribution method, which showed a decrease in $FVF$ from 0.399 for PPO to 0.35 for SPPO membrane. Modification of PPO by incorporation with a heteropolyacid (HPA) viz., phosphotungstic acid produced reasonable results. For a feed mixture composition of 5% CO$_2$ and 95% CH$_4$, the unmodified PPO membrane exhibited a reduction in CO$_2$ permeability from 4.7 to 2.5 Barrers with the feed pressure increasing from 5 to 40 kg/cm$^2$. PPO-HPA and SPPO membranes showed similar trends of reduction in permeability from 3.2 to 1.6 Barrers and 2.1 to 1.2 Barrers, respectively. These results are explained on the basis of a dual mode sorption phenomenon, wherein sorption of secondary components such as CH$_4$ becomes more and more competitive in the voids present in the amorphous regions of the polymer matrix, resulting in an increasing exclusion of CO$_2$ molecules from these voids [9].

The degree of sulfonation ($DS$) was varied in case of PC and PSF polymers to identify the optimum conditions. As the $DS$ was increased from 0 to 39.4%, the $FVF$ decreased from 0.31 to 0.19 for PC with a subsequent reduction in CO$_2$ permeability from 8.4 to 1.5 Barrers, but showing an increase in selectivity from 21.0 to 74.8. The
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decrease in free volume element size upon sulfonation could lead to a much greater steric hindrance for the diffusing species [12]. A reduction in diffusivity for both the gases is expected and therefore, a decrease in permeability would occur. However, the greater reduction is expected for methane whose molecular size (Lennard-Jones kinetic diameter) is 3.8 Å as compared to CO$_2$, whose molecular size is around 3.3 Å [9]. The effect of feed composition of the binary mixtures of CO$_2$ and CH$_4$ on the performance of unmodified PC and SPC membranes with DS of 14.4 % and 25 % was investigated.

With DS increasing from 0 to 38 %, the PSF membrane exhibited a decreasing pure CO$_2$ permeability from 6.7 to 2.8 Barrers with an enhancement of ideal selectivity from 29.1 to 46.6. Tensile strength and % elongation at break were reduced for all the polymers after sulfonation. Sulfonated polysulfone (SPSF) exhibited a decrease in tensile strength from 192 to 135 N/mm$^2$ with a lowering in elongation from 33 to 11 %. A comparison of the performance of PSF with polyethersulfone (PES) membrane showed that PSF membrane exhibited a pure CO$_2$ permeability of 6.7 Barrers when compared to 4.3 Barrers for PES membrane with an ideal selectivity of 29.1, which was marginally lower than that observed for PES (37.8). The straight and shorter chain structure of PES makes it amenable to pack more tightly in the glassy state as compared to the related polysulfones, which causes the gas molecules to permeate much slower in PES.

FTIR and X-RD spectra of the two polymers were compared to explain the permeability results. Asymmetric polysulfone (APSF) membranes were prepared by the phase inversion technique using the solution containing 20 % (w/v) solution of
PSF in a mixed solvent system comprising 60 % THF + 20 % DMF. SEM pictures representing the membrane morphology of APSF membranes showed a uniform surface morphology with no visible pores and the presence of porous support layer underneath the skin in the cross-sectional view. The selectivity of APSF for both CO₂/CH₄ and H₂S/CH₄ mixed gas systems were about 85-90 % of the intrinsic value, indicating its defect-free morphology.

Chapter V deals with studies on the most promising and upscalable polymer, viz., poly(ether-block-amide) (Pebax), its modifications and fabrication in the form of a commercially viable thin film composite (TFC) membrane. The chapter begins with the synthesis of another TFC membrane, polyamide, by the interfacial polymerization technique on an ultraporous polysulfone substrate using m-phenylene diamine as the aqueous reactant and isophthaloyl chloride as the organic reactant. The membrane was characterized by SEM, FTIR, X-RD and DSC; it exhibited moderate results for CO₂/CH₄ separation. At a feed pressure of 10 kg/cm², H₂S exhibited the maximum mobility with a permeance of 51.6 GPU followed by CO₂ with 15.2 GPU. The ideal selectivity of 49.1 for H₂S/CH₄ was also much higher (14.4) than that of CO₂/CH₄. H₂S and CO₂ are polar gases that undergo dissolution in polyamide membrane, which consists of polar –NHCO functional groups [9].

Pebax polymers of two different grades, 1657 and 2533, were used for the preparation of TFC membranes. Pebax 1657 was cast on a microporous polyvinylidene fluoride (PVDF) support using a 7:3 mixed solvent system of isopropanol/m-cresol, followed by heating in an oven at 150°C for 3-5 min, whereas Pebax 2533 was cast from iso-butanol solution on a tight PES substrate. To improve

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the selectivity of Pebax 2533, mixed matrix membranes were prepared by incorporating silver and activated carbon [13]. SEM studies on the surface and cross-section of the mixed matrix membranes revealed a uniform distribution of the fillers and defect-free surfaces. Silver incorporation by the addition of 36 % AgBF$_4$ in the dope made the membrane highly selective.

