Transport of acids through polymeric membranes

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Under the guidance of

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STATEMENT BY THE CANDIDATE

As required by the University ordinances 770, I wish to state that the work embodied in this thesis titled **"Transport of Acids Through Polymeric Membranes"** forms my own contribution to the research work carried out under the guidance of **Dr. B. D. Kulkarni,** at the National Chemical Laboratory, Pune. This work has not been submitted for any other degree of this or any other University. Whenever references have been made to previous works of other, it has been clearly indicated as such and included in the Bibliography.

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Dedicated to My Family

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Chapter 1

Acid separation: A brief literature survey

1.1. Introduction

Inorganic as well as organic acids are the integral part of many industrial process streams. They are used in various industrial processes such as; steel treatment, surface treatment, metal refining, electronic and glass industry, pigment and chemical production [Kim 2006, Koltuniewicz (2008a)]. Additionally, there is a large potential for the synthesis of various chemicals from organic acids. These acids can be converted to wide variety of chemicals, because of their multiple functional groups and high reactivity [Varadrajan (1999)]. Organic acids are also used in food, pharmaceutical, cosmetics, textile, chemical industries, etc. [Zigova (2000), Datta (2006), Dhillon (2011)]. Huge quantities of various (organic or inorganic) acids are used worldwide. For example, in 2002 worldwide HNO_3 production was reported as, 46×10^6 tonnes [Clarke (2004)]. For various organic acids, the approximate yearly production varies as: lactic acid 259,000 tonnes/y [Mujtaba (2012)], acetic acid 7,000,000 tonnes/y [Sauer (2008)], gluconic acid 45,000 tonnes/y [Koltuniewicz (2008a)], citric acid 1,700,000 tonnes/y [Dhillon (2012)], etc. An yearly growth of ~4 % in the production of organic acid has been estimated in the literature [Koltuniewicz (2008a)]. For lactic acid, the growth rate is 5-8 % annually; while commercial success of polylactic acid and lactate esters would increase its demand upto 14-19 % [Reddy (2008), Wasewar (2004), Vijayakumar (2008)].

Synthesis of these organic acids is one of the major industries. There is a large potential market for chemical production from fermentation derived organic acids [Varadrajan (1999)]. They are majorly produced from a diversity of potential feedstocks in the form of residues from forest products, agricultural and other established industries [Varadrajan (1999), Lynd (1999), Das (2004), Koltuniewicz (2008a), Dhillon (2011)]. Biotechnological production is advantageous over chemical synthesis since cheap raw materials such as agro-industrial byproducts can be used [John (2009)]. The dominant factor impeding biological production of commodity products is the high cost of current processing technology [Lynd (1999)]. For biologically produced organic acids to be

competitive in the market place, the production of these chemicals must be inexpensive [Tsao (1999)]. One of the ways to achieve this goal is to improve the fermentation process, while lowering the cost [Tsao (1999)]. Produced acids need to be separated from fermentation broth and purified before their use in further applications. The separation of acids is one of the cost intensive stages. For example, during the production of lactic acid by fermentation, its separation and purification by conventional precipitation method account up to 50 % of its production costs [Wasewar (2004)]. The conventional process of neutralization-precipitation has limitations of large chemical consumption (e.g. lime, H_2SO_4) and generation of huge quantity of solid waste [Datta (1995), Dhillon (2011)].

During the application of acids (organic or inorganic) in various industrial processes, the concentration of used acid is depleted. It can also get contaminated with different organic or inorganic impurities. These acids at depleted concentrations along with metallic or organic impurities contribute to the significant part of spent liquor. Various industrial effluents contain huge quantities of acids as a major component. According to literature report, the spent pickling solution can contain different acids at varying concentrations as; upto 150 g/dm^3 of H_2SO_4, 237 g/dm^3 of HCl, 200 g/dm^3 of HNO_3 and 150 g/dm^3 of HF [Regel-Rosocka (2010)]. One of the reported composition of semiconductor etching waste showed acids as main component containing, HNO_3 (3.4 %), H_3PO_4 (77.9 %), acetic acid (5.4 %) along with metallic and organic co-solutes [Kim (2006)]. These large quantities of acids making up the major portion of industrial wastes is a significant environmental issue and needs to be addresses before the discharge of effluents.

Recovery of acid from a process streams is often required in these industries, as unutilized acids results in major loss of reactants, which may not be advisable. It also needs to be treated before discharge as per environmental norms, causing chemical consumption adding economical concerns. The acids may be organic or inorganic in nature and may be present as a product or an undesirable impurity. Spent streams from various industries (metal refining, electronics, glass, pigment, chemicals, etc.) contain organic as well as inorganic acids [Kim (2006), Koltuniewicz (2008a)]. Such streams contain depleted acids, along with non-acidic components, such as salts (e.g. $FeSO_4$, $FeCl_2$, $ZnCl_2$, $SnCl_2$, metallic phosphates, sulphates), organic materials (oils, fats, poly-

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Si, SiN$_x$) etc. [Schwartz (2000), Kladnig (2003), Chojnacki (2005), Perry (2005), Kim (2006), Van Der Merwe (2010)]. These streams need to be treated for the separation of acid from non-acidic components, before its recycle. Presence of impurities would affect acid recyclability, their stability during storage and transportation or sludge disposal after neutralization [Evans (1996), Schwartz (2000), Kladnig (2003)]. In most of these cases, considerable amount of acid must be treated before its disposal [Koltuniewicz (2008a)].

Various methods for acid treatment reported in literature are briefly reviewed below.

1.2.   Conventional methods

1.2.1.   Direct use

In this method, acids can either be recycled after possible concentration make up [Stocks (2005)] or utilized in other processes [Evans (1996), Chojnacki (2005), Van Der Merwe (2010)] depending upon the process requirements. Though reuse of acid leads to its better utilization; this method requires low level of impurities in the process streams. This is obeyed by only few processes. For example, spent sulfuric acid from petrochemical industry was used in wet-process phosphoric acid technology [Chojnacki (2005)] and spent solid phosphoric acid catalyst was utilized for the fertilizer synthesis [Van Der Merwe (2010)]. Industrial spent acids contain various inorganic or organic components as an impurity [Schwartz (2000), Kladnig (2003), Stocks (2005), Kim (2006)]. Presence of these impurities may affect the efficiency of process and need to be separated before the acid can be reused [Evans (1996), Schwartz (2000), Kladnig (2003)].

1.2.2.   Direct discharge

The discharge of acid into environmental resources which can be used as sink (like waterbodies) though is reported [Evans (1996)], the allowable discharge limit is in pH range of 6-9 [Regel-Rosocka (2010)]. This pH make up would require addition of chemicals leading to neutralization–precipitation as discussed below. Used effluent from various industries consists of many heavy metallic and organic impurities and can be detrimental to biological organisms when exposed to the environment [Platt (2004)].

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Stringent regulatory norms imposed by many nations make this process almost redundant.

1.2.3. *Deacidification*

1.2.3.1. Neutralization – precipitation

This method is widely used for the separation of organic acid produced by a suitable method such as fermentation. Acid is isolated in the form of precipitated salt, which is then subsequently treated with a strong inorganic acid to recover the product organic acid [Joglekar (2006), Yamamoto (2011), Wang (2011)]. The formed salt of inorganic acid (e.g. calcium sulphate) is usually disposed off as waste [Joglekar (2006), Shin (2009), Yamamoto (2011), Wang (2011)]. This method is well practiced for the recovery of organic acid from fermentation broths e.g. lactic acid [Datta (1995), Wasewar (2004), Vaidya (2005), Wee (2006)], citric acid [Kubicek (1986), Tongwen (2002), Soccol (2006)], gluconic acid [Singh (2007)], propionic acid [Keshav (2008)], etc. This method is also used in other process streams such as the separation of short chain aliphatic carboxylic acid (adipic and butyric) from reaction mixture for synthesis of cyclohexanone from cyclohexane [Wang (2006)], separation of malic acid and unreacted fumaric acid during the enzymatic conversion of fumaric acid to L-malic acid [Belafi-Bako (2004)], etc. Neutralization–precipitation method is also practiced for the treatment of spent acids (neutralization before discharge) [Evans (1996), Kladnig (2003), Koltuniewicz (2008a), Shin (2009), Yamamoto (2011)]. For example, the treatment of waste streams from semiconductor manufacturing process [Yamamoto (2011)] and nitration spent acids (containing HNO_3 and H_2SO_4 used for organic nitration process) [Evans (1996)].

Though the process is easy to use and practiced conventionally, it has number of draw-backs. Consumption of chemicals and production of large quantities of salts (e.g. calcium sulfate, which has low commercial value) is a major drawback of this method (e.g. during lactic acid production, ~1 tonne [Datta (1995)] to ~2.5 tonne [Wasewar (2004)] of by-product, majorly gypsum is generated per tonne of lactic acid produced). Solutions containing salts of strong inorganic acids, mixed with organic and inorganic impurities would also be generated. The disposal of these waste streams is an ecological

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problem [Shin (2009)]. In cases where the salt (e.g. gypsum) is non-saleable product, it needs to be stockpiled leading to concerns of both storage space and leaching of contaminants into ground water [Evans (1996)], leading to contamination of waterbodies. Moreover, this method is destructive for inorganic acids since it looses acid value, while for organic acids, it is expensive. It is reported that during the production of lactic acid by fermentation, separation and purification stages account for up to 50 % of its production costs [Wasewar (2004)]. This method of treatment is economically unattractive and environmentally unacceptable.

1.2.3.2. *Chemical deacidification*

One of the options for treatment of spent acids is the addition of suitable chemicals, which would lead to release of gases. This method has limited applicability for the treatment of spent acids. Its use has been reported for the treatment of nitric acid from nitration spent (e.g. from production of mononitro-toluene, dinitro-toluene or trinitro-toluene) by addition of a compound from the urea/sulphamic acid family to form free nitrogen [Evans (1996)]. The process ensures removal of acid upto the trace levels. It is a destructive method and reduces the acid value.

1.2.3.3. *Steam stripping*

Steam stripping recovers acid value from the spent acid by evaporation and breakdown of species to release oxides. These gases can subsequently be recovered as acid by absorption in water. The process is usually carried out in a glass or glass lined steel packed columns. It is reported for the treatment of nitration spent acids and denitration of nitroglycerine spent acid [Evans (1996)]. Use of this method for the treatment for acids other than HNO_3 is not reported, to our knowledge.

1.2.4. **Distillation based methods**

1.2.4.1. *Distillation*

High vapor pressure and difference in boiling points of an acidic component to be separated is the basic requirement of this method. It can be better used for low boiling acids. For example, separation of acetic acid from fermentation broth [Raspor (2008)], separation of HF and HNO_3 from semiconductor manufacturing process [Yamamoto

(2011)], etc. Though distillation process is well reported, its practical use in acids separation is very feeble. Due to hydrophilic nature of acids, they form azeotrope with water. As an example, HNO_3–water azeotrope approaches at the concentration of 68 % wt., at boiling point of 393.8 K [Hensley (2007), Yamamoto (2011)]. This necessitates use of other methods such as extractive distillation by the addition of entrainer. Separation of HNO_3–water is achieved by addition of H_2SO_4 or magnesium nitrate as an entrainer [Hensley (2007)]. This requires further separation of the entrainer [Hensley (2007)]. Similarly, the physical and chemical nature of by-products and co-solutes affect their separation. In case of acids like lactic acid, high boiling internal esters like dimers or polymers can be formed [Wasewar (2004)]. This makes the separation difficult. Moreover, it is highly energy intensive process [Hensley (2007)].

1.2.4.2. *Reactive distillation (esterification–distillation–hydrolysis sequence)*

In this method, first esterification of organic acid is performed by a suitable alcohol. Formed ester is then distilled, followed by its hydrolysis to recover the pure acid. Esterification is efficiently carried out in the presence of cation exchange resin columns acting as packing, as well as catalyst [Joglekar (2006)]. It is a method used for effective separation of various organic acids [Joglekar (2006)] with high yield and purity. It is reported that 99.5 % pure lactic acid can be obtained by this process [Cockrem (1993)]. Separation of acid from fermentation broth by this method requires pre-treatment of fermentation broth to remove residual sugars and colors [Joglekar (2006)]. It also requires use of excess alcohol. It is reported that ~9 mol of methanol is required to remove 1 mol of lactic acid from an 82 % solution while leaving behind thick residue of impurities and partially reacted material [Vaidya (2005)]. The method is thus cost intensive [Joglekar (2006)].

1.2.5. *Sorption/desorption based methods*

1.2.5.1. *Adsorption*

The adsorption utilizes solid sorbents which are selective towards acids [Joglekar (2006)]. Acid sorption is followed by its elution using suitable eluants. Important characteristics of solid sorbents are high adsorption capacity, high selectivity

for the acid as opposed to water and other substrates (e.g. glucose), regeneration ability and biocompatibility with microorganisms, depending upon the process requirements [Joglekar (2006)]. The process has been reported for separation of various carboxylic acids using polymeric adsorbent of pyridine skeletal [Joglekar (2006), Wasewar (2005)]. Separation of inorganic acids (e.g. HNO_3) using polymeric adsorbent containing phosphonic acid ester group is also reported [Sato (1995)]. If a solid sorbent can be used in situ or in an external recycle loop in a fermentor, higher overall yields can be achieved [Joglekar (2006)] with recovery of acid [Wasewar (2005)]. Elution of sorbed acid from adsorbent requires use of solvents or chemicals, which requires further processing to purify the acid (e.g. purification by esterification is necessary after adsorption for lactic acid [Joglekar (2006)]).

1.2.5.2. *Ion-exchange*

Ion exchange works upon the transfer of ions across a boundary; i.e. movement of ions from one phase (liquid) to another which is insoluble in that liquid [Dyer (2000)]. It includes exchange of counter ions attached to the fixed ions of resin [Dyer (2000)], leading to formation of addition product. This is followed by elusion of the product acid from the ion exchange resin [Eyal (2000)] by using suitable chemical, usually stronger acid solution. Important characteristics of ion exchange resins are high exchange capacity for the acid, a rapid rate of exchange, chemical and thermal stability, resistance to poisoning and compatibility depending upon demand [Dyer (2000)]. This process has been well reported for the separation of organic acids (e.g. lactic acid [Wasewar (2005), Joglekar (2006), Gonzalez (2007)]) and inorganic acids (e.g. HCl, HF and HNO_3 [Regel-Rosocka (2010)]). Ion exchange allows both, lactate conversion into undissociated lactic acid and salt removal [Gonzalez (2007)]. The feed solution needs to be clarified before use [Gonzalez (2007)]. This method needs to use chemicals such as HCl or NaOH for regeneration followed by rinsing column by water [Gonzalez (2006), Gonzalez (2007)]. This gives rise to waste stream containing salts and other chemicals [Wasewar (2004)], which need further treatment.

1.2.6. Extraction based methods

1.2.6.1. Extraction

Extraction works on partitioning of acid between two immiscible solvents. Three important criteria have been established for the solvent selection: (i) high distribution coefficient (K_d), (ii) easy back extraction and regeneration and (iii) low emulsion formation tendency [Wasewar (2005)]. For practical viability, this method also needs to have high selectivity, cost feasibility and should use non-toxic extractant. Extraction of the strong mineral acids by an inert solvent is very low and thus has very less practical significance. Organic acids like lactic acid since are hydrophilic, are poorly extractable by common organic solvents [Joglekar (2006)]. Conventional oxygen-bearing hydrocarbons such as octanol and methyl isobutyl ketone (MIBK) are known to have very low distribution coefficients for organic acids [Wasewar (2005)]. This low distribution coefficient restricts applicability of the process.

1.2.6.2. Reactive extraction

In this method, the extractant in organic phase reacts with an acid present in the aqueous phase and reaction complex is solubilized into the organic phase [Wasewar (2004), Joglekar (2006)]. The extracted acid can be back extracted by suitable method of variation in temperature (temperature swing re-extraction), diluent (diluent swing re-extraction) or pH (by contacting with acid like HCl or base like NaOH) [Joglekar (2006)]. Extraction with reactive extractant gives higher distribution coefficient (greater than 1 for extraction step [Joglekar (2006)]) and thus has been proposed as a promising technique for the recovery of acids [Wasewar (2004)]. Various materials like organophosphates (e.g. trioctylphosphine oxide and tri-n-butyl phosphate) and long chain aliphatic amines have been reported for acid separation [Wasewar (2005)]. Separation of organic acids (e.g. lactic acid [Wasewar (2004), Wasewar (2005), Joglekar (2006)]) or inorganic acids [Bucher (1975), Sato (1976)] by reactive extraction has been reported in the literature. Though the process has high selectivity towards acid, it has certain drawbacks while separating acids produced by fermentation. Toxicity of the organic solvent and extractant to microbes is a critical problem in extractive fermentation [Schugerl (2000), Wasewar (2004), Wasewar (2005), Joglekar (2006)]. Extraction of

organic acids was reported to be effective only at pH lower than the pK_a (e.g. 3.86 for lactic acid). At such a low pH, acid-fermenting microorganisms are severely inhibited [Schugerl (2000), Wasewar (2004), Wasewar (2005)]. Back extraction of free acid is difficult and yields tend to be between 60–70 % [Schugerl (2000), Wasewar (2004), Wasewar (2005)]. In case of inorganic acids, reaction can occur between solvent and residual compounds in the spent acid to produce frothing during subsequent steps (e.g. black nitroso-organic compounds are formed during nitric acid treatment) [Evans (1996)].

1.3. Membrane based methods

Membranes work on physical separation without affecting chemical properties of the solutes to be separated. Membrane based separations are non-equilibrium processes with crucial advantages over conventional processes. They have operational simplicity, flexible in operation, modular in nature and do not require use of hazardous chemicals for the separations to occur [Sirkar (1997)]. Modularity of a membrane based processes makes the design simple and easy to scale up linearly [Li (2005)] and makes them less voluminous (smaller foot prints). The incorporated modularity of design gives easy scale-up options like stacking or cascading.

When acid separation is concerned, membrane based processes hold peculiar advantages over conventional methods. The separation can be carried out continuously and under milder conditions. This would reduce the requirement of storage and after treatment to obtain final product. Membrane based processes since rely on physical separation, use of solvents (e.g. extractant) or other chemicals (like alkali) for the separation is avoided. This in turn eliminates the requirement for further treatment for acid recovery and disposal of solid waste. The membranes based techniques (like ED, DD) recover acids in acidic form only. The membrane based techniques can be combined with fermemtator, leading to continuous acid production (e.g. lactic acid production by using membrane cell-recycle bio-reactor [Kwon (2001)]). These peculiarities give an edge for membrane based methods over conventional techniques. Various membranes based techniques reported for acid treatments are described below.

1.3.1.   Extraction with liquid membranes

The reactive extraction though has high selectivity towards acid; it has certain issues during practical application for the separation of acids as discussed earlier (Section 1.2.6.2). Considering these limitations during extraction, acid separation was tried by extraction in the form of liquid membranes (LMs). Transport of solutes by LMs is based on idea that, two completely miscible liquid phases separated by a third liquid immiscible with either of them, can exchange solutes [Boyadzhiv (2000)]. The solute exchange depends upon a chemical potential difference between the two phases and the ability of intermediate liquid to transport [Boyadzhiv (2000)]. The liquid membrane process can be regarded as a combination of extraction and a stripping process, which take place simultaneously in the same device [Boyadzhiv (2000)]. LMs have been reported for the separation of various inorganic acids (e.g. HNO_3 [Chiarizia (1991)]) and organic acids (e.g. lactic acid [Wasewar (2005)]). The liquid membranes can be used in either of bulk (BLM), emulsion (ELM) or supported (SLM) liquid membrane form [Boyadzhiv (2000)]. SLM using a porous membrane support soaked with complexing carriers to separate feed and strip phases is one of the feasible types of liquid membranes [Wasewar (2005)]. Its use for the recovery of acid offers unique advantages as; large surface area for mass transfer in a compact unit, no fear of back mixing, no direct exposure of microorganisms to extractants (in case of separation of acid from fermentation broth) thereby ensuring biocompatibility, no need for agitation, potential high efficiency and high separation factors in a single stage [Wasewar (2004), Joglekar (2006)]. It suffers from lower membrane stability, tendency to form emulsion and complex operation [Wasewar (2004), Joglekar (2006)].

1.3.2.   Nanofiltration (NF)

NF is also termed as loose RO. These membranes have low rejections (10-50 %) of mono-valent salts (e.g. NaCl), but exhibit high rejections (> 95 %) of divalent ions (e.g. SO_4^{2-}) as well as organic compounds of molecular weight of 200 or greater [Sirkar (1997)]. It requires high trans-membrane operational pressure (e.g. maximum rejection of impurities and lactate recovery were obtained at 20 bar, with partial rejection ~40 % of sulfate and phosphate ions [Vijayakumar (2008)]). Inorganic acids usually

permeate through NF membranes freely, while metal salts are more or less retained [Tanninen (2002)]. In case of organic acids, NF was able to efficiently remove magnesium and calcium ions from an acid salt (e.g. sodium lactate) in the fermentation broth [Vijayakumar (2008)]. Process has been reported for the separation of inorganic acids (e.g. HNO_3 [Tanninen (2002)], HCl, H_2SO_4, HNO_3 and HF from metal rinse, steel pickling and mining [Platt (2004)]) and organic acids (e.g. acetic acid, formic acid [Sirkar (1997)], lactic acid [Timmer (1994)]). It is a clean technology, which does not require addition of chemical and recovered acid can be recycled back directly or after concentration. It has certain issues such as, requirement of pretreatment by suitable technique like ultrafiltration [Timmer (1994)]. During fermentative acid production, protein fouling is the main issue leading to reduced membrane performance [Timmer (1994)]. Though the process is easy in operation, its performance was excellent at neutral pH but decreased drastically at low pH [Platt (2004)]. It also has limitations due to acid and caustic concentrations (pH 2–12) required for cleaning of the fouled membranes [Platt (2004)].