Over a feed pressure range of 10–40 kg/cm$^2$, the selectivity of plain Pebax 2533 varied from 15.3 to 20.4, whereas that of Ag-PEBAX ranged from 36.2 to 47.6, which indicates a 2.3-fold increase upon incorporation of silver. The permeance of Ag-Pebax membrane reduced (1.8–2.7 GPU) to almost one-third of the values (5.1–7.7 GPU) obtained for pristine Pebax due to the greater membrane casting thickness employed in the case of former membrane to avoid defects/gaps that can be induced in the presence of large quantities of inorganic fillers (36 % AgBF$_4$) in the dope. FTIR studies exhibited metal-ligand interactions in case of Ag-Pebax, whereas SEM studies showed a homogeneous dispersion of silver particles in a fibrous form onto the surface of Pebax without any agglomerations. Marginal improvement in the permeance was obtained for 50 % carbon-loaded Pebax 2533 membrane without any change in selectivity.

Crosslinking with 2 % (v/v) toluene diisocyanate (TDI) in $n$-hexane was more effective in case of Pebax 1657, which showed a two-fold improvement in ideal selectivity from 21.2 to 43.1 at 20 kg/cm$^2$ pressure. FTIR and X-RD studies confirmed the crosslinking between isocyanate groups of TDI and terminal hydroxyl groups in Pebax 1657. With an increase in crosslinking time from 0 to 60 min, ideal selectivity of the membrane to CO$_2$ increased from 21.2 to 52.4.
Chapter VI covers the scale-up studies on the most promising Pebax membrane into spiral wound modules of 0.2–0.25 m² area to establish its commercial viability. The advantages and drawbacks of different modular configurations such as tubular, hollow fiber, spiral wound and plate-and-frame are discussed with illustrations. Different ultraporous substrates made of PVDF, PES and PSF were prepared for supporting the Pebax 2533 layer. The tightness of the support and its pore structure appeared to play a vital role in determining the gas separation performance of Pebax membrane. To reduce the effective skin thickness to 2 μm, the TFC Pebax 2533 membranes were prepared by a dip coating method in a 6 % (w/v) polymer solution for 5 min followed by heating to 110°C for another 5 min.

Spiral modules of 15” length and 1.4” OD were fabricated indigenously, which consisted of essentially five components: (i) perforated central tube, which collects the permeate, (ii) permeate spacer, which carries the permeate to the central tube, (iii) membrane, which is the active separation media, (iv) feed spacer that separates the two membrane leaves, facilitating the flow of feed gas across the membrane, and (v) gas seal (brine seal) to prevent the bypass of feed in membrane housing. Modules were housed in stainless-steel pressure vessels of 15.6” length and 1.5” ID. PSF support seemed to be the most suitable for Pebax 2533 membrane, since a relatively higher selectivity of 29.5 could be obtained at a permeability of 56.0 Barrers. As the feed CO₂ concentration increased from 2 % to 20 mol %, the CO₂ permeability also increased from 40 to 49 Barrers along with selectivity from 19.2 to 26.7.
Data collected from experiments with spiral modules were used for the simulation study to predict the performance of a commercial gas permeator capable of processing crude natural gas of 100 m$^3$/h feed capacity in cross flow mode. Mathematical modeling was carried out to obtain the numerical solution for a plug flow model using the step-wise method, wherein membrane area was divided into numerous incremental areas. Equations, which represent the material balance across an incremental area were solved to construct a simulation program in Microsoft Excel capable of giving outputs of membrane area requirement as well as product and permeate compositions for inputs of membrane properties, stage cut, feed capacity, pressure and feed composition [14]. For a feed capacity of 100 m$^3$/h, feed composition of 95 % CH$_4$ + 5 % CO$_2$ and pressure of 60 kg/cm$^2$, the computer program showed that the desired product concentration of at least 98 % CH$_4$ was reached at a stage cut of 0.15 for which membrane area requirement was 64 m$^2$.

A commercial gas permeator of the same capacity was designed for purification of natural gas to pipeline quality. A process flow diagram consisting of two spiral wound membrane modules of 36 m$^2$ area each along with the other pretreatment equipment such as micron filter, glycol dehydration unit and post-treatment system like ZnO adsorbent bed is presented. An economic estimate showed that a capital investment of Rs. 21.3 Lakhs is required to set up the commercial plant, which incurred an operating cost of Rs. 0.25 per cubic metre of gas treated.

The list of papers published/in press/communicated is included at the end of this chapter.
VII.2. REFERENCES