1.3.3. *Reverse osmosis (RO)*

Reverse osmosis is defined as a process during which an outer pressure (higher than osmotic pressure) is applied to force the solvent through a membrane, which is permeable for the solvent and rejects the solute [Spohn (2000)]. The process operates at high pressure. For acid separation, it has been employed for the selective permeation of HF while rejecting fluosilisic acid and other metallic impurities in the semiconductor etching solutions [Sirkar (1997)]. It requires pretreatment of the solutions to avoid fouling problems [Timmer (1994)]. Though the knowhow of RO is well reported in literature (for purification of sea water and brackish water), not many reports are available for the selective permeation of acid. On the other hand, RO membranes have been reported to have strong rejection properties for various acids [Ragaini (2004), Diltz (2007), Sagne (2009)]. It can be better utilized in combination with suitable technique like NF to recover acids (e.g. lactic acid separation from fermentation broth [Li (2008)], acetic/formic acid separation by Zenon Nanofiltration Technology [Sirkar (1997)]).

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1.3.4. *Membrane distillation (MD)*

MD is a process in which two liquids or solutions at different temperatures are separated by a porous membrane [Mulder (1998)]. The temperature difference results in vapor pressure difference. The process involves evaporation on high-temperature side and transport of vapor molecules through the pores of the membrane from high vapor pressure side to a low vapor pressure side [Mulder (1998)]. In this process, membrane is not directly involved in separation, but act as a barrier between two phases and the selectivity is determined by the vapor-liquid equilibrium [Mulder (1998)]. The liquids or solutions must not wet the membrane or they would block the pores [Mulder (1998)]. The process is reported for the separation of inorganic acid (e.g. HCl separation from spent pickling solution [Regel-Rosocka (2010)]) or their dehydration (e.g. HNO_3 dehydration [Thiruvenkatachari (2006)]). The use of MD in acid separation is challenging due to the strong acidic environment. Only membrane materials stable in such environment are glass, high grade stainless steel, specialty alloys. Only at moderate concentrations, hydrophobic fluoropolymers such as perfluorinated ionomers may provide suitable permselective membrane [Thiruvenkatachari (2006), Regel-Rosocka (2010)].

1.3.5. *Pervaporation (PV)*

It is a process in which pure liquid or liquid mixture in contact with the membrane on feed or upstream side at atmospheric pressure and permeate is removed as vapor because of a low vapor pressure existing on the permeate or downstream side [Mulder (1998)]. The low (partial) vapor pressure can be achieved by employing a carrier gas or using vacuum [Mulder (1998)]. PV has been used for the separation of acid and water. It has been used for the transport of acetic acid [Bai (1993), Yoshikawa (1993), Li (2004a)] or water from the acetic acid-water mixture [Gorri (2005), Isiklan (2005), Van Baelen (2005)]. PV is used for dehydration of hydriiodic acid [Orme (2005)], HNO_3 by using Nafion membranes [Scott Sportsman (2002), Ames (2005)]. The process can be used for volatile acids only, in case of other acids it has been reported for dehydration purpose.

1.3.6.   Diffusion dialysis (DD)

DD is a diffusion process in which ions are transported across ionic membrane due to concentration difference [Mulder (1998)]. It generally uses an ion exchange membrane, allowing anions and the protons to pass through into a water stream [Akgemci (2004), Koltuniewicz (2008a)]. Acid is reconstituted on the permeate side of the membranes and can be directed back to the process tank [Akgemci (2004)]. Various anion exchange membranes (e.g. Neosepta (AFN, ACM and AMH) [Akgemci (2004), Palaty (2000)], polyether sulphone based SB-6407 [Ersoz (2001)], polytetrafluoroethylene-fluoroethylenpropylene based perfluorinated membranes (PTFE-FEP) [Cohen (1986)] and brominated-aminated poly(*2,6*-dimethyl-*1,4*-phenylene oxide) [Tongwen (2001)]), Nafion and Flemion based membranes [Wodzki (1997)] are reported for the separation of organic as well as inorganic acids. It requires no external forces to promote separation, only electrical energy is required to pump the solutions [Akgemci (2004)]. This substantially reduces operational cost and is their biggest advantage [Palaty (2004a)]. The operation is effective only at high acid and low salt concentrations. Acid transport rate is affected by the presence of salt molecules in feed solution and is accompanied by co-transport of salt / cations [Nagamura (1983), Cohen (1986), Elmidaui (1991), Cwirko (1992), Tongwen (2001), Palaty (2004a), Palaty (2004b)]. The process suffers from membrane fouling, which requires frequent cleaning of the dialyzer [Wasewar (2004)].

1.3.7.   Electrodialysis (ED)

Electrodialysis is a process in which ion exchange membranes in combination with an electrical potential difference (which acts as driving force) are used to remove ionic species from an aqueous solution [Strathman (2000)]. Monopolar (desalting) ED can be used for the recovery and concentration of acid salts, while bipolar (or water splitting) ED can be used to produce free acid and free base [Schugerl (2000), Datta (2006)]. A double ED process, uses desalting ED unit to remove the multivalent salts and concentrate acid salt, followed by water splitting ED with bipolar membranes to produce concentrated acid and alkali for recycle [Datta (2006)]. It has been reported for the separation of organic acids (e.g. lactic acid from fermentation broth [Wasewar (2005),

Datta (2006)]) and inorganic acids (e.g. HNO_3 [Ponce-de-Leon (2000)], HF and HNO_3 from pickling operation [Sirkar (1997)]). Major advantage of ED is that, it can lead to simultaneous separation and concentration of acid [Wasewar (2004)]. It can lead to an increase in the fermentation rate by up to 60 % [Wasewar (2005)]. The method has high requirement of electrical energy, which has been reported to be 0.88 kWh/kg [Datta (2006)] - 1.8 kWh/kg [Joglekar (2006)] of lactic acid produced. Membrane fouling by cell culture is another issue, which needs to be removed by NaOH; which damages the bi-polar membranes. This implies that only cell-free broth can be used in this method [Schugerl (2000)]. This leads to higher operating cost [Wasewar (2004), Wasewar (2005)]. Transport of small amount of by-product salts and proteinaceous impurities along with acid are also reported [Wasewar (2004), Wasewar (2005)].

1.4.   Need for alternate method for acid separation

Though various methods are reported in the literature for acid treatment (recovery, separation or disposal) they have their own drawbacks, when practical application is concerned. During the synthesis of organic acid, emphasis is on the separation and purification of acids. On the other hand, during the treatment of spent acid, recovery of acid along with separation of commercially important co-solutes is advisable. In both these cases, the prerequisite of a process is to separate acidic moieties from complex mixture of components, in which other components can be commercially important or contribute to sludge. Different processes for acid treatment mentioned above have various shortfalls, when their industrial applicability is concerned. The methods of direct use or discharge and deacidification (except neutralization-precipitation) could be used for the treatment of spent acids only. Conventional sequence of neutralization-precipitation is widely used in the treatment of organic [Joglekar (2006)] or inorganic acids [Evans (1996)]; which consumes large quantity of chemicals (e.g. lime) producing huge quantities of salts (e.g. gypsum) [Datta (1995), Evans (1996), Wasewar (2004)]. Stockpiling of these wastes leads to concerns of storage space and their leaching leading to contamination of ground water [Evans (1996)]. Various regulations have been forced to limit the discharge of metals and acids [Regel-Rosocka (2010)]. This makes treatment and recovery of acid a crucial issue regarding both

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environmental protection and economy of the process. Though several processes are reported in the literature for acid separation, issues like waste generation and its disposal (neutralization-precipitation, adsorption and ion-exchange), high energy requirements (ED), inability to combined with fermentation broth due to feed toxicity (reactive extraction), membrane fouling (ED, DD and NF-RO), instability (LMs), etc. restricts their commercial applicability.

These issues can be addressed by advancement in the method for separation of acids. A suitable method of acid treatment aimed towards their separation and recovery can lead to several advantages, *viz.*; (i) better method for isolation of product (e.g. acid during fermentation based synthesis) or by-product, (ii) better product quality and refinement (e.g. deacidification of fruit juice would enhance its usability in various food products [Calle (2002), Vera (2003)]), (iii) lowering of ecological issues (e.g. reduction in the sludge disposal and ground water contamination) and (iv) attractive economical benefits.

Multiple economic benefits can be withdrawn by an efficient and cost effective method for separation and recovery of acids. From the economical point of view, plants tend to reuse as much chemicals as possible, while unused or free acids in spent adds to the losses. For example, ~40 % cost can be saved in steel galvanizing plant by acid recycling [Stocks (2005)]. During the synthesis of lactic acid by fermentation, the separation and purification accounts for up to 50 % of the production costs [Wasewar (2004)]. Additionally, fermentation operates most effectively at near neutral pH, as the accumulation of acid is inhibitory to cell growth [Datta (2006), Carpenter (2009)]. This requires neutralization of acid and produces salt, instead of the acid itself [Joglekar (2006), Datta (2006)], which requires further treatment. If acid separation could be combined with its production by fermentation, the fermentation process can be operated on a continuous mode without need of pH maintenance. This would reduce the requirement of chemicals, minimize sludge production and disposal issues. It could also lead to a large cost reduction in terms of nutrients and salts requirement. It is reported that, to produce the same amount of lactic acid, repeat batch production of lactic acid requires only 26 % of the yeast extract dosage as compared with conventional batch fermentation [Wee (2006)]. The recovery of spent acids from waste can also be helpful

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in the separation of valuable chemicals like heavy metals from process streams. The secondary sources of materials are becoming increasingly important from the economic point of view and are of prospective use for future technology. This would also reduce potential hazard to the environment.

Ideal solution to the acid treatment and separation issues would be application of a technology with 'near zero discharge'. In such method, every stream in the process is recycled and utilized as much as possible, to produce no wastes and use as little amount of fresh water and chemicals as possible [Regel-Rosocka (2010)]. The objective of near zero discharge can be achieved by applying a process which can be termed as clean technology. Such technologies reduce pollutant emission at the source rather than capturing them after they have been generated [Koltuniewicz (2008b)]. Thus in case of acid treatment, the objective of a clean technology would be efficient separation or recovery of acids from various process streams while addressing present techno-economical limitations. This would lead to improved economy also addressing environmental concerns. This instigated the need of an alternate process for the separation of acid from fermentation broth and other process streams. Present work aims at technical feasibility evaluations of a new process, we term as "Chemodialysis".

1.5. Methodology

As elaborated in earlier section, there is requirement of a process with the aim of separation of acid from non-acidic components (organic or inorganic) present in the process streams. Existing non-membrane based equilibrium-driven separation technologies (e.g., absorption, adsorption, distillation, extraction, ion exchange, stripping) have significant shortcomings, like, operational difficulties (emulsification, foaming, entrainment, weeping, etc.), lack of flexibility (flooding, loading, need for difference in density or boiling point, etc.), slower rates, need for hazardous chemicals, lack of modularity, high capital costs, higher energy requirements and need for large equipment volume [Sirkar (1997)]. These shortcomings are exacerbated by new separation demands and environmental pollution control laws [Sirkar (1997)]. Considering these facts and in the view of some of the advantages of currently practiced

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processes, it was thought that a membrane based process would be advantageous for required application of acid separation.

In terms of membrane based process, there is a need of selective transport of acid across the membrane, rejecting non-acidic (organic or inorganic) molecules present in the solution. The membranes can be porous or non-porous in nature. The use of porous membranes would lead to size based separation, which would result in poor selectivity for the transport of acid over other small molecular weight solutes (e. g. inorganic salts or organic molecules) across the membranes. Hence, non-porous membranes need to be used in the process for desired separation. Though the porous membranes are reported for acid separation in nanofiltration (NF), they have issues like efficient operation at neutral pH and also they have low rejection for mono-valent salts, as discussed (Section 1.3.2). Among the available processes using non-porous membranes, reverse osmosis uses external pressure higher than the osmotic pressure of solution, to reverse the flow of solvent by osmosis. This ability of solvent transport rejecting solute has been utilized for the concentration of acid as discussed earlier (Section 1.3.3). This would require controlling of acid concentration or pH of the process streams (e.g. acid production by fermentation). Also in case of spent processing, where the acids need to be separated from non-acidic components, RO may not be applicable. The stability of polymeric membranes to acidity also remains a major drawback. The present issue of acid separation requires a process which would transport acid as the solute. Thus, a pressure driven processes cannot serve the current purpose and thus are not considered. Pervaporation for acid separation though is known, it works on the transport of acid across the membrane and its removal by evaporation. Thus this process has a limitation that only volatile acids can be separated (Section 1.3.5). Majority of acids used in various processes are non-volatile or corrosive in high temperature environment, this eliminates the possibility of using a temperature driven processes for their separation. The electricity driven process (ED) for acid separation is reported to have higher energy consumption and co-transport of salts across membrane, affecting product purity.

Hence a process of chemodialysis is proposed for the selective transport of acid. It would use polymeric membranes possessing chemically active functionality (like, amine), which would selectively sorb only acid molecules from the feed solution by

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interactions (e.g. acid-base type complexation). This would generate a concentration gradient across the membrane thickness. This concentration gradient would act as a driving force for the transport of sorbed acid molecules, depending upon reversibility of complex between acid and functional group. This transport of acid molecules from feed surface towards permeate side would continue till all the functional sites would get saturated by them. The saturation would cease further migration of acid molecules. When the permeate side is contacted to a suitable stripping agent which could leach acid molecules by overcoming acid-functional group interactions, it would lead to stripping of acid present on the permeate side surface. This would create vacant interaction sites in the membrane matrix and would facilitate further migration of acid molecules from the neighboring interaction sites. This would lead to continuous transport of acid molecules from feed solution to stripping side, with concentration gradient as a driving force.

Membranes prepared using such chemically active polymers would be mounted in a suitable plate and frame module. A feed solution containing acid and a stripping agent would be circulated on either side of the membrane. It would transport the acid molecules due to interaction, depending upon their chemical and physical properties as discussed above. This process results in selective transport of acid in a single stage. It would result in the reduction of various steps in the acid separation processes reported in literature. At the same time, biggest advantage of the process would be low energy consumption (energy would be required only for circulation of the feed and stripping solution across the membranes). The process has certain added advantages along with peculiar advantages reported for membrane based processes as discussed already (Section 1.3). Various possible advantages of the method are discussed in detail below.

1.5.1. *Possible advantages of the proposed "Chemodialysis" as a method*

1.5.1.1. *Lower capital and operating cost*

In the proposed technique of 'chemodialysis', membrane would sorb the acid molecules from the solution on feed side and transport them by concentration gradient as a driving force. Thus, it requires only pumps for circulating feed and permeate solutions. Hence its installation costs will be significantly lower as compared with other process like ED (higher installation cost for dialyzer) or ion-exchange (high cost for ion-

exchange resin and pre-treatment facility). Only possible major cost is for the replacement of membrane. As the process works with concentration gradient as a driving force, it does not need any external stimuli. The only energy requirement is for circulation of solutions on feed and permeate side of the membrane. Hence energy requirement is very low as compared to the processes like distillation, ED, RO, PV, etc. The operational cost would be significantly lower as there is no consumptions of chemicals (e.g. lime, sulphuric acid required in neutralization-precipitation, chemicals required for regeneration of ion-exchange resin or cleaning of dialyzer in electrodialysis, etc.), solvents and extractants (e.g. reactive extraction), resins (adsorption and ion-exchange) and no requirement of extractant replacement (e.g. liquid membranes). In combination with these advantages, the proposed technique (chemodialysis) is simple to operate and can be operated unattended for longer periods. The process being simple in operation would require minimum skilled manpower. All these factors sum up to the possible low capital and operating cost.

1.5.1.2. *High product purity and possible to combine with acid production*

The separation of acid by chemodialysis can be possibly carried out in a continuous mode and under milder conditions. Separation of acid would utilize interactions between these molecules and functional group present on the polymer matrix. This would help to achieve higher selectivity for the transport of acid, in turn obtaining high purity acid as a product. This process has features with the possibility to combine with acid production process like fermentation. Continuous removal of acid would eliminate its build up and thus adverse effects on the life of micro-organisms. This would also eliminate the requirement of pH maintenance and addition of base is not required. Continuous removal of acid during its biotechnological production would also enhance the productivity and make the acid production and separation economically attractive. This is especially important during the processing of organic acids which are sensitive to the changes in solution environment. At the same time since acids are recovered in acidic form itself, their use as a primary product by suitable concentration or reuse in secondary processing becomes easy.

1.5.1.3. Economical and environmental benefits

During the process of 'chemodialysis', use of water as a stripping agent would lead to the recovery of acid in acidic form only. This eliminates the requirement for other chemicals (like alkali in neutralization-precipitation). This would eliminate the salt generation and its disposal issues, making the process environmentally benign. The recovered acid can be recycled after sufficient concentration, which can lead to substantial economical benefits. In case of separation of organic acids during fermentation based synthesis, this process can reduce multiple steps compared with conventional separation methods.

To achieve these advantages, there is a need of membrane for selective transport of acid prepared from suitable polymer having chemically active functional groups those are stable with acidic environment. These membranes need to be investigated for acid transport properties and the selectivity over non-acidic co-solutes. The effects of various process and operational parameters on their stability and transport properties need to be investigated. These investigations will be carried out as: (i) selection of suitable polymers and the membrane preparation with them, (ii) investigations of effect of different process parameters (polymer properties, nature of feed acid to be separated, nature of stripping agent, other operational parameters like temperature, concentration and their effects) on the acid transport by using the membranes prepared from the material with suitable permeation properties and (iii) enhancement of acid transport properties by suitable modification in structure.

1.6. Rationale of the work

Various processes reported in the literature for acid recovery have their own advantages and drawbacks. Among these processes, diffusion dialysis (DD) and liquid membrane based acid separation have some of the peculiar advantages over other methods. The liquid membrane based extraction has shown high separation factor and selectivity towards acids [Wasewar (2004), Wasewar (2005)]. It suffers from issues like membrane instability and toxic nature of extractants and diluents [Wasewar (2004), Joglekar (2006)]. DD uses polymeric anion exchange membranes which are stable during acid separation operation and holds the advantage of low energy consumption

(requires energy for circulation of feed and stripping solutions) [Wodzki (1999), Palaty (2004a), Palaty (2004b), Akgemci (2004)]. It shows transport of co-solute (salts) across the membrane affecting product purity and is effective at high acid and low salt concentration in feed solution [Elmidaoui (1991), Tongwen (2001), Palaty (2001), Palaty (2004a), Palaty (2004b)]. The advantages of both these process were thought to be combined to overcome their individual drawbacks and a membrane based process (chemodialysis) has been proposed. The membranes were prepared using polymers with chemically active functionality on the repeat unit. These chemically active functional groups on polymer repeat unit would lead to selective acid uptake, resulting in high selectivity for acid (as seen in liquid membrane based separation). Additionally, use of polymeric membrane (similar to DD) would eliminate the stability issue associated with liquid membranes.

Extractant with amine functionality were reported to possess high distribution coefficients for the extraction of carboxylic acids [Wasewar (2005), Joglekar (2006)]. Similarly, strong binding of acid with basic amine containing sorbents (polymer or small organics) is well documented in literature [Baroncelli (1962), Bak (1970), Chanda (1985), Joglekar (2006), Liu (2006)]. Use of PEI for the separation of lactic acid in aqueous two-phase system (ATPS) based fermentation has been reported earlier [Kwon (1996)]. Owing to this, polymers containing amine $-N=$, $-NH-$, $-NH_2$ groups on the repeat unit would be used for acid transport investigations.

Commercial viability of a membrane process is largely dictated by the transport rate and selectivity towards desired component. Intrinsic permeability and selectivity properties of the polymer used for membrane preparation are governed by its physical properties. These include chain packing density, segmental motions (glass transition and sub-T_g relaxations), interactions with penetrants, etc. For a membrane of given polymer, transport through membrane can be enhanced using porogen concept [Baniel (1990), Eyal (1992a), Eyal (1992b), Sun (1993)]. The porogen derived membranes (PDMs) prepared with polymer having high selectivity for acid can be investigated. This would lead to enhanced transport rate.

1.7.   Scope of the work

Though various processes have been reported for the separation of acid, they have their own techno-economical or environmental concerns. Out of these processes, reactive extraction using liquid membranes has shown high selectivity for acids; while diffusion dialysis has low energy consumption. We thought to combine these two approaches in a process of termed as 'chemodialysis', wherein transport of acids through chemically active polymeric membranes is proposed. The concept of using polymeric membranes containing chemically active functional groups on its repeat unit, for acid transport is not reported in the literature.

This work requires identification of polymer containing suitable functional groups for acid sorption, preparation of membranes in suitable form and analyzing them for stability and acid transport properties. It was thought to use polymers containing amine functional groups as discussed in details earlier. Three polymers (ASR, PEI and PBI) containing amine functionality were identified for the initial membrane preparation and acid transport investigations. For ASR and PEI, these investigations would be carried out by preparing their thin film composite (TFC) membranes since preparation of their dense membrane is difficult. The dense membranes would be used in case of PBI. Effect of various parameters on the formation of these membranes, their stability and acid transport properties need to be established. Effect of various process parameters and polymer structure on the acid transport properties need to be examined. The mechanism for transport of acid through these membranes, their selectivity and effect of chemically active functional group on the transport properties need to be established.

As per the literature reports, the use of porogen derived membranes (PDMs) can be used to enhance the transport properties [Baniel (1990), Eyal (1992a), Eyal (1992b), Sun (1993)]. It was thought to prepare the PBI based PDMs for acid transport. A polymeric porogen would help to provide longer path for solute diffusion. For a polymer to be used as porogen, it needs to have miscibility with base material (PBI). Formation of a compatible blend between PBI and aromatic polyester is well reported in literature [Chung (1989), Chung (1990a), Chung (1990b)]. Hence the aromatic polyesters were thought to be used as a porogen in current investigations. Formation of PDMs with any polymer as a porogen to be leached out by chemical degradation is not reported in

the literature. The polyester content in premembrane, leaching conditions required for its degradation and removal, other after treatments and their effects on membrane structure and its transport properties need to be optimized in view of rearrangement in membrane matrix during the leaching of porogen as hypothesized in literature [Baniel (1990)].

1.8. Objectives

Objectives of the work presented in this thesis can be divided into three larger classes;

(i) To explore applicability of polymers possessing chemically active functionality as membrane materials for acid transport and validate the concept of "Chemodialysis". For this purpose, three polymers containing amine functionality were selected *viz.*, (i) aminated silicon rubber (ASR), (ii) polyethyleneimine (PEI) and (iii) different members from polybenzimidazole (PBI) family. Investigations with ASR and PEI were carried out by forming thin film composite (TFC) membranes. Various parameters such as coating conditions, polymer concentrations and crosslinking agent were optimized during TFC membrane formation. The initial investigations with PBI as membrane material were carried out in dense membrane form. This part of the work was focused on membrane material selection and basic investigations of their properties.

(ii) The next section of the work was aimed at investigating acid transport through polymeric membranes in presence of co-solute of organic and inorganic in nature and investigate the selectivity of acid molecules over these two types of co-solutes. Glucose and NaCl were chosen as the representative of organic and inorganic type, respectively, based on their nature that would usually encounter in practical application like fermentation. Based on above investigations, PBI based membrane was found to be suitable for further investigations. Various process parameters, *viz.*, sorption of acid in PBI, its effects on mechanical properties of membrane, temperature of operation, feed concentration, properties of feed acid and stripping agent needed to be investigated.

(iii) The next objective was to study effects of structural variations in PBI on transport properties. It was thought to investigate porogen membranes with PBI as a base

material and aromatic polyester to act as a porogen, in order to enhance transport rate. Various parameters responsible for porogen membrane formation, removal of porogen needed in view of new class of porogen (polyester) thought to be used in this study.

1.9.   Organization of thesis

The work done towards achieving above goals is presented in following 6 chapters.

Chapter 1 briefly reviews the need of acid either separation as a product, by-product or prior to the disposal of waste streams. Different methods used for acid treatment have been discussed with their advantages and limitations. The need for an alternate separation method is discussed, leading to a concept of 'Chemodialysis'. This is followed by methodology of the work, scope and objectives. This chapter ends with the organization of the thesis.

Chapter 2 deals with the identification of suitable polymer to be used for preparation of membrane for acid separation by chemodialysis. Explorations with rubbery polymers (aminated silicon rubber and polyethyleneimine) towards membrane preparations, their transport, selectivity over non-acidic co-solutes and stability investigations are discussed. This is followed by use of polybenzimidazole (PBI), as the membrane material.

Chapter 3 deals with investigations of parameters affecting the transport of acid through PBI based membranes. It also describes synthesis of different PBIs, their characterizations and investigations on acid transport properties. Effects of parameters like feed acid properties, operational temperature and concentration feed and stripping agent are discussed.

Chapter 4 deals with the formation of porogen derived membranes, in a bid to enhance acid permeation rate. The formation of porogen derived membranes (PDMs) based on PBI while using aromatic polyester *viz.*, poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen has been discussed. Various parameters affecting PDM formation, its acid sorption and transport properties were studied.

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Chapter 5 deals with exploring applicability of Chemodialysis for the separation of inorganic acids *viz.*, HCl, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$ using PBI based membranes. Effects of feed acid concentration, structural variation of PBI, type of stripping agent, acid sorption and variation in membrane structure from dense to PDMs were investigated.

Chapter 6 summarizes the process of chemodialysis and applicability of PBI membranes towards acid separation and the conclusions drawn during the work.

Chapter 2

Selection of membrane material

2.1.   Introduction

2.1.1.   *Criteria for membrane material*

For the aimed application of acid separation, combination of two phenomena *viz.*, selective extraction of acid by liquid membranes and acid transport by diffusion dialysis (DD) in a single process would be desirable. By this way, advantages of both the processes could be retained, provided adequate membrane material could be developed. A process of acid separation using nonporous polymeric membrane containing chemically active functionality on the polymer backbone is proposed. It would lead to the selective acid uptake due to interaction between acid molecules and active functional groups on the membrane, similar to the liquid membranes. Sorbed acid would be transported across the membrane by the concentration gradient as driving force. Since, transport would be governed by selective sorption of acid and the nature of membrane being nonporous, selectivity of acids over non-acidic solutes can be anticipated to be high based on their differential sorption. This way, draw-backs of low selectivity in DD membranes can be minimized. The issues related with liquid membranes can also be eliminated by using polymeric membranes.

The very first choice of chemically active functionality to be present on polymer backbone is amine group (either primary, secondary or tertiary). These groups would form complex with acid molecules present on the feed side of membrane. It would lead to sorption of acid on the membrane surface and generate a concentration gradient across the membrane thickness. These sorbed acid molecules would keep migrating towards permeate side due to this concentration gradient, provided the acid-amine complex formation is reversible (which is known in the literature [Yang (1991), Wasewar (2004), Joglekar (2006)]). After attaining the saturation of complex formation in membrane matrix, a steady state would be attained. At this stage, if the permeate side of membrane is contacted with a stronger base than amine, the acid-base complex would break and acid would now form a complex with the base present on permeate side. This 'stronger-base'

could be triethyl amine (Et₃N) or even an inorganic base. In later case, a salt of acid would be produced on the permeate side. Thus, formed salt would be incapable of getting complexed again with the amine group of membrane and hence it would be an irreversible process. This would make base (amine) functionality on permeate side of the membrane now available for complexation with new acid molecules and would accept the acid from neighboring sites. This process is expected to lead to migration of acid from feed to permeate side. Such transport phenomenon could be dependent on several factors. These include; (i) characteristics of the transporting acid molecules, (ii) properties of the polymeric membrane material, (iii) acid-base interactions, etc. These are briefly discussed in following sections, which would form guidelines for the design of membrane material and process parameters.

2.1.1.1. Characteristics of transporting acid molecules and co-solutes

Acid separation is required in the diverse types of industrial applications, such as fermentation based acid synthesis, food processing, etc.; involving different kinds of co-solutes and variations in process parameters. The acid to be transported by a basic membrane could be organic or inorganic in nature and may be present as a product, by-product, residual feed component or an undesirable impurity.

Interaction capacity of acid molecules with amine can be expressed in terms of acidity or pK_a. It is also dependent on various other factors like, presence of more than one acidic protons (H^+ in case of an inorganic acid, e.g. H_2SO_4, H_3PO_4 or carboxylic group, -COOH in case of organic acid, e.g. oxalic acid, citric acid) on the molecule, sulfonic acid or other functional groups (such as NO_2, halogen, etc.) present on the organic acid, presence of more than one interactive groups (e.g. amine functionality for amino acid, -OH group in case lactic acid, etc.), molecular size, nature (hydrophilic/hydrophobic), etc. Process parameters which might affect the separation would be temperature, concentration of the acid in feed solution, presence of non-acidic solutes in the process stream, viscosity of solution, etc. Such factors can be crucial in governing the transport of acid through chemically active membrane. The separation performance would depend upon the relative sorption rates of different solutes present in the solution. Since driving force of the proposed process is concentration gradient between the feed and permeate side, use of pressure (which is a major parameter in usual

membrane processes) may not be really applicable here. Similarly, other forms of driving forces such as temperature, electric current, etc. are not considered during present evaluations.

Process stream can contain various co-solutes, which could be salts, organics, colorants, etc.; depending upon to the process involved. A fermentation based acid synthesis would contain unutilized carbohydrates, salt and other nutrients (*viz.*, amino acids, vitamins, proteins and minerals). For example, lactic acid fermentation broth contains carbohydrates, amino acids, vitamins, peptone and minerals (like K_2HPO_4, sodium acetate, Na_2SO_4, $FeSO_4.7H_2O$, $MnSO_4.4H_2O$, etc.) [Wee (2006), Vijayakumar (2008)]. For example, short chain aliphatic carboxylic acid (adipic and butyric) is produced as a by-product during synthesis of cyclohexanone from cyclohexane [Wang (2006)]. In case of spent streams, acids need to be separated from various non-acidic components (salts and organic). For example, steel pickling plant spent would contain oils, fats, organic compound such as aldehydes, ketones, urea, ferrous salts, etc. [Kladnig (2003)]. The semiconductor etching solution waste stream would contain HF, fluosilisic acid, H_3PO_4, HNO_3, acetic acid, toxic metallic impurities, poly-Si, SiN_x, etc. [Sirkar (1997), Kim (2006)]. The spent solid phosphoric acid catalyst from petroleum refineries contains inorganic molecules and volatile organic compounds [Van Der Merwe (2010)]. All such residual reactants or other products would be a part of the process stream from which acids need to be separated. For catering the need of such diversity, there is a need of membrane based process which can combine the advantages of high selectivity of liquid membranes by the use of functional groups like amine and stability provided by use of polymer as a membrane material (as in diffusion dialysis).

2.1.1.2. *Properties of host polymeric material*

Proposed process would work upon selective sorption of acid in polymeric membrane and its transport across the membrane by concentration gradient as a driving force. Basic requirement for any polymer to be used as a membrane material is good film forming ability. For its use as a membrane material in this process, it should have good acid sorption capacity and should show high acid permeation rate. Moreover, leaching of the permeated acid using a suitable stripping agent should be feasible. For the easy removal of transported acid molecules on stripping side, complex formation between acid

molecules and functional group on the polymer matrix should be reversible or could be made reversible by suitable method. Acid should be possibly leached from the complex with basic functional group by contacting with stronger base, variation in temperature, pH or solvent. The membranes prepared from selected polymer should be stable in presence of acid and stripping agent.

Various polymeric materials have been reported for acid separation as an application. Nafion and Flemion based membranes have been reported for the transport of organic acids by DD [Wodzki (1997)]. Various other polymeric membranes reported are polyether sulphone based SB-6407 [Ersoz (2001)], polytetrafluoroethylene-fluoroethylenpropylene based perfluorinated membranes [Cohen (1986)] and brominated-aminated poly(*2,6*-dimethyl-*1,4*-phenylene oxide) [Tongwen (2001)]). For acid separation by adsorption, polymeric adsorbants containing pyridine and phosphonic acid ester groups have been reported in literature [Sato (1995), Wasewar (2005), Joglekar (2006), Gonzalez (2007)]. These methods have various limitations; especially low selectivity for acid over non-acidic moieties.

The sorption of acid by basic amine containing sorbents (polymer or small organics) is well reported in literature [Chanda (1985), Wasewar (2005), Liu (2006), Joglekar (2006)]. Polyethyleneimine has been used for the separation of lactic acid, during its production by aqueous two phase extractive fermentation [Kwon (1996)]. During reactive extraction, extractants containing amine group showed higher extraction efficiency over phosphorous bonded oxygen containing extractants [Wasewar (2005), Joglekar (2006)]. Acid can be re-extracted from amine-acid complex by suitable method of variation in temperature (temperature swing re-extraction), diluent (diluent swing re-extraction) or pH (by contacting with acid like HCl or base like NaOH, ammonia or trimethyl amine) [Yang (1991), Joglekar (2006)]. Owing to this, the polymers containing amine (–N=, –NH–, –NH$_2$) functionality on repeat unit would be useful as membrane material for acid separation.

The amine functionality possesses a lone pair of electrons on its nitrogen. It would facilitate ion-pair formation with acidic moieties [Eyal (1995)]. This acid-base type complex formation between acid molecules and amine functionality on polymeric membranes would result in selective sorption of acid over non-acidic molecules. It is also

reported that, tertiary amine based extractants (e.g. Alamine 336) extracted only acid molecules and not their salts [Yang (1991), Eyal (1995)]. This acid sorption would generate a concentration gradient across the membrane and can be used as driving force for acid transport. To our knowledge, such acid transport through basic polymeric membranes with free amine functionality is not reported in the literature. In proposed process, interaction between solute (acid molecules) and amine functionality on the membrane matrix is an important criterion for selective acid transport across the membranes.

2.1.2. *Selection of polymers and transport investigations*

Three potential polymers were selected for the initial screening of membrane preparation and acid transport properties: (i) aminated silicon rubber (ASR, amine value = 30 mg KOH/g, equivalent to 0.94 mol % amine content), (ii) polyethyleneimine (PEI) and (iii) polymers from polybenzimidzole (PBI) family. Initially rubbery polymers (ASR and PEI) were preferred anticipating a faster diffusion rate through rubbery matrix, as known in the case of gas permeation [Zoland (1992)]. ASR was selected due to its hydrophobic backbone, which would lead to selective sorption of acids with minimum water uptake. This should lead to the separation of acid from aqueous solution. On the other hand, PEI was known to show a good partition of lactic acid during aqueous two phase fermentation [Kwon (1996)]. Third polymer PBI, though is glassy in nature, is known to possess high sorption of inorganic and carboxylic acids [Chanda (1985), Chanda (1999), Li (2009), Kumbharkar (2009), Leykin (2010)]. After sorption of acid, the PBI membranes showed phase transition from being completely glassy to rubbery nature [He (2006), Kumbharkar (2009)]. Such plasticization of PBI membrane matrix would enhance the acid transport. It is also reported that acid doped PBI membranes loose acid by leaching during PEMFC operation [Liu (2006)], in contact with water [Leykin (2010)] or when treated with 0.1 M NaOH [Chanda (1985)]. High acid sorption and easy desorption properties can be combined for their selective transport through the PBI based membranes.

Investigations with ASR and PEI were carried out by preparing thin film composite (TFC) membranes. These membranes were formed by using a suitable crosslinker (*viz.*, glutaraldehyde, polyacrylic acid, *1,3,5*-benzene tricarbonyl trichloride

and toluene-*2,4*-diisocynate). Ultrafiltration (UF) membranes based on either polyacrylonitrile (PAN) or polysulfone (PSF) were used as the porous support. In case of PBI family, initial investigations were carried out using dense membranes prepared from a common member, poly(*2,2'-m*-phenylene-*5,5'*-dibenzimidazole) (PBI-I). Acid transport was investigated using aq. solution containing 10 % lactic acid as a feed solution. The membrane stability and acid transport properties were investigated using stripping solution consisting of aqueous solution of inorganic base (Na_2CO_3, $NaHCO_3$ or $NaOH$) and triethyl amine (Et_3N) or salt of Et_3N and benzoic acid in organic solvent.

2.2.   Experimental

2.2.1.   *Materials*

Polyethyleneimine (PEI, 50 % aq. solution, average molecular weight ~750,000), polyacrylic acid (PAA, average molecular weight = 750,000), toluene-*2,4*-diisocyanate (TDI), *1,3,5*-benzenetricarbonyl trichloride (TMC), benzoic acid (BA), ovalbumin (grade-V), *3,3'*-diaminobenzidine (DAB), isophthalic acid (IPA) and rhodamine were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, ca. 84 % as P_2O_5) was procured from Alfa Aesar. Aminated silicon rubber (ASR, amine value = 30 mg of KOH; defined as equivalents to the basic nitrogen content in 1 g sample of ASR, expressed in mg KOH/g) was procured from Reliance Silicones. Polyacrylonitrile (PAN, viscosity-averaged molecular weight = 24,800) was gifted by IPCL. Polysulfone (PSF, UDEL-3700) was procured from Amoco Corporation. The nonwoven polyester fabric Viledon H-1006 was obtained from Frudenberg and was used as the support for preparation of PAN based UF membrane. PSF based UF membranes were prepared on the top of nonwoven polyester support Hollytex-3329, procured from Alhstrom. Glutaraldehyde (GA, 25 % aq. solution), *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc), hexane (H), isopropanol (IPA), isobutanol (IBA), triethylamine (Et_3N), Na_2CO_3, $NaHCO_3$, NaOH, HCl, H_2SO_4, lactic acid (90 % aq. solution) (LA), citric acid, disodium hydrogen orthophosphate (Na_2HPO_4), $CaCl_2$, *3,5*-dinitrosalicylic acid (DNSA) of GR/extrapure grade were procured from Merck. *D*-Glucose was procured from Qualigens Chemicals. All the chemicals were used as received. Pure gases (N_2, He and CO_2) used for assessing the integrity of thin film composite (TFC) membranes were obtained from Inox Gases with minimum purity of 99.9 %.

2.2.2. *Preparation and characterization of ultrafiltration (UF) membrane*

PSF and PAN based UF membranes were prepared by the phase inversion method. In case of PAN, the dope solution was prepared by dissolving 32 g of $ZnCl_2$ and 200 g of PAN in 768 g of DMF [Chendake (2010)]. It was casted onto running non-woven polyester support (Viledon H-1006), with 8 min air-dry time before entering into gelation bath containing water as a non-solvent at 27 °C. Formed UF membranes were washed in running water for 16 h, to remove the residual solvent and then stored at 4 °C, wetted with 0.1 % formalin solution until use. PSF based UF membranes were prepared with a dope solution containing 200 g of polymer in 800 g of DMF [Achalpurkar (2007)]. Dope solution was casted onto running non-woven polyester support (Hollytex-3329), with 8 min air-dry time before entering into gelation bath containing water as a non-solvent at 8 °C. It was followed by curing the membranes at 60 °C. Formed UF membranes were washed in running water for 16 h, to remove the residual solvent. These membranes were stored at 4 °C, wetted with 0.1 % formalin solution until use.

UF membranes were analyzed for water flux, protein rejection and bubble point (water–air) [Lohokare (2006)]. Water flux was measured using Amicon type stirred cell assembly in a dead end mode, with an active membrane area of 11 cm^2 at 1.02 Kg/cm^2 upstream pressure. Initially, 50 ml of deionized (DI) water was allowed to permeate through the membrane, in order to remove the formalin from pores before measurement of water flux. Bubble point of the membranes was determined by using water–air pair (surface tension, σ: 76 dyne/cm). A continuous flow of air was measured through the prewetted membranes.

Protein (ovalbumin, average molecular weight: 43 kDa) rejection was investigated at pH 7.5 using McIlvaine buffer (0.1 M citric acid and 0.2 M Na_2HPO_4), in a stirred dead end assembly. Its concentration in the feed and permeate solution was analyzed at 280 and 260 nm wavelength by the double beam UV spectrophotometer (Chemito, Spectrascan UV 2700). Percent rejection (*% R*) was calculated by using Eq. (1)

$$\% R = \left[1 - \left(\frac{C_p}{C_f} \right) \right] \times 100 \qquad (1)$$

where, C_p and C_f are permeate and feed concentrations, respectively.

The scanning electron microscopic (SEM) images of these UF membranes were obtained using Leica SEM (Model Stereoscan 440).

2.2.3. *Thin film composite (TFC) membrane preparation*

ASR and PEI based TFC membranes were prepared by dip coating method. Thin polymer skin layer was formed on the top of UF membranes samples of 15×8 cm^2 size, as discussed below.

2.2.3.1. ASR based TFC membranes

PAN based UF membranes were used as a support during the preparation of ASR based TFC membranes. ASR layer was coated on the top of these membranes by dip coating, followed by crosslinking using GA or PAA. The crosslinking reactions are given in Scheme 2.1.
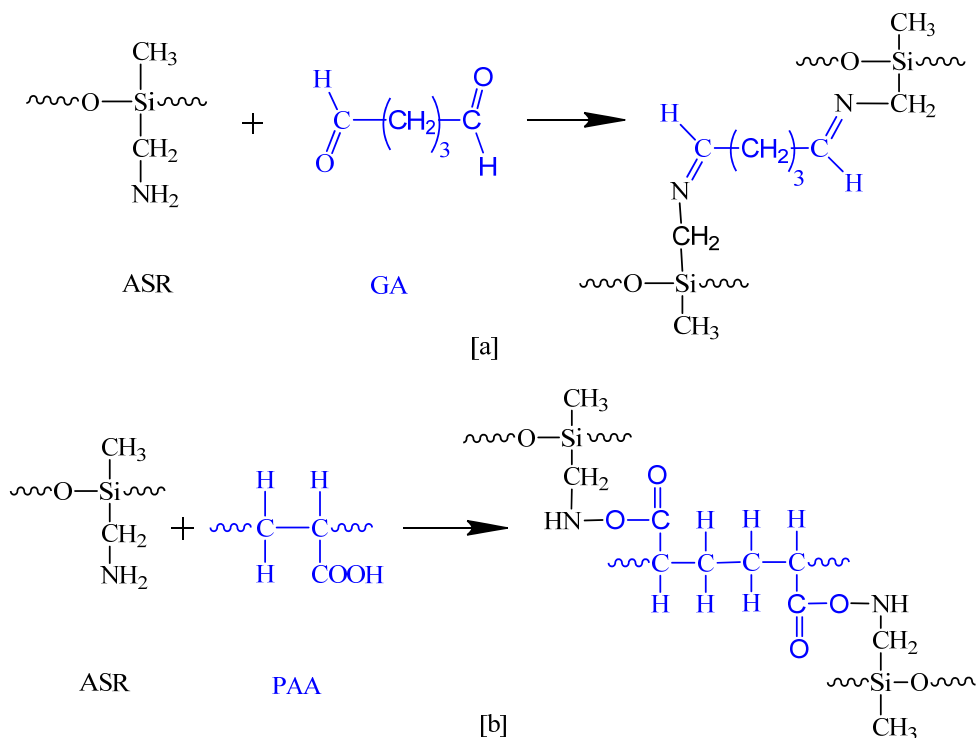
Scheme 2.1. Crosslinking of ASR with (a) GA and (b) PAA during TFC membrane formation

UF membrane was initially mounted on a glass plate with all four sides taped using a scotch tape. Water in the pores of UF support was replaced by sequential solvent exchange, using IPA followed by hexane (dip time of 12 h in each case). A 4 % (w/v)

ASR solution was prepared using hexane as a solvent. The support UF membranes were air dried for 2 min and then dipped in ASR bath for 2 min. This was followed by air dry (2 min) and then dipped in either GA (aq. 2 % solution, dip time = 45 sec) or PAA (aq. 2 % solution, dip time = 30 sec). The membranes were air dried for 2 min and then in an oven at 70 °C for 90 min. Formation of defect free membrane was assessed by gas permeation (CO_2 and N_2) analysis and their (CO_2/N_2) selectivity at 15 psi$_g$, using variable volume method [Stern (1963)].

2.2.3.2. *PEI based TFC membranes*

PSF membranes were used as a support for the formation of PEI based TFC membranes. Three different crosslinking agents, *viz.*, TMC, GA or TDI were used for membrane preparation. The support UF membranes were initially mounted on a glass plate with all four sides taped using a scotch tape and used for further coating. In case of TMC or TDI as a crosslinking agent, the membranes were dipped in 1 % aq. solution of PEI (1 min). It was followed by air dry (8 min) and then dipped in either TMC (0.3 % solution in hexane, dip time = 30 sec) or TDI (0.5 % solution in hexane, dip time = 1 min) bath. The membranes were air dried for 2 min and then in an oven at 70 °C for 90 min (Table 2.1). For the preparation of TFC membranes with GA as a crosslinking agent, an aqueous solution containing 1 % PEI was prepared and acidified with HCl (till pH = 6). GA was added to this solution till 1 % concentration. UF membranes were mounted on a glass plate with all four sides tapped by scotch tape and dipped in the solution for 15 h. It was followed by drying in oven at 70 °C for 90 min (Table 2.1). Formed membranes were assessed for continuous skin layer formation by rhodamine test. A 0.1 % aqueous solution of rhodamine dye was spread on the surface of formed TFC membranes. After draining the dye, the uncoated membrane surface would show stains. Absence of such area was a primary indication of good membrane formation. Formed TFC membranes were analyzed for gas (He and CO_2) permeation and He/CO_2 selectivity at 15 psi$_g$ using variable volume method [Stern (1963)]. Selective membranes were then used for the acid transport investigations. The crosslinking reactions of PEI with these crosslinking agents are given in Scheme 2.2. Their membrane preparation parameters are summarized in Table 2.1.
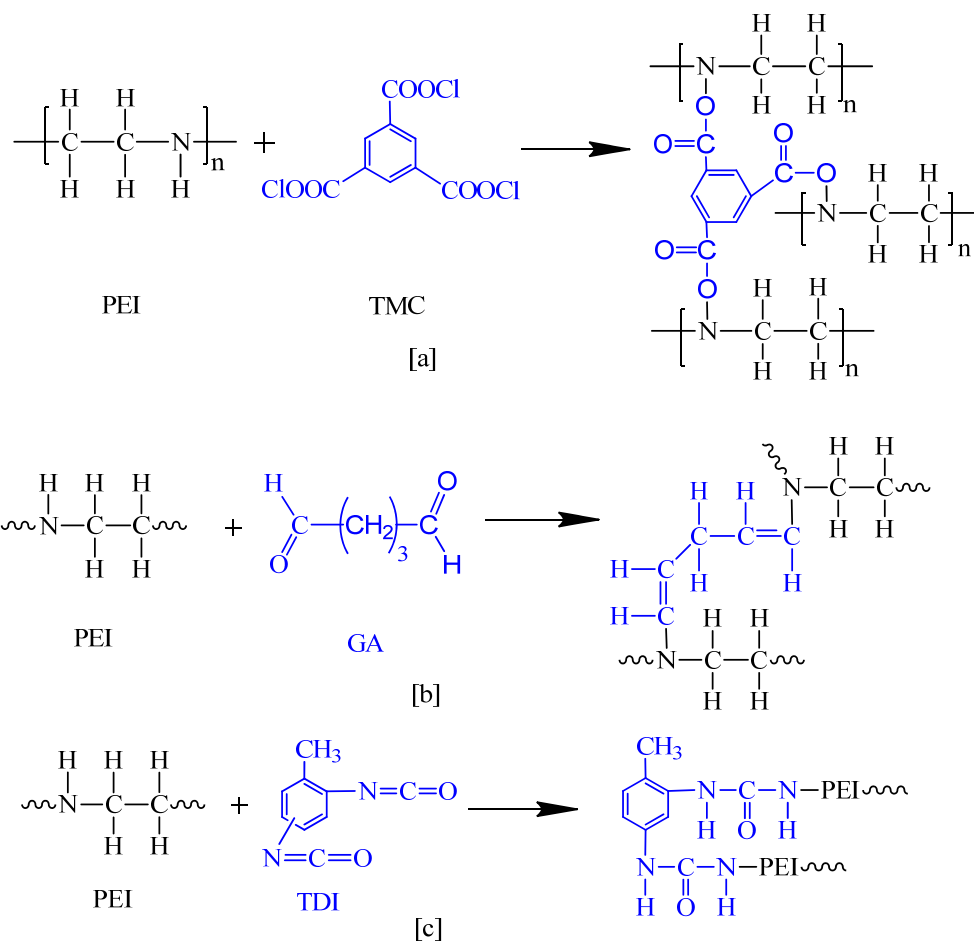
Scheme 2.2. Crosslinking of PEI with (a) TMC, (b) GA and (c) TDI during TFC membrane formation

Table 2.1. Preparation conditions for PEI based TFC membranes

1st coat		Air dry	2nd Coat		Oven dry
Coating solution	Dip time (min)	time (min)	Coating solution	Dip time (min)	time (min) at 70 °C
Aq. PEI, 1 %	1	8	TMC, 0.3 % in H	0.5	90
Aq. PEI, 1 % (pH = 6) + GA, 1 %	900	-	-	-	90
Aq. PEI 1 %	1	8	TDI, 0.5 % in H	1	90

2.2.4. *Synthesis of polybenzimidazole (PBI) and its dense membrane preparation*

Polybenzimidazole, PBI-I was synthesized using DAB and IPA, by solution polycondensation in PPA at 200 ºC as reported earlier [Kumbharkar (2006)]. Typically, a

three-neck round bottom flask equipped with a mechanical stirrer, N_2 inlet and an outlet fitted with $CaCl_2$ guard tube was charged with 450 g of PPA and heated to 120 °C under constant flow of N_2. A 15 g (0.07009 mol) of DAB was added with continuous stirring, temperature was raised to 140 °C and an equimolar quantity of IPA was added. The temperature was slowly raised to 170 ºC and maintained for 5 h. It was further raised to 200 ºC and maintained for 12 h. Obtained reaction mixture was poured into stirred water to precipitate the polymer. It was sequentially washed with water, $NaHCO_3$ solution and again with water; till the filtrate was neutral to pH. The polymer was dried at 100 °C under vacuum for a week. It was purified by dissolving in DMAc at 80 °C, centrifugation at 2800 rpm (2 h), followed by precipitation in stirred water. Precipitated polymer was dried at 100 °C under vacuum for a week. Structures of monomers and polymer are given in Scheme 2.3.
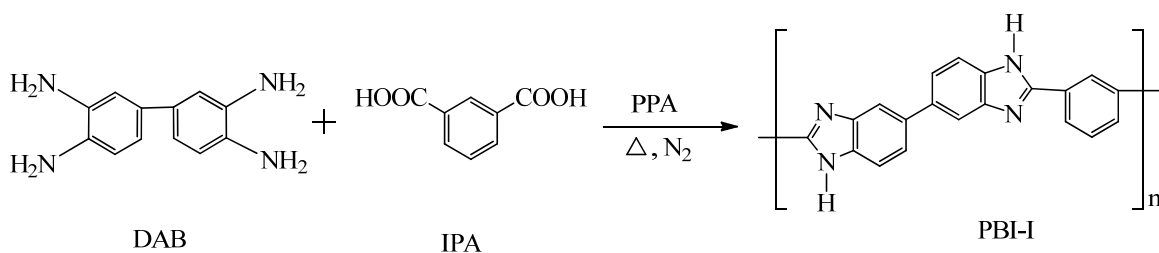
Scheme 2.3. Structure and abbreviations of monomers and polybenzimidazole (PBI-I)

Inherent viscosity of the synthesized PBI-I was determined using its 0.2 g/dL solution in 98 % H_2SO_4 at 35 °C. It was found to be 1.2 dL/g. This viscosity is high enough for formation of membranes, which would be stable in the presence of acids, as per our earlier experience [Kumbharkar (2009)]. Dense membranes of PBI were prepared by solution casting method. A 2 % (w/v) solution of PBI in DMAc was poured on a flat glass surface and the solvent was allowed to evaporate at 80 ºC for 18 h under dry conditions. Formed membranes (thickness: $20 - 30 \pm 4\ \mu m$) were peeled off from the glass plate. They were kept in water at 60 ºC for 3 days to remove the traces of solvent. They were finally dried under vacuum at 100 °C for a week and preserved in a desiccator until use.

2.2.5. Permeation equipment

A plate and frame module (prepared from either SS 316 or polypropylene) (Fig. 2.1) was used for the acid transport investigations.
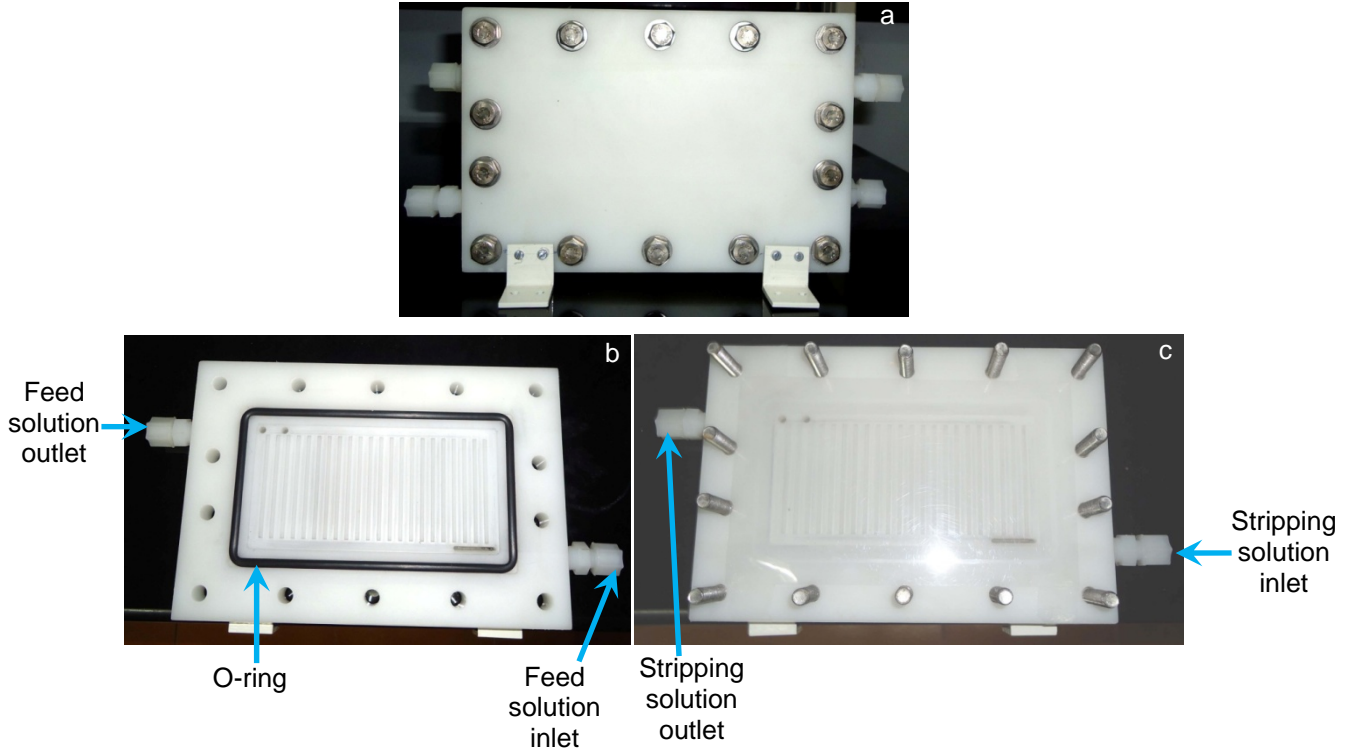
Fig. 2.1. Plate and frame module used for acid transport investigations (a: permeation cell, b: feed plate and c: stripping plate)

Feed and retentate connections on opposite plates were arranged in such a way that feed and stripping solutions would flow in the counter current direction. Channels were grooved on both plates, which assist in the distribution of solution and also provide a support to the membrane. This reduces the possibility of membrane damage due to external pressure during operation. Membrane was mounted in two plates of plate and frame module, supported by an O-ring. The active membrane area was ~100 cm^2.

2.2.6. Acid transport investigations

These membranes were investigated for transport of lactic acid (10 %, w/v) with glucose as co-solute in feed solution. The membranes were initially soaked in feed acid

solution for 3 days and then mounted in a plate and frame module, immersed in a thermostat (Fig. 2.2). The photograph of the experimental setup is shown in Fig. 2.3.
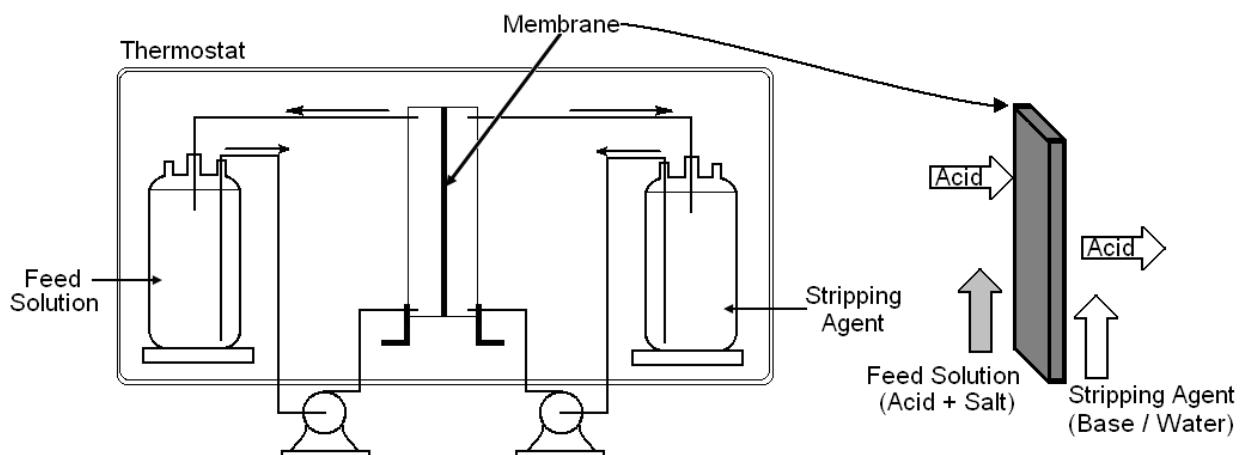
Fig. 2.2. Schematic representation of the acid transport setup
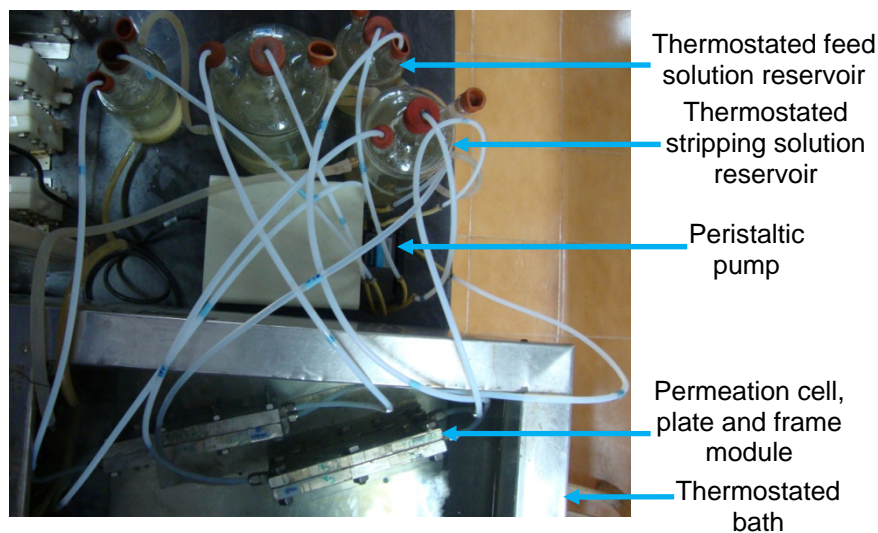
Fig. 2.3. Setup for acid transport investigations

On feed side of the membrane, 300 ml feed solution containing acid was circulated; while on other side 1500 ml of stripping agent was circulated in a counter current manner. Either aq. Na_2CO_3 (9.03 %, w/v), aq. $NaHCO_3$ (9.33 %, w/v), aq. NaOH (2.5 %, w/v), Et_3N in hexane (10 %, w/v) or salt of benzoic acid (BA) (8 %) and Et_3N (6.65 %) in isobutanol + hexane (50 %, v/v) were investigated as the stripping agent. Flow rate on both the sides of membrane was maintained at ~1.6 ml/min. Samples at various time intervals were analyzed by titration to determine the acid transport. Glucose

analysis was done by DNSA method [Canizares-Macias (2001)]. At the end of experiment, lactic acid and glucose concentrations in feed and stripping solution reservoir were also determined using HPLC (Column: Aminex HPX87H Biorad 300 mm, with 5 mM H_2SO_4 as the mobile phase, at 50 ºC, 0.6 ml/min flow rate and an injection volume of 20 μl). Flux through the membrane was calculated using Eq. (2).

$$J = \frac{M}{A \cdot t}$$
(2)

where, J is the flux of penetrant (g/m^2.h), M is the mass of penetrant transported (g) across the membrane of cross-sectional area A (m^2), within duration t (h).

2.3. Results and discussion

2.3.1. UF membrane properties

The PAN or PSF based UF membranes were studied for water flux, bubble point and rejection characteristics (Table 2.2). These membranes showed acceptable water flux at 1.02 Kg/cm^2 upstream pressure. This indicated the presence of appreciable porosity in membranes, which would allow easy transport of penetrant permeated through skin layer. The porosity of these membranes can be seen from scanning electron microscopic images (Fig. 2.4).
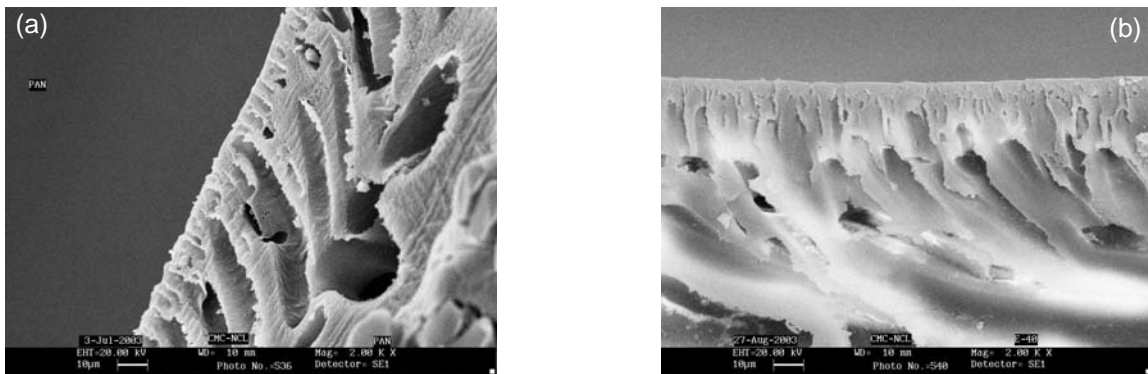
Fig. 2.4. Scanning electron microscopic images of ultrafiltration membranes; (a) PAN and (b) PSF

This water flux, appreciable rejection of ovalbumin coupled with high bubble point (> 4.1 Kg/cm^2) indicated that these UF membranes do not posses abnormally large pores. Absence of such pores is necessary for the uniform coating of selective polymer

and formation of defect free skin layer. From our previous experiences, water flux, rejection and bubble point of these UF membranes are adequate and they can be used as a support for TFC membrane preparation [Achalpurkar (2007), Chendake (2010)]. Hence these membranes were used as a support in the preparation of TFC membranes with ASR or PEI as skin layer.

Table 2.2. Properties of UF membranes used as support for TFC membrane preparation

Membrane	Water flux (l/m^2.h)	(%) Rejection (Ovalbumin, MW: 43 kDa)	Bubble point (Kg/cm^2)
PAN	37	93	> 4.1
PSF	16	94	> 4.1

2.3.2.   *Investigations with TFC membranes*

TFC membranes were prepared by in-situ crosslinking of ASR and PEI by suitable crosslinking agent, on the top of either PAN or PSF based UF membranes as a support. Crosslinking was controlled by varying crosslinking agent or by optimizing dip time. Controlled amount of crosslinking was necessary to increase the stability of formed membrane. The higher degree of crosslinking would reduce chain mobility, which may lead to decrease in permeance [Achalpurkar (2007)], which is not desirable.

2.3.2.1. *ASR based TFC membranes*

These membranes were prepared by coating a solution of ASR in hexane as a solvent, on the top of PAN based UF membranes as support. Water in their pores was replaced by hexane before coating by sequential solvent exchange by dipping in IPA followed by hexane, prior to dipping these membranes in solution. Through our earlier work, we have shown that, if solvent used for preparation of coating solution is already present in the pores of UF support membrane, it assists in the formation of selective and defect free membrane [Chendake (2010)]. Hence water in the pores of membranes was needed to be replaced by hexane. Hexane used a solvent for ASR is immiscible with water. Hence the water from the pores of UF membrane was sequentially replaced by IPA followed by hexane. ASR was crosslinked by using two crosslinking agents; (i) GA or (ii) PAA, to obtain stable TFC membranes.

(i)   GA as a crosslinking agent

Initial investigations were carried out with the membrane skin layer prepared from ASR using GA as a crosslinking agent. Prior to use in acid transport investigations, formed membranes were analyzed for gas (N_2 and CO_2) permeation. They showed appreciable selectivity for CO_2/N_2 (7.5-8.2) (Table 2.3), which is a sign of defect free skin layer formation. Similar selectivity has been reported earlier for the formation of ASR based TFC membranes [Achalpurkar (2007)]. This formation of defect free skin layer was necessary for selective acid transport. Selective membranes were used in acid transport investigations, using aqueous feed solution containing 10 % LA and 10 % glucose. LA concentration in feed solution is taken as 10 % (w/v) to check the applicability of proposed process for separation of acid from fermentation broth. Typically, bio-platform molecule (generated from biomass by fermentation) is present at ≤ 10 % (wt) within broth along with several by-products, minerals and nutrients [Clark (2009)]. Glucose was taken as the representative of organic substrate (molasis, starch or sugars [Koltuniewicz (2008a)]) used for fermentation based biotechnological synthesis of acid.

To start with, the acid transport was investigated using aq. $NaHCO_3$ as a stripping agent. Initially, the investigations were continued for more than 150 h to obtain equilibrium transport properties. A large variation in the transport rate was observed during initial 70 h, after which it was almost linear (Fig 2.5).
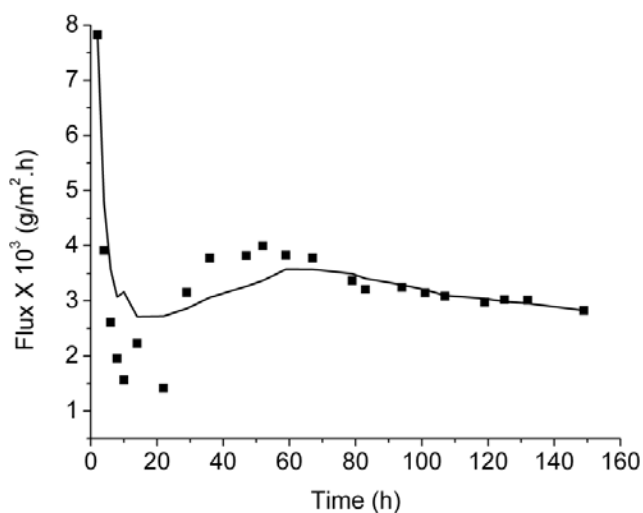
Fig. 2.5. Variation in LA flux through the ASR based TFC membrane

The flux was decreased sharply for initial 30 h and then it was stabilized with time. Inital sharp change in flux could be attributed to the equilibration of membranes with acid in feed solution before mounting to transport cell. This would lead to the sorption of acid by interaction with amine functionality on polymer matrix. These membranes on contacting with the alkaline solution as a stripping agent, would leach out acid molecules from membrane surface. This would result in creation of vacant interaction site on the membrane matrix and transport of molecules from neighboring interaction sites. This might have resulted in the initial high transport rate, which was stabilized after a period of time. Hence, further experiments were continued for 72 h and equilibrium transport rate was obtained (Table 2.3).

Table 2.3. ASR based TFC membranes prepared using GA as crosslinking agent

Gas permeation before acid transport study			Stripping agent	LA Flux $(g/m^2.h)$	Average gas permeation after acid transport study			Other observations
$P_r(N_2)$	$P_r(CO_2)$	$S(CO_2/N_2)$			$P_r(N_2)$	$P_r(CO_2)$	$S(CO_2/N_2)$	
163	1222	7.5	9.33 % aq. $NaHCO_3$	Very low < 0.01or NT**	109	719	6.6	LA transport observed for only one experiment
235	1938	8.2	9.33 % aq. Na_2CO_3	NT**	High*	High*	-	Membranes damaged during transport investigation
266	2087	7.8	2.5 % aq. NaOH	NT**	High*	High*	-	Membrane damaged during investigation, leaching of backing observed
234	1695	7.2	10 % Et_3N in H	NT**	500	1406	2.8	Membranes damaged in ~ 24 h and Et_3N was transported to feed side
141	1140	8.1	8 % BA + 6.65 % Et_3N in IBA + H (50 %)	32.85 (± 2.5)	100	866	8.7	Membrane was intact at the end of experiment and two immiscible layers formed in stripping solution

*: Gas permeance beyond measurement limits,

**: NT = Nil acid transport (below detection limits),

P_r = permeance measured in GPU (1 GPU = 10^{-6} cm^3 (STP) / cm^2.sec. cm Hg),

$S(CO_2/N_2)$ = selectivity for the CO_2 over N_2 (ratio of pure gas permeance of CO_2 to N_2).

Transport of LA, through the ASR based membranes was either very low or below detection level with aq. $NaHCO_3$ as a stripping agent (Table 2.3). LA transport in these conditions could be measured only once. For all the other experiments it was below detection level. Non-transport of acid through ASR based membranes with aq. base as a stripping agent could be attributed to the hydrophobic nature of polymer. LA is highly hydrophilic in nature [Joglekar (2006)]. Its aqueous solution was used in the transport investigations, which might be imposing limitations on LA in hydrophobic ASR matrix. At the same time, use of aq. base solution as a stripping agent would also act as an additional resistance for the leaching of acid from 'N' in hydrophobic ASR matrix. Low acid uptake and additional resistance for its stripping could be a reason for non-transport of LA, with aqueous alkali as a stripping agent. Similar observations were seen with aq. Na_2CO_3 or aq. NaOH as a stripping agent, which showed nil or below detection level transport for LA through ASR based TFC membranes (Table 2.3).

ASR based membranes after using for LA transport investigations with aq. $NaHCO_3$ as a stripping agent showed nominal reduction in CO_2/N_2 selectivity from 7.5 to 6.6. This reduction of gas selectivity in contact with aqueous alkali as a stripping agent could be due to the hydrolysis of backing (which was nonwoven polyester), used as a support for UF membrane preparation. This hydrolysis of backing would result in damage of the membrane. When these membranes were used in LA transport investigations with aq. Na_2CO_3 and aq. NaOH as a stripping agent, their gas permeance could not be measured after experiment. This was a sign of membrane damage. Visual observations showed damage of the membrane backing with aq. Na_2CO_3 and aq. NaOH as a stripping agent (Table 2.3). In case of aq. NaOH as a stripping agent, leaching of the support backing was also observed. Hydrolysis of the polyester in contact of aqueous alkali has been reported in literature [Zaikov (1984)].

To avoid the issues with aq. alkali as a stripping agent for LA transport through ASR based TFC membranes, Et_3N in hexane was used as stripping agent. Use of hexane as a solvent would reduce the resistance for acid transport, by eliminating the resistance for stripping during use of aq. alkali as a stripping agent. Further, hexane would lead to swelling of ASR selective layer and reduce the resistance for acid transport. Membranes were damaged within ~24 h and transport of Et_3N towards feed side of the membrane was observed (Table 2.3). This could be attributed to the swelling of ASR selective layer

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due to sorption of hexane. This swelling would weaken the skin layer and would damage membrane, which would result into transport of Et_3N across the membrane. This was further conformed by gas permeation analysis; where the membranes showed 61 % reduction in CO_2/N_2 selectivity, after they were used in acid transport investigations (Table 2.3).

To overcome this problem, it was thought to use the salt of BA and Et_3N as a stripping agent. Formation of salt of Et_3N with BA would restrict its transport across the ASR membrane towards feed side, while BA being weak acid could be easily replaced from the salt by transported LA. Similar to the regeneration of LA by contacting with stronger acid like HCl, during its extraction by amine based extractants, as reported in literature [Wasewar (2004), Joglekar (2006)]. The salt (BA + Et_3N) is insoluble in hexane alone; hence hexane + IBA (50 %) were used as solvent. Additionally, use of combination of solvents would reduce the possibility of skin layer damage, observed during use of only hexane as a solvent for stripping agent. The ASR based membranes showed good transport rate with Et_3N + BA salt as a stripping agent; at the same time membranes were stable during transport investigations (retained the CO_2/N_2 selectivity) (Table 2.3). Two immiscible layers were observed in the stripping side solution. Such extra layer formation might be due to acid-amine complex formation which is immiscible with the solvent (hexane + IBA). Though this system provided appreciable transport for LA, it required further separation steps for the recovery of transported acid from stripping solution. Hence, it was not used as a stripping agent during further investigations.

(ii)   PAA as a crosslinking agent

To counter stability issues with the membranes prepared by using GA as a stripping agent, ASR based TFC membranes were prepared with PAA as a crosslinking agent. It was thought that, PAA being polymeric in nature, it would result in better crosslinked structure. This would enhance the strength and stability of membrane skin layer. The membranes were analyzed for gas permeation and showed acceptable selectivity (average CO_2/N_2 selectivity = 7.4). This indicated formation of TFC membranes with defect free skin layer. These membranes were used in LA transport investigations with Et_3N in hexane as a stripping agent.

These membranes showed appreciable transport for LA with a flux of 14.9 ($\pm$ 2) g/m^2.h. This could be attributed to the swelling of ASR layer by hexane. It would reduce the resistance for diffusion of sorbed acid molecules through membrane matrix. At the same time, use of hexane as a solvent for Et$_3$N would lead to easy leaching of LA from membrane matrix. Both these properties combinely resulted in appreciable transport of LA through these membranes. The membrane stability was low in this case also. Though the membranes could be used for more than single experiment (each of 72 h duration) for acid transport investigations, its CO$_2$/N$_2$ selectivity was reduced to a large extent (from 7.4 to 2.6) during one operation. In addition, transport of Et$_3$N towards feed side was also observed. Swelling of ASR by hexane would lead to reduction in stability and damage to selective skin layer. This would result in the reduction of gas selectivity and transport of Et$_3$N towards feed side.

Thus, the ASR based membranes showed low transport for LA with Et$_3$N as a stripping agent, while it was nil with aqueous base as a stripping agent. The membranes have low stability and were damaged during acid transport investigations. This generated a need for alternate membrane material. We thought that use of PEI, a hydrophilic polymer would result in easy uptake of LA from aqueous feed solution and help its transport across the membrane.

2.3.2.2. PEI based TFC membranes

PEI based TFC membranes were prepared by using PSF based UF membranes as base material. Three crosslinking agents: (i) TMC (ii) GA or (iii) TDI, were used for preparation of PEI based TFC membranes. Initially TMC was used to prepare the TFC membranes. Prepared membranes were investigated for LA transport using Et$_3$N in hexane as a stripping agent. Use of Et$_3$N in hexane would lead to easy recovery of transported LA by heating, due to their volatile nature as discussed above. Additionally, non-woven polyester backing was stable in contact with Et$_3$N in hexane. Hence it would reduce the issues of membrane damage due to hydrolysis of polyester backing.

(i)   TMC as a crosslinking agent

These membranes were prepared by sequential coating of PSF membranes with aq. PEI solution and crosslinking by dipping in TMC solution with hexane as solvent

(Table 2.1). Aqueous solution of PEI was used for coating, hence the PSF membranes from water were directly used for coating. Prepared membranes were analyzed for gas permeation (He and CO_2) showed a low selectivity for He/CO_2 (2.9) (Table 2.4). Though, these selectivities were not promising; it indicated formation of skin layer and non-porous membrane structure. Hence the membranes were further used for LA transport.

Table 2.4. Analysis of PEI based TFC membranes for LA transport

Crosslinking agent	Initial gas permeation before acid transport study			LA flux $(g/m^2.h)$	Selectivity (LA/glucose)	Average gas permeation after acid transport study		
	$P_r(He)$	$P_r(CO_2)$	$S(He/CO_2)$			$P_r(He)$	$P_r(CO_2)$	$S(He/CO_2)$
TMC	725	247	2.9	36.3	1.3	222	96	2.3
GA	9.6	2.5	3.8	0.69	1.6	4.9	1.5	3.3
TDI	23.5	0.39	60	NT**	-	23.9	0.42	57

**: NT = Nil acid transport (below detection limits),

P_r = permeance measured in GPU (1 GPU = 10^{-6} cm^3 (STP) / cm^2.sec. cm Hg),

$S(He/CO_2)$ = selectivity for the He over CO_2 (ratio of pure gas permeance of He to CO_2).

Formed membranes showed good transport for LA, with the flux of 36.3 g/m^2.h. Presence of –NH– functionality on PEI polymer chain would lead to sorption of acid in the membrane matrix. It would generate a concentration gradient and lead to transport of acid to permeate side. The permeated acid would be leached by Et$_3$N in hexane as a stripping agent. The membranes also showed transport of glucose along with acid and the acid/glucose selectivity was 1.3. PEI used for coating is highly hydrophilic polymer. It would lead to swelling of skin layer due to sorption of water. This resulted in transport of glucose through the water sorbed in skin layer. Observed LA/glucose selectivity was very low for the use of these membranes in practical application. At the same time, membrane stability was low (could not be used for more than one experiment of 72 h). These membranes showed a reduction in He/CO_2 selectivity (from 2.9 to 2.3), after they were used for acid transport investigations (Table 2.4). This reduction in selectivity was an indication of damage to the membrane skin layer. This could be due to the leaching of uncrosslinked PEI, in contact with water used as a solvent for feed solution.

Hence, it was thought that use of stronger crosslinking agent and crosslinking throughout the thickness of skin layer would reduce possibility of skin layer leaching and increase the stability of resultant membrane.

(ii)   GA as a crosslinking agent

The coating solution was composed of 1 % aq. PEI solution acidified to 6 pH by addition of HCl; GA was added to the solution till 1 % concentration. Both PEI and GA are water soluble and their aqueous solutions were used for coating. They undergo instantaneous crosslinking if their solutions are mixed directly. Hence, the conventional way of coating with polymer solution followed by dipping into crosslinker solution could not be used as it would result into crosslinking at surface layer. This crosslinked layer would arrest further passage of GA into PEI layer and hence its crosslinking. Addition of HCl in PEI solution to acidic pH would result in sorption of HCl by interaction with 'N' on the PEI repeat unit. This sorption of acid on 'N' of PEI would protect it from the instantaneous reaction with GA, during its dissolution and coating of the solution on membrane.

TFC membranes were prepared by dipping PSF support membranes in the coating solution for 15 h, followed by curing in oven at 70 °C for 90 min. A higher dip time (15 h) was used for coating to increase the penetration of coating solution in the pores of support membrane. This would anchor polymer in the pores and help to increase stability of formed TFC membranes. After coating the membranes were cured by heating in an oven at 70 °C for 90 min. This heating of membranes during curing would release the sorbed HCl, making 'N' sites on PEI free for crosslinking. Subsequent crosslinking reaction with the GA present in vicinity would result in crosslinking throughout the thickness of skin layer. This would help to reduce leaching of skin layer and result in formation of a stable membrane.

Prepared membranes were investigated for gas permeation before application for acid transport. They showed selectivity of 3.8 for He/CO_2 (Table 2.4). Though the gas selectivity was not high, but was higher than with TMC as crosslinking agent. This indicated formation of skin layer; hence they were investigated for LA transport properties. These membranes showed lower transport rate for LA (0.69 $g/m^2.h$) than the membranes prepared using TMC as a crosslinking agent (36.3 $g/m^2.h$) (Table 2.4). This

reduction in transport rate could be due to higher overall membrane thickness. The dip time of 15 h would lead to the penetration of coating solution in the pores of support membrane. It would result in higher effective thickness of skin layer. Additionally, higher crosslinking of PEI throughout the skin layer thickness would increase permeation resistance and reduce acid transport rate through the membrane. Combined effect of both these factors (increased permeation resistance and higher effective thickness) resulted in large reduction of acid transport rate (flux ratio of the TFC membranes with TMC/ GA = 52.6). Glucose was also transported across the membranes along with LA and the acid/glucose selectivity was just 1.6 (Table 2.4). Eventhough, LA/glucose selectivity was increased marginally, as compared with the membranes prepared with TMC as a crosslinking agent (1.6 from 1.3). This selectivity is still very low, for practical significance of the process. At the same time a large reduction in transport rate made it an unattractive option. The membranes were analyzed for gas permeation after their use in LA transport investigations. They showed a reduction in He/CO_2 selectivity (from 3.8 to 3.3) (Table 2.4). This indicated leaching of unreacted PEI resulting in damage of skin layer.

(iii)   TDI as crosslinking agent

PEI based TFC membranes with TDI as crosslinking agent were prepared with sequential dipping in the respective solutions as detailed in Table 2.1. Formed membranes were analyzed by gas permeation and showed higher He/CO_2 selectivity (60), as compared to those with TMC or GA as a crosslinking agent (Table 2.4). Higher crosslinking by TDI as a crosslinking agent lead to formation of defect free skin layer, which resulted in higher selectivity for these gases. Highly crosslinked PEI based TFC membranes prepared using TDI as crosslinking agent are known in reverse osmosis as NS-100 [Rozelle (1977)]. It was thought that use of concentration gradient as a driving force and sorption of acid by N on PEI would lead to preferable transport of acid (solute) rather than water (solvent). When these membranes were investigated for LA transport, they showed no transport for LA as well as glucose. The membranes were stable in contact with acid and stripping solution with a marginal reduction in gas selectivity (Table 2.4). This could be attributed to the formation of stable membrane with high crosslinking. This higher crosslinking due to use of TDI as a crosslinking agent might

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restrict polymer chain motion, which would reduce sorption and transport of LA. At the same time, higher crosslinking would consume available 'N' on the surface of TFC membrane, which would reduce availability of free 'N' for acid uptake.

Thus, PEI based TFC membranes either showed low transport for LA with poor selectivity over glucose (TMC and GA based) or were impermeable to acid and glucose (TDI based). With the variation in crosslinking agents from TMC to GA, the LA transport rate was reduced to a large extent (from 36.3 to 0.69 g/m^2.h). Moreover, the increase in LA/glucose selectivity (1.3 to 1.6) was not very promising. The TFC membranes prepared with TDI as a crosslinking agent showed nil transport for LA. This indicated that crosslinking with variation in crosslinking agent might have increased in the order TMC < GA < TDI, which makes membranes more tight for the LA transport to occur. This resulted in lower sorption and transport for LA through the PEI based membranes. This showed that, PEI may not be a suitable candidate for current application of acid transport.

Both these rubbery polymers investigated (ASR and PEI), with suitable crosslinking were unable to offer stable membranes with acceptable acid transport characteristics. This originated the need for some better polymer possessing chemically active functionality on its repeat unit, stable during operating conditions and offer acceptable sorption and transport properties.

2.3.3. *Investigations on polybenzimidazole (PBI) as a membrane material*

In view of failure with amine containing rubbery materials, focus was shifted to the glassy polymeric materials. Hence we thought to evaluate polybenzimidazole (PBI) as a family for acid transport. The poly(*2,2'-m*-phenylene-*5,5'*-dibenzimidazole) (PBI-I), a member from PBI family was tried initially for the membrane preparation and acid transport investigations. Its properties of high stability, high acid sorption and easy leaching of sorbed acid made it obvious choice as a membrane material for acid separation. Dense membranes of PBI-I were used in the LA transport investigations, using aq. NaOH or Et_3N in hexane as a stripping agent. These membranes showed appreciable transport for LA with aq. NaOH as a stripping agent, while it was nil with Et_3N in hexane as a stripping agent (Table 2.5).

Table 2.5. Transport of LA through PBI-I based membranes

Stripping agent	LA flux ($g/m^2.h$)	Glucose flux ($g/m^2.h$)
Aq. NaOH	4.1	No transport
Et$_3$N in hexane	No transport	No transport

PBI posses basic 'N' in the –N= and –NH– on its repeat unit. It leads to sorption of LA by acid-base type interaction (ion-pair formation) with 'N' on its repeat unit. Sorption of acids in PBI based membranes has been reported in literature [Chanda (1985), Chanda (1999), Li (2009), Kumbharkar (2009), Leykin (2010)]. This sorbed acid would generate a concentration gradient across the membrane, which would result in permeation of sorbed acid towards permeate side. This phenomenon would continue till equilibrium is reached in membrane matrix. When this membrane is contacted with stronger alkali (aq. NaOH) as a stripping agent on the permeate side, it would lead to leaching of sorbed acid by overcoming the interactions with PBI. The leaching of carboxylic acids from PBI by aq. NaOH has been reported in literature [Chanda (1985)]. Vacant interaction site on the membrane matrix would lead to further migration of LA molecules from neighboring interacting sites. LA leached from permeate side would form sodium lactate with NaOH present in the stripping solution, making the process irreversible. It would result in continuous transport of LA from feed to stripping solution on permeate side. Inability for transport of LA with Et$_3$N in hexane as a stripping agent could be attributed to the combination of hydrophilic nature of PBI and hydrophobic nature of hexane. This is in line with the nil transport for LA, across the hydrophobic ASR based membranes with aqueous alkali as a stripping agent.

PBI-I based membranes showed nil transport for glucose used as co-solute during LA transport investigations (Table 2.5). These membranes were further investigated for the transport of various non-acidic species (aq. Et$_3$N, inorganic bases, glucose and NaCl) in a single component study, with water as a stripping agent. The membranes showed 'nil' transport for these non-acidic species. Transport of permeant through PBI membranes depends upon its sorption in membrane matrix by interaction. Sorption is followed by its permeation through membrane matrix by concentration gradient as a driving force. In absence of interactions and thus sorption, nil transport of

these non-acidic molecules across the PBI based membranes could be justified. Thus these membranes have practically infinite selectivity for transport of acid over non-acidic molecules.

Inspiring from these results, detailed investigations on the sorption and transport of acids in PBI was planned. Effects of various parameters (*viz.*, properties of stripping agent, properties of acid to be transported, structure of polymer and other operating parameters like temperature, concentration of acid in feed solution, stripping solution concentration) on the transport of acid through PBI based membranes were investigated as discussed in next chapters.

2.4.   Conclusions

Three polymers (ASR, PEI and PBI-I) having basic amine functionality on the repeat unit were investigated for the transport of lactic acid. ASR and PEI were used in the TFC membrane form. They showed either low transport rate for acid with co-transport of glucose or no transport at all. Also, the acid/glucose selectivity was very low ($\leq$ 1.6). Hence, these membranes cannot be used in the practical acid recovery applications. Additionally, some of the TFC membranes were damaged during investigations. To overcome these problems, dense membrane of PBI-I was used. They showed good transport for LA with aq. NaOH as a stripping agent. These membranes showed nil transport for NaCl, Et$_3$N, inorganic Bases (NaOH, Na$_2$CO$_3$ or NaHCO$_3$) and glucose (alone or in presence of acid).

Transport of acid and its selectivity over non-acidic solutes through the membranes based on chemically active polymers containing basic amine functionality was dependent upon the interaction between acid and polymer. At the same time, the leaching of transported acid from membrane surface was also highly dependent upon the nature of stripping agent and interactions between acid molecules and stripping agent. Hence the process was termed as 'Chemodialysis'. The transport of acids through PBI based membranes is investigated and discussed in detail, in the next chapters. The chapters aimed towards investigations and optimization of various parameters affecting the process of chemodialysis (*viz.*, properties of stripping agent, properties of acid to be transported, structure of polymer, membrane morphology and other operating parameters like temperature, concentration of acid in feed solution, stripping solution concentration).

Chapter 3

Transport of organic acids through polybenzimidazole based membranes by Chemodialysis

3.1.   Introduction

During our earlier work towards the selection of membrane material for separation of acid by chemodialysis, the polybenzimidazole (PBI) based membranes showed selective transport of acids. Polybenzimidazole, a family of high performance polymer is well known for its thermochemical and mechanical properties. The polymer structure and thus the physical properties can be tuned by varying either of the monomer, i.e. tetramine or dicarboxylic acid. Gas permeation properties as well as acid sorption in various members of PBI family are known to vary to a large extent depending on the PBI structural parameters resulting in deviations in physical properties [Kumbharkar (2009), Leykin (2010)]. PBIs based on *4,4'*-(hexafluoroisopropylidene)bis(benzoic acid) and *5-tert*-butyl isophthalic acid exhibited 10–40 times higher permeability than that of PBI based on isophthalic acid [Kumbharkar (2006)]. At the same time, a variation in sorption of different acids in a single PBI is well reported [Chanda (1985), Kumbharkar (2009), Leykin (2010)]. During the sorption of aq. tetrafluropropanol, an increase in the swelling (permeant uptake) of PBI based membranes with temperature is reported [Wang (2007a)]. An increase in the sorption of H_3PO_4 with the bath concentration though could be easily anticipated, it is not a linear function of bath concentration [Kumbharkar (2009), Leykin (2010)] and depends on polymer properties, solute-polymer interactions, etc. Such interactions with stripping agent and acid molecules on the transport properties of acid were observed during the material selection investigations [Chapter 2].

Thus, it was planned to investigate the sorption and transport of acids through chosen members of PBI family and investigate effects of various parameters responsible for the transport to occur. Three PBIs, *viz.*, PBI-I, PBI-BuI and PBI-Py (based on *3,3'*-diaminobenzidine (DAB) condensed with isophthalic acid (IPA), *5-tert*-butylisophthalic acid (BuI) or *2,6*-pyridinedicarboxylic acid (Py), respectively were selected as the

membrane materials for investigating transport of organic acids. Effect of various parameters such as concentration, temperature, type of stripping solvent on acid sorption and transport are evaluated. Initially, transport of lactic acid (LA) through PBI-I based membranes was investigated at varying feed concentration and stripping agent (water, aqueous or organic solution of NaOH, Na_2CO_3, triethyl amine). LA transport was also investigated using PBI-BuI and PBI-Py based membranes in order to investigate the effect of structural variations in PBI. Transport of acetic acid and citric acid through PBI-I membranes was investigated to evaluate the feasibility of proposed method of 'Chemodialysis' for the separation of other organic acids from non-acidic solutes.

3.2. Experimental

3.2.1. Materials

3,3'-Diaminobenzidine (DAB), isophthalic acid (IPA), 5-tert-butylisophthalic acid (BuI) and 2,6-pyridinedicarboxylic acid (Py) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, ca. 84 % as P_2O_5) was procured from Lancaster. D-glucose was procured from Qualigens Fine Chemicals. Hexane, N,N-dimethyl acetamide (DMAc), lactic acid (90 % aq. solution) (LA), acetic acid (AA), citric acid (CA), H_2SO_4, NaOH, Na_2CO_3, triethyl amine (Et_3N), $NaHCO_3$, NaCl, 3,5-dinitrosalicylic acid (DNSA) and calcium chloride ($CaCl_2$) (GR/extrapure grade) were obtained from Merck. All these chemicals were used without further purification.

3.2.2. Synthesis of polybenzimidazoles (PBIs) and dense membrane preparation

Three polybenzimidazoles (PBIs) based on DAB and a dicarboxylic acid (IPA, BuI or Py) were synthesized as described earlier [Kumbharkar (2009)]. Typically, a three-neck round bottom flask equipped with a mechanical stirrer, N_2 inlet and an outlet fitted with $CaCl_2$ guard tube was charged with 2400 g of PPA and heated to 120 °C under constant flow of N_2. A 80 g (0.3738 mol) of DAB was added with stirring, temperature was raised to 140 °C and an equimolar quantity of a dicarboxylic acid was added. The temperature was raised to 170 ºC and maintained for 5 h. It was further raised to 200 ºC and maintained for 12 h. Obtained reaction mixture was poured into stirred water to precipitate the polymer. It was sequentially washed with water, $NaHCO_3$ solution and again with water; till the filtrate was neutral to pH. The polymer was dried

at 100 °C under vacuum for a week. Obtained polymer was further purified by dissolving in DMAc at 120 °C, centrifugation at 2800 rpm (2 h), followed by precipitation in stirred water. The precipitated polymer was dried at 100 °C under vacuum for a week. Structure and abbreviations of monomers and PBIs are given in Scheme 3.1.
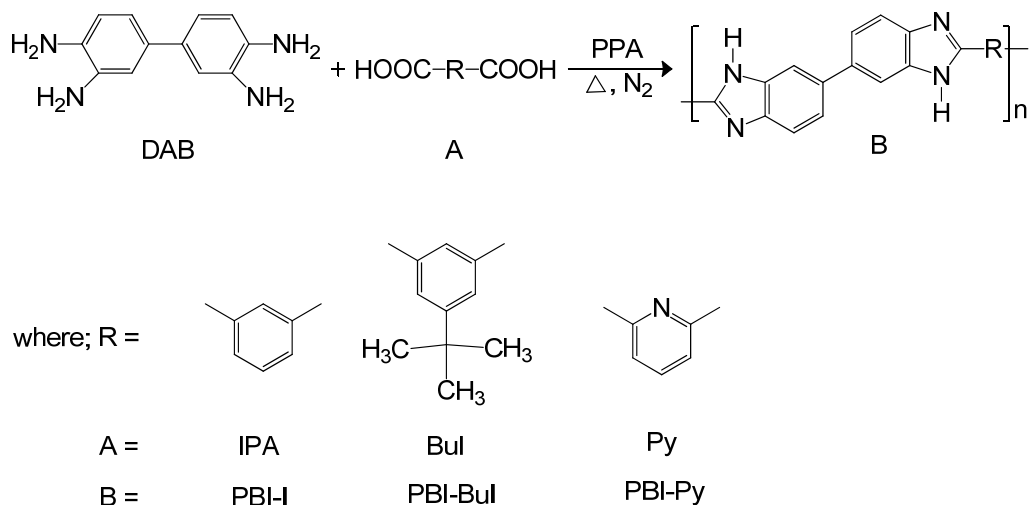
Scheme 3.1. Structure and abbreviation of monomers and PBIs

Dense membranes were prepared by solution casting method using 2 % (w/v) PBI solution in DMAc on a flat glass surface. The solvent was evaporated at 80 ºC under dry conditions. Formed membranes were peeled off from the glass plate (thickness variation within ± 3 μm), kept in water bath at 60 ºC for 3 days in order to remove traces of the solvent and finally vacuum dried at 100 °C for a week.

3.2.3. *Physical properties*

Inherent viscosity of PBIs was determined using its 0.2 g/dL solution in conc. H_2SO_4 at 35 °C. They were characterized by FT-IR (recorded on Perkin Elmer-16-PC FT-IR spectrophotometer) and thermogravimetric analysis (TGA-5000, TA instruments, under N_2 atmosphere with a heating rate of 10 °C/min).

3.2.4. *Sorption studies*

Dry PBI samples were immersed in a screw cap bottle containing solution of a solute (NaCl, glucose or acid) of known concentration is kept in a thermostated shaker. Sorption of LA in PBI-I and PBI-BuI was studied at varying temperatures (30, 40, 50

and 60, ± 0.1 °C); while sorption of other acids was studied at 40 °C. Sorption of the LA in PBI-I and PBI-BuI was also investigated at varying bath concentrations (1, 3, 5, 6, 7, 10 and 12 %, w/v). Sorption of LA in PBI-Py was studied with 10 % (w/v) bath concentration, while sorption of water, 10 % aq. AA and 10 % aq. CA was investigated only in PBI-I. The progress of acid sorption in PBI was monitored by measuring solution conductivity. After attaining the equilibrium, bath concentration of acid was deduced by titration against standardized NaOH solution. Acid uptake in PBI was deduced from the difference in initial and equilibrium bath concentrations and was calculated using Eq. 1. Obtained data is given in Table 3.1, 3.2 and Fig. 3.3.

$$Acid \ uptake \ in \ PBI \left(\frac{mol}{RU} \right) = \frac{\left(M_i - M_f \right)}{N} \tag{1}$$

where; M_i, M_f are initial and equilibrium bath concentrations, respectively; while N represents moles of PBI repeat unit.

Weight and dimensions of the membrane samples after attaining the equilibrium were also measured to determine membrane swelling (Eq. 2) as well as weight uptake (Eq. 3).

$$Swelling \ ratio \ (\%) = \frac{\left(A_f - A_i \right)}{A_i} \times 100 \tag{2}$$

$$Weight \ uptake \ (\%) = \frac{\left(W_f - W_i \right)}{W_i} \times 100 \tag{3}$$

where; A_i and A_f are area of membrane samples under dry and acid sorbed states, respectively; while W_i, W_f are weights of PBI before and after acid sorption.

3.2.5. *Acid transport*

Transport of organic acids (LA, AA and CA) was investigated using 10 % (w/v) acid concentration containing 10 % glucose as a co-solute. PBI membranes already dipped in the feed solution for 72 h was mounted in a plate and frame module (active area: 102 cm^2) and kept in a thermostat, as shown schematically in Fig. 2.2. Feed (300 ml) and stripping solution (water, aq. NaOH, aq. Na$_2$CO$_3$ or Et$_3$N in water/hexane) were circulated in a counter current manner. Flow rate on both sides of the membrane was maintained as ~1.6 ml/min. Transport of lactic acid was investigated at varying

temperatures (28, 40, 50 and 60 °C), while for other acids it was studied at 40 °C. Samples from feed and permeate sides (2 ml) were drawn at various intervals of time and analyzed by titration to determine the acid concentration on respective side. Glucose was analyzed by DNSA method [Canizares-Macias (2001)]. At end of the experiment, the glucose concentration was also determined using HPLC (Column: Aminex HPX87H Biorad 300 mm, with 5 mM H_2SO_4 as the mobile phase, at 50 °C, 0.6 ml/min flow rate and an injection volume of 20 µl).

Acid flux was calculated using Eq. 4.

$$J = \frac{M}{A \cdot t} \tag{4}$$

where; J is the flux (g/m^2.h), while M is acid transported (g) across the membrane of cross-sectional area A (m^2) during time t (h). Acid flux through the membrane can be given by integrating Fick's law over the thickness of membrane [Wijmans (1995)];

$$J = \frac{D_i}{l}(C_{if(m)} - C_{is(m)}) \tag{5}$$

where; l is thickness of the membrane, $C_{if(m)}$ and $C_{is(m)}$ are acid concentrations in feed and stripping side interface, respectively.

$$C_{if(m)} = K_i \cdot C_{if} \tag{6}$$

where; K_i is the sorption coefficient and C_{if} the acid concentration in feed solution [Wijmans (1995)].

On permeate side of membrane; the same procedure can be followed leading to equivalent expression,

$$C_{is(m)} = K_i \cdot C_{is} \tag{7}$$

where; C_{is} is acid concentration in stripping solution.

Concentrations of permeant within the membrane phase at two interfaces can be substituted from Eq. 6 and 7 into Eq. 5, to give expression describing permeation through membranes.

$$J = \frac{D_i \cdot K_i}{l}(C_{if} - C_{is}) \tag{8}$$

The product $D_i \times K_i$ is normally referred as the permeability coefficient, P_i.

$$J = \frac{P_i}{l}(C_{if} - C_{is}) \tag{9}$$

Thus;

$$P_i = \frac{J \cdot l}{(C_{if} - C_{is})} \tag{10}$$

D_i, K_i and thus P_i are concentration dependent. Thus, Eq. 8-10 implies the use of values for D_i, K_i and P_i that are averaged over membrane thickness [Wijmans (1995)]. As the samples were analyzed at varying time intervals, the overall flux and permeability over the duration of experiment was calculated using Eq. 11 and 12, assuming steady state between two consecutive samples. These values of flux and permeability (with a variation in range of 0.18 - 6 % for various cases) are presented in Table 3.3-3.5 and Fig. 3.4, 3.5.

$$J_{avg} = \frac{1}{T}\sum_{t=0}^{t=T} J_t \cdot \Delta t \tag{11}$$

$$P_{avg} = \frac{1}{T}\sum_{t=0}^{t=T} P_t \cdot \Delta t \tag{12}$$

where, J_{avg} and P_{avg} is the average flux (g/m^2.h) and permeability (m^2/sec) respectively, J_t and P_t is the flux and permeability at the time t and Δt is the duration between two consecutive samples and T is the total duration of experiment (h).

In a separate experiment, membranes were also investigated for the transport of NaCl (0.1 % feed concentration) with water as the stripping agent. The conductivity probe was inserted in stripping solution reservoir to monitor changes in the conductivity.

3.3.   Results and discussion

3.3.1.   *Basis for selection of membrane material*

Three PBIs (*viz.*, PBI-I, PBI-BuI and PBI-Py) were chosen as membrane materials due to variations in their structural and physical properties. PBI-I, possessing high sorption of H_3PO_4 and H_2SO_4 [Li (2009), Kumbharkar (2009)] was thought to be used to prove the hypothesis of selective acid transport. PBI-BuI contains bulky *tert*-butyl group on repeat unit, which led to 9.62-28 time enhancement in permeability of different gases as compared to PBI-I [Kumbharkar (2006)]. The third polymer, PBI-Py

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possessing additional 'N' in its acid moiety (*2,6*-pyridine dicarboxylic acid) was evaluated in order to assess the effect of additional basicity on acid transport.

3.3.2.   *PBI synthesis, their physical characteristics and membrane preparation*

The PBIs were synthesized as detailed in experimental section using polyphosphoric acid as the solvent. After PBI precipitation in water, it was rigorously washed with water, aq. $NaHCO_3$ and water; followed by its purification by reprecipitating DMAc solution. This was necessitated in order to remove H_3PO_4 completely from the polymer matrix, otherwise its solubility (and thus membrane formation by solution casting) is affected. The inherent viscosity of PBI-I, PBI-BuI and PBI-Py was 1.2, 1.15 and 0.9 dL/g for; respectively.

Formation of each PBI was confirmed by comparing their IR and TGA pattern with that of reported earlier [Kumbharkar (2009)]. A typical broad band in IR spectra at 3688-2042 cm^{-1} (PBI-I), 3716-2336 cm^{-1} (PBI-BuI) and 3700-2142 cm^{-1} (PBI-Py) were as found earlier and attributed to the hydrogen bonding of N-H/N and non-hydrogen bonded N-H stretching (Fig. 3.1). Also a band responsible for C-H stretching (3082 cm^{-1} for PBI-I, 3076 cm^{-1} for PBI-BuI and 3096 cm^{-1} for PBI-Py); characteristic band for imidazole C=C and C=N in the range of 1650-1450 cm^{-1}, bands in the fingerprint region (in-plane C-H deformations at 1230-1090 cm^{-1}, typical benzene ring modes at 1011 and 980 cm^{-1}, out-of-plane deformations of substituted benzene rings at 900-800 cm^{-1}) conformed the formation of respective PBIs (Fig. 3.1).
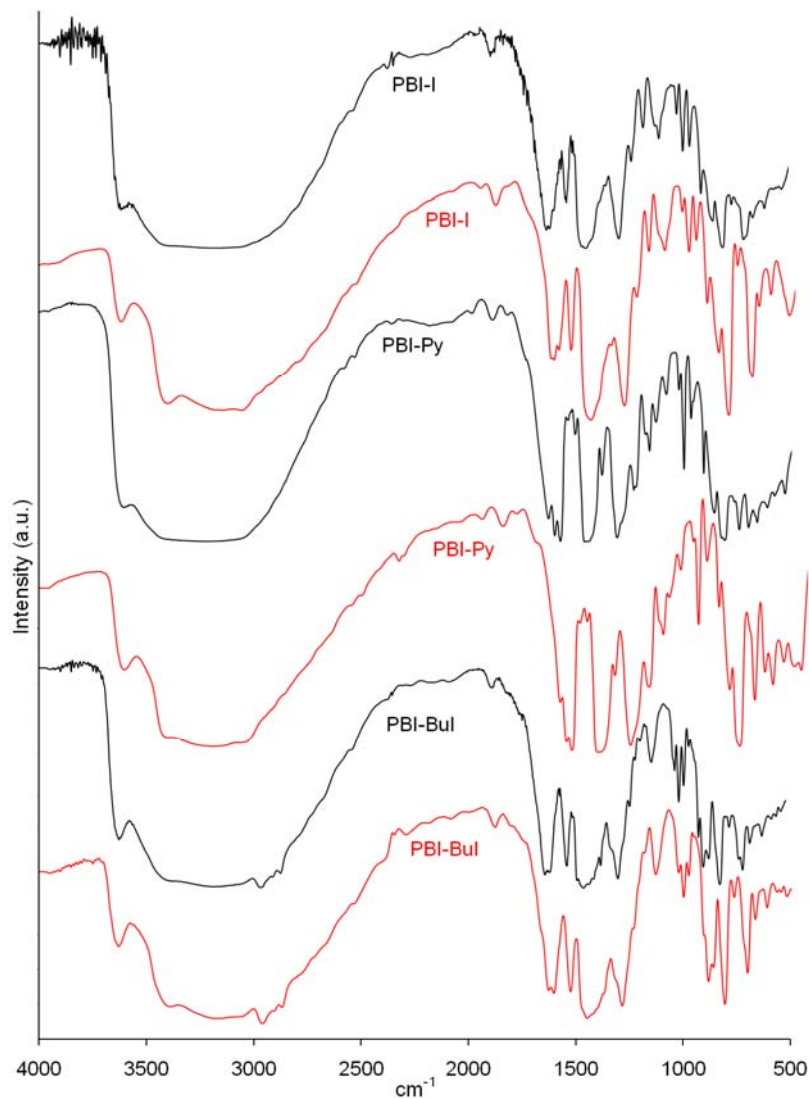
Fig. 3.1. Comparison of the FT-IR spectra of synthesized PBIs with the previously reported; (where, spectra in black previously reported and spectra in red obtained during current study)

This was further substantiated by their similar initial decomposition temperature (PBI-I: 611 ℃, PBI-BuI: 524 ℃ and PBI-Py: 594 ℃; which were reported to be 600, 525 and 600 ℃, respectively) (Fig. 3.2).
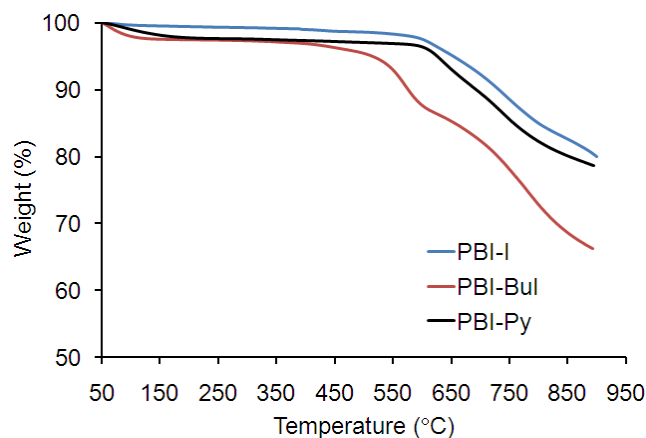
Fig. 3.2. TGA spectra of synthesized PBIs

The dense membranes of these PBIs were prepared by solution casting using 2 % (w/v) solution in DMAc. Formed membranes were treated with water, followed by keeping in vacuum oven for the removal of residual solvent.

3.3.3. *Sorption analysis*

3.3.3.1. *Sorption of non-acidic solutes*

Sorption of NaCl and glucose was evaluated using 5 and 10 % (w/v) solution by immersing the PBI sample in solution for 72 hours. Gravimetric analysis of samples in triplicate (after vacuum oven treatment to remove sorbed water) conveyed that there is no sorption of NaCl or glucose in any of the PBI membrane (PBI-I, PBI-BuI or PBI-Py) investigated. This observation could be attributed to the nature of PBI. Due to H-bonding, PBI is known to be densely packed [Kumbharkar (2006)]. NaCl being salt and glucose being a bigger molecule, their sorption being nil (beyond detection limit) in PBIs could be anticipated. It is reported that amine based extractants (e.g. alamine 336) extract only acids and not their salts [Yang (1991)]. Success of reverse osmosis process relies on absence of NaCl sorption in polyamide membranes.

3.3.3.2. *Sorption of lactic acid: Effect of concentration, temperature and nature of PBI*

As could be seen from Fig. 3.3, for a given temperature and a PBI, a linear increase in the sorption of LA was observed with an increase in initial bath concentration from 1-12 %. Since the acid sorption takes place by interaction between acid molecules from the bath and basic nitrogen of PBI, increase in sorption with bath concentration is

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as anticipated. Such increase of acid sorption in PBI with increase in bath concentration is well known [Chanda (1985), Kumbharkar (2009), Leykin (2010)].
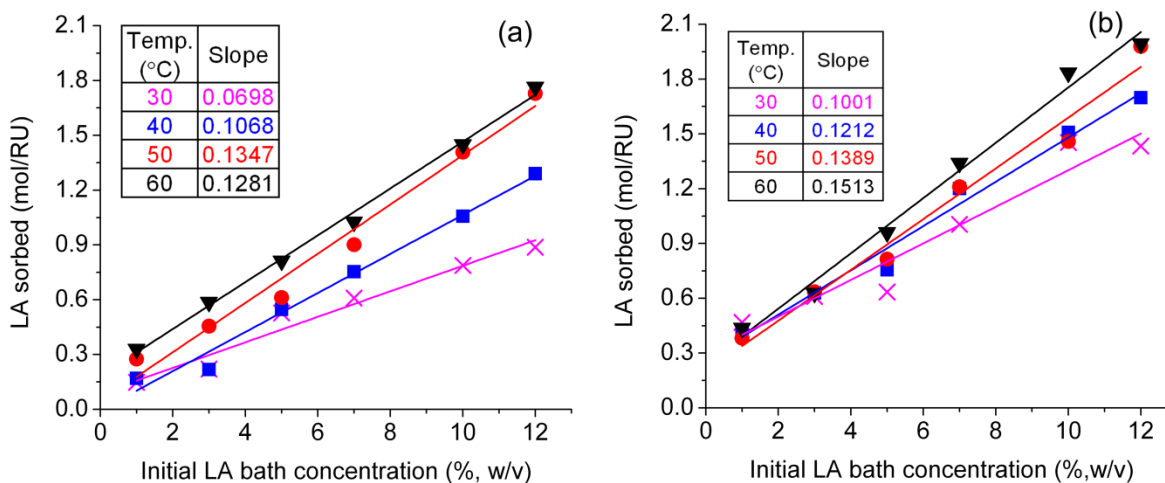
Fig. 3.3. Effect of temperature and bath concentration on the sorption of LA in PBI, where (a) PBI-I and (b) PBI-BuI; (×: 30 °C, ■: 40 °C, ●: 50 °C, ▼: 60 °C)

Both PBI-I and PBI-BuI showed an increase in LA sorption with increase in temperature (Fig. 3.3), at a given bath concentration. This could be attributed to the increase in swelling of polymer chains, aided by temperature and acidic environment. PBI is known to sorb large water (20.4, 12.3 and 17.6 % w/w, for PBI-I, PBI-BuI and PBI-Py, respectively [Kumbharkar (2009)]). As the temperature increases, swelling due to water might facilitate entry of acid molecules into the polymer matrix, which would overcome H-bonding interactions present in PBI (since acid-base interactions in PBI are anticipated to be more dominant than H-bonding within the PBI-polymer chains). An increase in sorption due to increased swelling of PBI by aq. tetrafluoropropanol is reported [Wang (2007a)]. An increase in sorption with increase in temperature is known in other polymers such as chitosan [Shieh (1997)], polyacrylonitrile [Tsai (2005)], Nafion [Jalani (2005), Choi (2006)], etc.; which are highly polar in nature. Temperature induced reduction in interchain interactions leading to high benzoic acid sorption in the range of 4-25 °C is reported for polyurethane (PU) membranes [Rzeszutek (1998)].

When the nature of PBI is to be considered, PBI-BuI showed higher sorption of lactic acid than PBI-I (Fig. 3.3) at all temperatures and bath concentrations (Fig. 3.3).

PBI-BuI is known to be loosely packed (possess higher *d*-spacing) than PBI-I in dry state [Kumbharkar (2006)]. Comparatively higher free volume of PBI-BuI would offer higher sorption of water and lactic acid molecules inside the membrane bulk, than in the case of PBI-I. This is conveyed by generally higher slopes of acid sorption isotherm at a particular temperature for PBI-BuI than that of PBI-I (Fig. 3.3). Higher sorption of H_3PO_4 and H_2SO_4 in PBI-BuI than PBI-I has been observed earlier [Kumbharkar (2009)]. Significance of increased *d*-spacing or free volume in increasing the sorption of water and alcohols in polyimides is reviewed [Jiang (2009)].

Table 3.1 details the sorption of LA in PBI-I, PBI-BuI and PBI-Py at 40 °C and at bath concentration of 10 %. It is interesting to see that though PBI-BuI showed higher LA-sorption than that of PBI-I as explained above, the weight uptake as well as swelling ratio (dimensional variation) for PBI-BuI is lesser than that of PBI-I. This can be explained on the basis of hydrophobic *tert*-butyl group being present in the PBI-BuI, which is known to possess lesser water uptake than that of PBI-I [Kumbharkar (2009)]. In other words, though weight uptake by PBI-I is higher, the water content in the membrane seems to be higher than that in the case of PBI-BuI. The PBI-Py being more basic in nature by virtue of pyridine basicity, it showed higher acid uptake (1.38 mol/RU) than that of PBI-I (1.06 mol/RU). Its lower acid uptake than that of PBI-BuI can be explained based on higher packing density (lower *d*-spacing) of PBI-Py than the later [Kumbharkar (2009)]. During this work, we had observed similar trend for the sorption of H_3PO_4 in these PBIs.

Table 3.1. Sorption of aq. solution of LA (10 %, w/v) in various PBIs at 40 °C

Polymer	Acid uptake (mol/RU)	Weight uptake (%)	Swelling ratio (%)
PBI-I	1.06	45.8	21.12
PBI-BuI	1.51	37.47	10.76
PBI-Py	1.38	33.59	15.52

3.3.3.3. *Sorption of different acids in PBI-I*

Investigation of sorption of other organic acids was studied at 10 % (w/v) bath concentration and at 40 °C with PBI-I; which varied in the order: CA (0.91 mol/RU) <

LA (1.06 mol/RU) < AA (2.14 mol/RU; Table 3.2). We had maintained the bath concentration as 10 %, since this is the concentration of acid generally encountered during organic acid production by fermentation [Wee (2006), Soccol (2006), Rapsor (2008), Vijayakumar (2008), Clark (2009)]. The order of acid uptake can be explained on the basis of 'molar' bath concentrations (which was AA (1.67 M) > LA (1.11 M) > CA (0.52 M)), though the bath concentration on weight basis was same for all the cases (10 %).

Table 3.2. Sorption of aq. solution of organic acids (10 %, w/v) in PBI-I at 40 °C

Acid	Acid uptake (mol/RU)	Weight uptake (%)	Swelling ratio (%)
AA	2.14	36.3	15.05
LA	1.06	45.8	21.12
CA	0.91	19.0	10.48

3.3.4. *Transport of non-acidic solutes*

PBI based membranes were investigated for the transport of NaCl and glucose, individually. Glucose was taken as a representative of carbohydrate molecules (used as feed for the production of carboxylic acid by fermentation); while NaCl was taken as a representative of inorganic minerals and salts present in the fermentation broth. The concentration of glucose in the feed was 10 % (w/v); while that of NaCl, it was 0.1 % (w/v). Water was used as a stripping solvent. No transport for either of these molecules could be detected on the permeate side after a continuous circulation of respective feed solution for more than 72 h using PBI-I membranes. This inability of transport of nonacidic solutes could be explained on the basis of membrane type and transport mechanism. Since these membranes are dense in nature (without any induced porosity), transport of these molecules cannot occur based on diffusion through pores. For the transport to occur by solution-diffusion mechanism, sorption of solutes has to occur in the membrane matrix. As given in section 3.3.3.1, there is no sorption of these solutes in PBI matrix. Thus, diffusion and permeability of these molecules through PBI based membranes could not be detected. Moreover, present process works due to concentration gradient as the driving force and external stimuli (e.g. pressure) is not used.

3.3.5. *Acid transport analysis*

The concentration of acid and glucose in the feed was kept as 10 % (w/v) each, while the bath temperature was maintained as 40 °C in order to mimic the parameters usually associated with a fermentation process [Adachi (2003), Vaidya (2005), Wee (2006), Soccol (2006), Rapsor (2008), Vijayakumar (2008), Clark (2009)]. Though PBI membranes do not permeate glucose, it was used as one of the solute in the feed as a marker to confirm membrane integrity. Prior to the transport study, PBI membrane was suspended in the feed solution for 3 days in order to allow sorption of solute (acid) in the membrane matrix. This would help in reducing time lag for the transport process to occur. On the permeate side of the membrane, a solution (water or base) was circulated to strip away transported acid from the membrane surface.

3.3.5.1. *Transport of lactic acid through PBI-I membrane: Effect of stripping agent*

In view of applicability of this process for acid separation from other type of solutes of organic / inorganic in nature, water as a stripping solution is always advantageous so that the acid can directly be concentrated for further use. Unfortunately, with water as a stripping agent, lactic acid transport could not be detected. At the same time, glucose transport was also absent. These observations could be explained based on the solute sorption in the membrane matrix. Lack of glucose transport can be as anticipated based on its nil sorption in PBI (Section 3.3.1). As given in Table 3.3, sorption of LA in PBI-I was 1.06 mol/RU, at similar conditions as that studied for transport investigations (i.e. 10 % bath concentration and temperature of 40 °C). With 1.06 mol/RU as the sorption capacity, all sorbed acid molecules are anticipated to be bound to PBI by acid-base interactions. It is known that acid sorption in PBI occurs by two modes, one is bound and the other is free acid form [Li (2004b)]. Since the amount of sorbed LA is anticipated to be mostly in the bound form, water may not be able to extract the acid from permeate surface of the membrane; even though the membrane matrix has achieved its equilibrium state of sorption. It may be that for the acid transport to occur, stripping agent has to overcome the interactions between the LA and basic benzimidazole of PBI. This may not be possible with water as a stripping agent; resulting

in absence of LA transport. Thus, it was thought to use base solution as a stripping agent; which is anticipated to be stronger than the basicity of PBI (pK_b = 6 [Xing (1999)]).

Table 3.3. Effect of stripping agent on transport of LA through PBI-I based membranes (feed solution: 10 % LA + 10 % glucose, temperature: 40 ºC)

Stripping agent	Average thickness of acid sorbed membrane (µm)	Flux (g/m^2.h)	Permeability (m^2/sec)
Water	32.4	No transport	-
Aq. Na$_2$CO$_3$	47.5	3.92	5.6×10^{-13}
Aq. NaOH	26.4	4.1	3.9×10^{-13}
Aq. Et$_3$N	41.6	7	11.2×10^{-13}
Et$_3$N in Hexane	33.8	No transport	-

As could be seen from Table 3.3, appreciable transport of lactic acid was observed by the use of base solution as a stripping agent. While keeping the feed concentration same (10 % LA + 10 % glucose), acid permeability varied with the use of stripping base solution as NaOH < Na$_2$CO$_3$ < Et$_3$N. Surprisingly, this is opposite to the pK_b value of the bases used (14, 3.7 and 3.25, respectively [Ermakov (1995), Lesch (2005)]). This unexpected behavior could be explained based on the amphoteric nature of PBI. Use of strong base solution as a stripping agent would also lead to the interaction between alkali and PBI (in addition to the anticipated role of base, acting as a stripping agent to remove permeated acid from the membrane surface). This could lead to sorption of alkali in the PBI membrane, as known in the literature. Doping of PBI with bases, *viz.*, NaOH, KOH, LiOH and K$_2$CO$_3$ has been reported in the literature [Xing (2000), Hou (2008)] with appreciable doping levels (0.37 mol/RU for 1 M NaOH for poly(*2,5*-benzimidazole) [Luo (2012)], 0.55 mol/RU for 5 M KOH for poly[*2,2'*-(*4,4'*-diphenylether)-*5,5'*-bibenzimodazole] [Leykin (2009)]. Such sorption of bases in PBI matrix would not only engage PBI (and make it unavailable for acid binding); but also would increase the resistance for the permeation of acid across the PBI-membrane by neutralizing sorbed acid in the membrane matrix itself. This ultimately would result in lower permeability of the lactic acid than anticipated on the basis of basicity of stripping

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agent. To confirm this hypothesis, we analyzed the lactic acid transport while varying the concentration of aq. NaOH used on the stripping side. As could be seen from Fig. 3.4, a reduction in the lactic acid transport with increasing the concentration of stripping solution was indeed observed.
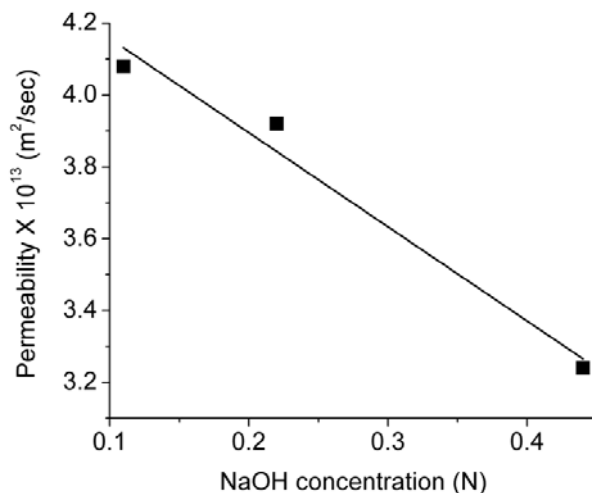
Fig. 3.4. Effect of stripping agent concentration (aq. NaOH) on the transport of LA through PBI-I based membranes, at 40 ºC

In all above cases, transport of glucose was nil (or beyond detection limits of HPLC. Thus, it could be inferred that the selectivity of lactic acid over glucose was very high (though looks infinity in terms of mathematical interpretation). In other words, lactic acid as a co-solute did not lead to any effect in offering glucose permeability. This is highly significant and promising finding in terms of practical applicability of the process.

Use of NaOH or Na_2CO_3 as a stripping leads to conversion of lactic acid into its salt form on the permeate side. Thus, though concentration gradient of the acid is maintained as that of the feed side concentration in order to drive the process, the transported acid into its salt is to be recovered on the permeate side. In order to use this acid for its application (either in food industry or conversion into polylactic acid as summarized in the introduction) the obtained salt needs conversion to the acid form again. The transport of lactic acid with aq. ET_3N as a stripping agent prompted use to use Et_3N in hexane as a stripping agent. Use of Et_3N (boiling point = 89 °C) and hexane (bp

= 69 °C) would be beneficial in terms of easy recovery of lactic acid. Unfortunately, no transport could take place when Et_3N in hexane was used as a stripping agent (Table 3.3). This could be due to the hydrophobic nature of hexane; which would have no interaction with PBI-membrane surface. This needs further investigations (either use of better polar as well as volatile solvent such as dioxane or THF); where phase transfer issues could be better prevalent.

3.3.5.2. Variation in lactic acid transport with temperature

With increase in temperature from 28 to 60 °C, transport of LA through PBI-I based membrane showed a linear increase in permeability from 3.22×10^{-13} to 5.77×10^{-13} m^2/sec (Fig. 3.5). This increase in permeability could be attributed to an increase in the sorption of LA in PBI matrix (Section 3.3.3.2), as well as anticipated increase in the diffusivity with temperature. It is said that increase in temperature can increase the thermal motion of polymer chain and generate more free volume in the polymer matrix to facilitate sorption and diffusion of permeant in membrane [Shieh (1997)]. An increase in transport rate of aq. tetrafluoropropanol is reported with an increase in temperature in case of PBI/PI dual layer hollow fiber membrane, which retains selectivity till ~60 °C [Wang (2007a)].
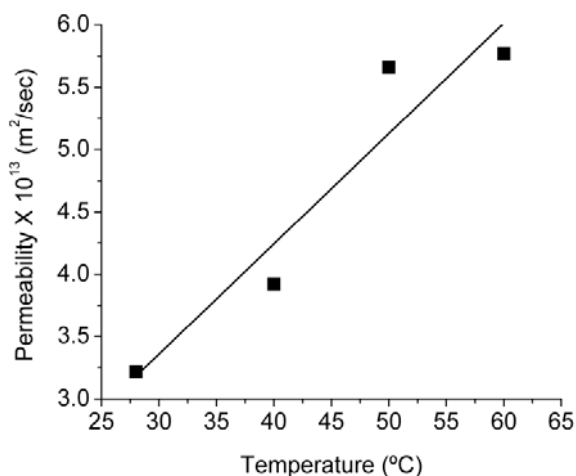
Fig. 3.5. Variations in LA transport with temperature through PBI-I based membranes (feed solution: 10 % LA + 10 % glucose, stripping agent: aq. NaOH)

3.3.5.3. Transport of lactic acid through various PBIs

The structural variation in PBI was found to affect lactic acid permeability in the order: PBI-I < PBI-Py < PBI-BuI (Table 3.4). This increase in the permeability followed the order of LA sorption in these PBIs (Table 3.1). Though acid sorption capacity could be one of the factor governing transport, diffusivity could also get affected due to difference in chain packing density under sorbed state. Thought swelling ratio (Table 3.1) could not be correlated with the observed transport, free volumes of these PBIs in dry state vary in the same order as PBI-I (0.3096 $cm^3.cm^{-3}$) < PBI-Py (0.3226 $cm^3.cm^{-3}$) < PBI-BuI (0.3393 $cm^3.cm^{-3}$) [Kumbharkar (2009)].

Table 3.4. LA transport through different PBI based membranes (stripping agent: 0.22 N aq. NaOH, feed solution: 10 % LA + 10 % glucose, temperature: 40 ºC)

PBI	Average thickness of acid sorbed membrane (µm)	Flux (g/m^2.h)	Permeability (m^2/sec)
PBI-I	26.4	4.1	3.9×10^{-13}
PBI-Py	46.8	6.1	9.1×10^{-13}
PBI-BuI	42.7	8.1	18.5×10^{-13}

3.3.5.4. Transport of other acids

In order to evaluate feasibility of *Chemodialysis* for transporting other industrially significant organic acids, acetic and citric acids (volatile and nonvolatile in nature) were chosen as representatives and their transport characteristics through PBI-I based membrane were determined as shown in Table 3.5.

Table 3.5. Transport of organic acids through PBI-I based membrane (feed solution: 10 % acid + 10 % glucose, temperature: 40 °C)

Acid	Stripping agent	Average thickness of acid sorbed membrane (µm)	Flux (g/m^2.h)	Permeability (m^2/sec)
AA	Aq. NaOH	19.8	35.1	113.4×10^{-13}
	Water	51.4	2.1	3.3×10^{-13}
LA	Aq. NaOH	26.4	4.1	3.9×10^{-13}
CA	Aq. NaOH	37.1	2.6	3.0×10^{-13}

Permeabilities for acids with aq. NaOH as a stripping agent were increased as: citric acid < lactic acid < acetic acid; which followed the same order as that of amount of acid sorbed (Table 3.2). Moreover, molecular size for these acids decrease in the same order (citric acid > lactic acid > acetic acid. Van der Waal volumes of these acids calculated by group contribution method are 30.21, 40.03 and 81.39, respectively [Van Krevlin (1997)]). Thus, in addition to sorption characteristics, size of the transporting acid also could be contributing to transport properties.

With water as a stripping agent, through lactic and citric acid transport could not be observed, acetic acid exhibited some transport (permeability = 3.3×10^{-13} m^2/sec); which is considerably lower than its flux when 1.33 M NaOH was used as the stripping agent. This could be correlated to acid sorption, in a same way, as explained above in section 3.3.4.1. Acetic acid show higher sorption of 2.14 mol/RU than its bound acid capacity of ~ 2 mol/RU [Li (2004b)]. Thus, a small excess of unbound acid molecules lead to AA transport through PBI membranes, even with water as a stripping agent. Leaching of unbound acid (H_3PO_4) from PBI matrix by water is known in the literature [Leykin (2010)].

3.4.   Conclusions

The PBI based membranes showed appreciable transport for various organic acids (e.g. acetic acid, lactic acid and citric acid). Transport was dependent upon various factors like, acid properties, stripping agent used, properties of the PBIs used for membrane preparation and other operational parameters like concentration of acid in feed, stripping agent, temperature, etc. Additionally, there was no transport for non-acidic molecules like, salt (NaCl), organic molecules (glucose) or bases; leading to practically infinite selectivity for acid transport. The acid transport was dependent upon its sorption in membrane, followed by permeation across the membrane by concentration gradient as a driving force. It does not require any external force for the transport, only energy is required for the circulation of solutions on either side of the membranes. Thus this method is highly energy efficient. It can be operated in combination with the fermentor and can be used for the continuous production of acids. This can reduce the number of stages required during separation of acid from fermentation broth by

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conventional method. Moreover, the fermentation can be operated continuously enhancing acid production and reducing the requirement of nutrients and minerals. It would reduce nutrient losses and avoid sludge generation during the separation of acid by conventional methods.

Though the transport was seen for different acids, these membranes require base as stripping agent for appreciable transport rate. The use of base solution leads to formation of salt which needs further treatment for the regeneration of acid, before use in further applications. This would not be advisable in terms of economical and environmental aspects. The transport rates with water as stripping were either low (for acetic acid) or nil (for lactic and citric acid). Hence, we thought, an introduction of molecular level porosity in the membrane would assist to overcome these issues. Hence further work is planned to introduce a molecular level porosity in the PBI based membranes by preparation of porogen derived membranes.

Chapter 4

Chemodialysis: Flux enhancement through polybenzimidazole based membranes using porogen concept

4.1. Introduction

Structural variations in PBI, as discussed in Chapter 3 though led to highly promising results in terms of offering high selectivity of acidic solutes over nonacid ones, the transport rate was either low (for acetic acid) or absent (for lactic and citric acid). Moreover, with base as a stripping agent, the permeated acid is obtained in its salt form. This necessitates its back conversion to acid form for the practical applicability. Since acetic acid transport was feasible with water as a stripping agent, acid sorption capability of the membrane matrix was concluded as the major controlling factor towards acid transport [Chapter 3]. In order to enhance acid sorption, we thought to generate molecular level porosity in the membrane matrix. The porosity needs to be small enough so that other neutral molecules such as sugars or salts (usually encountered with the acid production by fermentation) should not pass through the membrane. One of the most feasible options to generate such small porosity is use of porogen derived membranes (PDM); rather than through pores; which would have a threat of loosing selectivity. In PDMs, the pore connectivity though is absent; their solute sorption capacity is considerably elevated.

Various types of porogens are demonstrated in the literature including organic molecules (e.g. esters, glycerol and formic acid ester, triphenyl phosphate, surfactants [Mecerreyes (2004), Shen (2011), Wang (2012), Zheng (2010), Eyal (1992a), Eyal (1992b)], etc.); inorganic molecules (e.g. silica, alumina, NaCl, NaHCO$_3$, etc.) [Feng (2007), Freitas (2004), Gumusderelioglu (2004), Liu (2003), Yu (2008), Zhou (2008)]) and polymers (e.g. polyimide, polyethylene glycol, polypropylene glycol [Ding (2010), Yang (2002), Xi (2006), Zeng (2004), Nikpour (1999)]. These porogens are removed from polymer matrix by various methods such as dissolution in solvent [Nikpour (1999), Yu (2008), Zhao (2009), Zheng (2010)], treatment with acid [Zhou (2008)] or base [Feng (2007), Rukenstein (1997), Yang (2002), Zeng (1996)]), thermal treatment [Mecerreyes

(2004), Heo (2006)]; etc. Formed PDMs were reported to offer voids or pores of 2.45 nm to 100 μm size, depending upon host polymer, porogen used and their composition [Freitas (2004), Heo (2006), Nikpour (1999), Rukenstein (1997)]. They lead to considerable enhancement in the sorption and permeation properties. For example, In case of PBI based membranes, H_3PO_4 doping level increased from 132 % to 439 % using 70 % triphenyl phosphate as porogen [Mecerreyes (2004)]. PBI based PDMs are demonstrated using dialkyl/diphenyl phthalates and triphenyl phosphate as porogen, which are leached out using methanol/toluene or thermal evaporation (at 200 °C) [Mecerreyes (2004), Shen (2011), Wang (2012)]. Formed PDMs contained pores with varying sizes (from 100 nm to 15 μm), depending upon porogen content. A possibility of aggregation (resulting in formation of pores with varying sizes) or incomplete removal of porogens is known [Mecerreyes (2004), Heo (2006)]. It is said that miscible polymer blends offer potential for the fabrication of porous polymer films by selectively removing one of the components [Ding (2010)].

Since PBI is known to form miscible blends with polyester [Chung (1990a), Chung (1990b)], we thought to use a polymer of this family, *viz*.; poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen, which can be degraded in alkaline conditions. It could be anticipated that the one of the component of a perfect blend if could be removed selectively, it would lead to porosity without creating large voids. This way, the selectivity of acid transport through PBI based membrane by chemodialysis can be retained (since large voids could be absent). Various PDMs were prepared by using two PBIs (PBI-I and PBI-BuI) based on a tetramine; *3,3'*-diaminobenzidine (DAB) polymerized with isophthalic acid (IPA) or *5-tert*-butylisophthalic acid (BuI), respectively. Prepared PDMs were investigated for physical properties, sorption and transport characteristics of various organic acids and glucose and NaCl as a representative of small neutral molecules (non-acidic co-solutes).

4.2. Experimental

4.2.1. Materials

3,3'-Diaminobenzidine (DAB), isophthalic acid (IPA), *5-tert*-butylisophthalic acid (BuI), isophthaloyl chloride (IPC), terephthaloyl chloride (TPC) and

benzyltriethylammonium chloride (BTEAC) were procured from Aldrich Chemicals. Phenolphthalein was procured from Loba Chemie. Polyphosphoric acid (PPA, ca. 84 % as P_2O_5) was procured from Alfa Aesar. *D*-Glucose was procured from Qualigens Fine Chemicals. Dichloromethane (DCM), *N,N*-dimethyl acetamide (DMAc), hexane, ethanol, acetone, chloroform, *1,1,2,2*-tetrachloroethane (TCE), NaCl, NaOH, H_2SO_4, lactic acid (90 % aq. solution), acetic acid, citric acid, maleic acid, fumaric acid, succinic acid, malic acid, *3,5*-dinitrosalicylic acid (DNSA) and $CaCl_2$ (all GR/extrapure grade) were obtained from Merck. Recrystalization of IPC, TPC (using hexane) and phenolphthalein (using ethanol) was done prior to use; while other chemicals were used without further purification.

4.2.2. *Synthesis of polymers*

Two PBIs (PBI-I and PBI-BuI) based on DAB and a dicarboxylic acid (IPA or BuI, respectively) were synthesized by solution polycondensation using PPA as a solvent and purified as discussed in Chapter 3.

The polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) was synthesized by interfacial polycondensation as reported earlier [Charati (1991)]. Typically, a three-neck round bottom flask equipped with a mechanical stirrer was charged with 40 g (0.1257 mol) of phenolphthalein dissolved in 110 ml aqueous solution of NaOH (10.3 g, 0.2572 mol). A 0.7061 g (0.0031 mol) of BTEAC and 177 ml of DCM were added to the reaction mixture and stirred at 2000 rpm. A solution containing 13.01 g (0.0641 mol) each of IPC and TPC dissolved in 200 ml of DCM was added drop wise while stirring. The solution was further stirred for an hour. The polymer was obtained by precipitating organic phase in acetone while stirring. It was collected by filtration and dried in an oven at 60 °C for a day. It was further purified by dissolving in $CHCl_3$ and precipitating in stirred acetone and finally dried at 60 °C under vacuum for 2 days. Structure and abbreviation of monomers and Ppha-IT are given in Scheme 4.1.
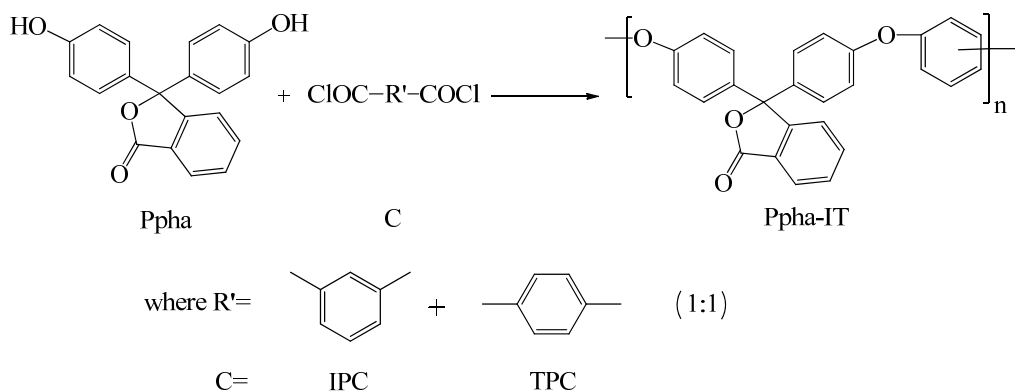
Scheme 4.1. Structure and abbreviation of monomers and polyester poly(phenolphthalein iso-terephthalate) (Ppha-IT)

4.2.3. Membrane preparation

The dense membranes of PBI-I, PBI-BuI and Ppha-IT were prepared by solution casting method. In the case of PBIs, 2 % (w/v) DMAc solution was poured on a flat glass surface and the solvent was evaporated at 80 °C for 18 h under dry atmosphere. Formed membranes were peeled off from the glass plate and immersed in water at 60 °C for 3 days and then dried under vacuum at 100 °C for a week in order to remove traces of solvents. The Ppha-IT based dense membranes were prepared by pouring its 2 % (w/v) solution in Ppha-IT onto a flat glass surface, evaporating solvent at 40 °C under dry atmosphere (8 h), peeling off the formed film, followed by vacuum dying at 60°C for a week. Prepared membranes were preserved in the desiccator until use.

The blend premembranes based on PBI-I and PBI-BuI with Ppha-IT (25, 35, 50, 60 and 75 w/w %) were prepared by solution casting method using 2 % (w/v) polymer solution in DMAc. The solution was poured on a flat glass surface and solvent was evaporated at 80 °C for 18 h under dry conditions. Formed premembranes were peeled off from the glass plate and kept in water (60 °C, 3 days) and finally dried in a vacuum oven at 100 °C for a week. These premembranes were treated with 5 % aq. NaOH bath at 60 °C for 20 days for the hydrolysis and leaching of Ppha-IT in the bath solution. Repeated water wash removed residual degradation products and NaOH and offered 'porogen derived membranes' (PDMs). These PDMs based on the premembranes containing PBI-I with Ppha-IT (25, 35, 50, 60 and 75 wt. %) were designated as PBI-I$_1$,

PBI-I$_2$, PBI-I$_3$, PBI-I$_4$ and PBI-I$_5$, respectively; while those based on PBI-BuI with Ppha-IT (25, 35, 50, 60 and 75 wt. %) were designated as PBI-BuI$_1$, PBI-BuI$_2$, PBI-BuI$_3$, PBI-BuI$_4$ and PBI-BuI$_5$, respectively (Table 4.1). These PDMs were preserved in water at 4 °C, till further use.

4.2.4. *Physical property analyses*

Inherent viscosity (IV) of the synthesized PBIs was determined using 0.2 g/dL solution in concentrated H$_2$SO$_4$ at 35 °C. The intrinsic viscosity of Ppha-IT was measured using its different concentration solutions (0.05, 0.2, 0.4 and 0.5 %, w/v) in TCE, by using Ubbelohde viscometer. Thin films (~12 μm thickness) of PBI-I, PBI-BuI, Ppha-IT, composite premembranes and formed PDMs were analyzed by Fourier transfer infrared (FT-IR) spectra (recorded on Perkin Elmer-16-PC FT-IR spectrophotometer) (Fig. 4.1). The membranes of PBI-I, PBI-BuI, Ppha-IT and composite premembranes were characterized by thermogravimetric analysis, as described in Chapter 3 (Fig. 4.2). They were also characterized in the film form by wide angle X-ray diffraction (WAXD) spectra, recorded using Rigaku X-ray diffractometer (D-max 2500) with Cu-Kα radiation in 2θ range of 4-40° (Fig. 4.5). Average *d*-spacing (*d$_{sp}$*) was calculated from the amorphous peak maxima, using Bragg's equation ($n\lambda = 2d.sin\theta$, where $\lambda = 1.5418$ Å) (Fig. 4.6). Scanning electron microscopic (SEM) images of membrane surface were recorded on FEI QUANTA 200 3D, for the premembranes and formed PDMs (Fig. 4.4, 4.8). Mechanical properties (tensile tests) of the dried PDMs in the film form ($2 \times 0.6 \times 0.004$ cm^3 size) were analyzed at the ambient temperature on Linkman TST-350 microtensile testing instrument operated at a speed of 100 μm/sec.

4.2.5. *Leaching analysis and porosity determination*

Pre-weighed membrane samples membranes were placed in a beaker containing aq. NaOH solution and kept in thermostated shaker at 60 °C. Change in the weight of membrane samples with time was recorded. After attaining constant weight, they were repeatedly washed with distilled water, till neutral to pH. Their weight and size were measured. The reduction in weight (%) was calculated by Eq. 1 and reduction in volume (%) was calculated by Eq. 2.

$$\% \text{ Weight reduction } = \frac{w_i - w_f}{w_i} \times 100 \tag{1}$$

where; w_i and w_f are weights of sample before and after leaching, respectively.

$$\% \text{ Volume reduction } = \frac{v_i - v_f}{v_i} \times 100 \tag{2}$$

where, v_i and v_f are the volumes of samples before and after leaching of Ppha-IT, respectively. The obtained values are given in Table 4.1.

Degradation of Ppha-IT dense membranes was investigated using varying concentration of aq. NaOH (1, 2.5 and 5 %, w/v) at 60 °C. Variation in weight loss (%) with time was as plotted in Fig. 4.7. Leaching of porogen from PBI-I and PBI-BuI based premembranes with varying concentration of Ppha-IT was investigated with 5 % aq. NaOH at 60 °C. Obtained PDM samples were further dried at 100 °C under vacuum for a week and the variation in weight and volume were measured (Table 4.1). Difference in weight and volume of these membranes in wet and dry conditions was used to determine the percent porosity of formed PDMs, by Eq. 3 [Yang (2002), Freitas (2004), Tang (2009)], and are given in Table 4.1.

$$\% \text{ Porosity } = \frac{(w_2 - w_1)}{(v_1 \cdot \rho_w)} \times 100 \tag{3}$$

where; w_1 and w_2 are weights of membrane samples before and after drying, v_1 is the volume of membrane sample before drying and ρ_w is the density of water at 60 °C (0.9832 g/cm^3).

4.2.6. Sorption studies

PDM (PBI-I$_3$) was investigated for the sorption of lactic acid at different bath concentrations (1, 3, 5, 7, 10 and 12 %, w/v) at 30 and 40 °C to investigate the effect of temperature, as described in Chapter 3. Acid uptake in the membrane per PBI repeat unit (RU) was determined from the difference between bath concentrations before and after sorption (Eq. 4) and given in (Fig. 4.9).

$$\text{Acid uptake in PDM} \left(\frac{mol}{RU \text{ of } PBI \text{ in } PDM} \right) = \frac{(M_1 - M_2)}{N} \tag{4}$$

where; M_1 and M_2 are the number of moles of acid present in bath before and after sorption, respectively, N is the number of moles of PBI repeat units present in the PDM sample.

4.2.7. Acid transport investigations

Transport of organic acids (lactic, acetic, citric, maleic, fumaric, succinic and malic acid) was investigated with equal amount (by wt.) of glucose as a co-solute through these PDMs. PDMs preconditioned with feed solution for 72 h were mounted in a plate and frame module and investigated for acid transport, as discussed in details in Chapter 3. Water or aq. NaOH was used as stripping agent, during the investigations. Lactic acid transport at 10 % (w/v) feed concentration was investigated at varying temperatures, *viz.*, 30, 40, 50, 60 and 70 °C; while for all the other acids it was studied at 40 °C. These membranes were also investigated for the transport of NaCl (0.1 %, w/v) and NaOH (1 N), using water as a stripping agent. Concentration of NaOH was measured by titration, while variation in conductivity was used to measure the NaCl concentration. Conductivity was monitored by inserting a conductivity probe in the permeate side solution reservoir. Flux and permeability was calculated as discussed in Chapter 3, and the values are presented in Table 4.2-4.5 and Fig. 4.10, 4.11.

4.3. Results and discussion

4.3.1. Physical characteristics of synthesized polymers

The PBIs (PBI-I and PBI-BuI were synthesized and obtained polymer was purified by reprecipitation, which was necessary to obtain soluble polymer for membrane preparation, as discussed earlier [Chapter 3]. All the properties (FT-IR and TGA) of these PBIs almost match with the same reported earlier [Kumbharkar (2006), Kumbharkar (2009)], which conform the formation of PBI-I and PBI-BuI.

FT-IR spectra of Ppha-IT showed a twin band corresponding to ester group at ~1775 and 1746 cm^{-1} and ether linkage band at 1206 cm^{-1} (Fig. 4.1). These ester group vibrations could be a sign of the formation of polyester, while ether linkage band was originated from phenolphthalein. The WAXD spectra of Ppha-IT showed a single peak with average d_{sp} of 5.12 Å, while its IDT was 460 °C.

4.3.2. *Use of PBI as base and Ppha-IT as porogen*

In the current investigations, the porogen derived membranes (PDMs) were prepared using PBI-I and PBI-BuI as a base material. Aromatic polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) synthesized as discussed in section 4.2.2 was chosen as a porogen. It was though that, the use of polymeric porogen compatible with base polymer would lead to the formation of co-continuous and uniform porosity. The compatibility of PBI and aromatic polyesters (Ardel and Durel) is known in literature [Chung (1989), Chung (1990a), Chung (1990b)]. Other properties required are good solubility in the casting solvent, stability at the casting temperature and easy leaching by a suitable method. Ppha-IT has excellent solubility in DMAc, (which is the solvent for PBI as well) and has good high thermal stability (IDT = 460 °C). Thus it can be used in membrane preparation by solution casting method using DMAc as a solvent at higher temperature. Additionally, Ppha-IT is highly susceptible to alkaline conditions and can be easily hydrolyzed in contact with alkali solution. This property would help in the degradation and leaching of Ppha-IT from PBI based membranes. Besides, the sorption of strong alkali in PBI is reported in literature [Xing (2000), Hou (2008)], which would assist this leaching of porogen.

4.3.3. *Formation of blend premembranes*

The blends of PBI (PBI-I or PBI-BuI) containing varying concentrations of Ppha-IT (25, 35, 50, 60 or 75 %, w/w) prepared as discussed in section 4.2.3 were used as premembranes for the formation of PDMs. They were transparent with light brown in color. These premembranes were characterized by FT-IR, TGA, SEM and WAXD to analyze blend compatibility. In case of PBI-I based premembranes (PBI-I$_1$, PBI-I$_2$ and PBI-I$_3$); IR spectra showed merging of the signals at 1775 and 1746 cm^{-1} of Ppha-IT to a single band at ~1747 cm^{-1}. The signal at 1208 cm^{-1} was broadened in PBI-I$_2$ and PBI-I$_3$ premembranes at same position, while it was shifted to 1218 cm^{-1} along with broadening for PBI-I$_1$ premembrane (Fig. 4.1a).
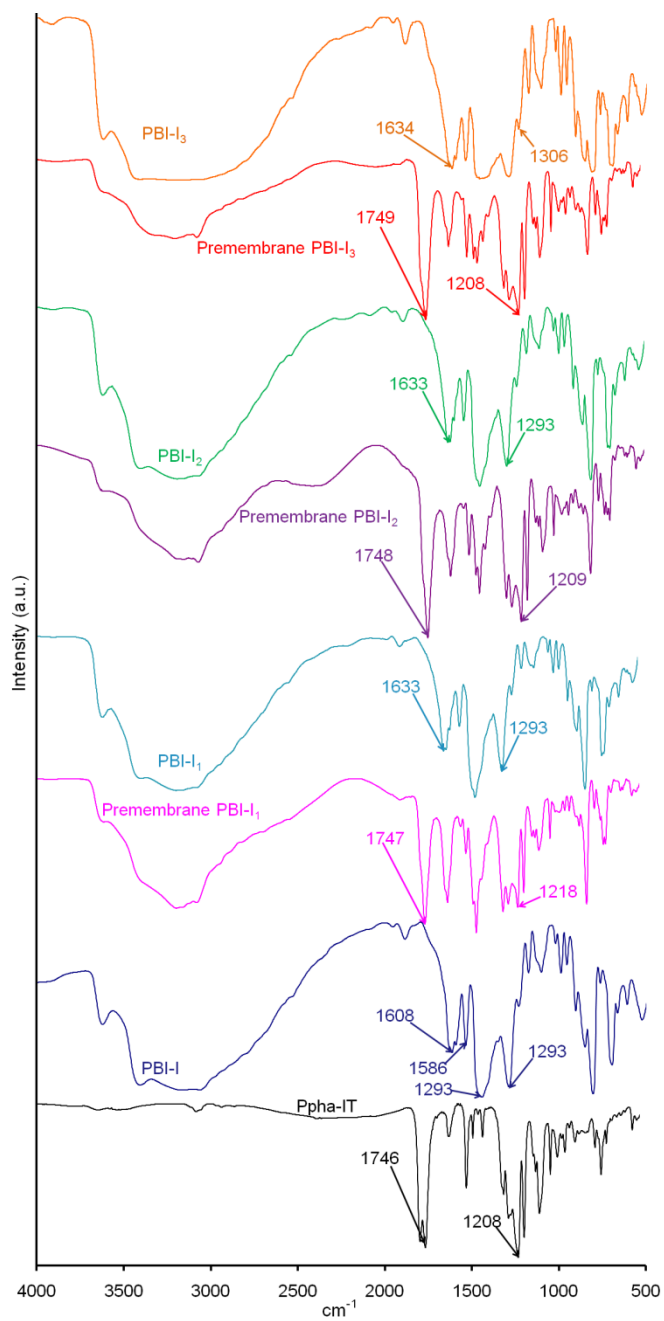
Fig. 4.1a. FT-IR spectra of PBI-I, Ppha-IT, premembrane PBI-I$_1$, premembrane PBI-I$_2$, premembrane PBI-I$_3$ and the dried PDMs base on them
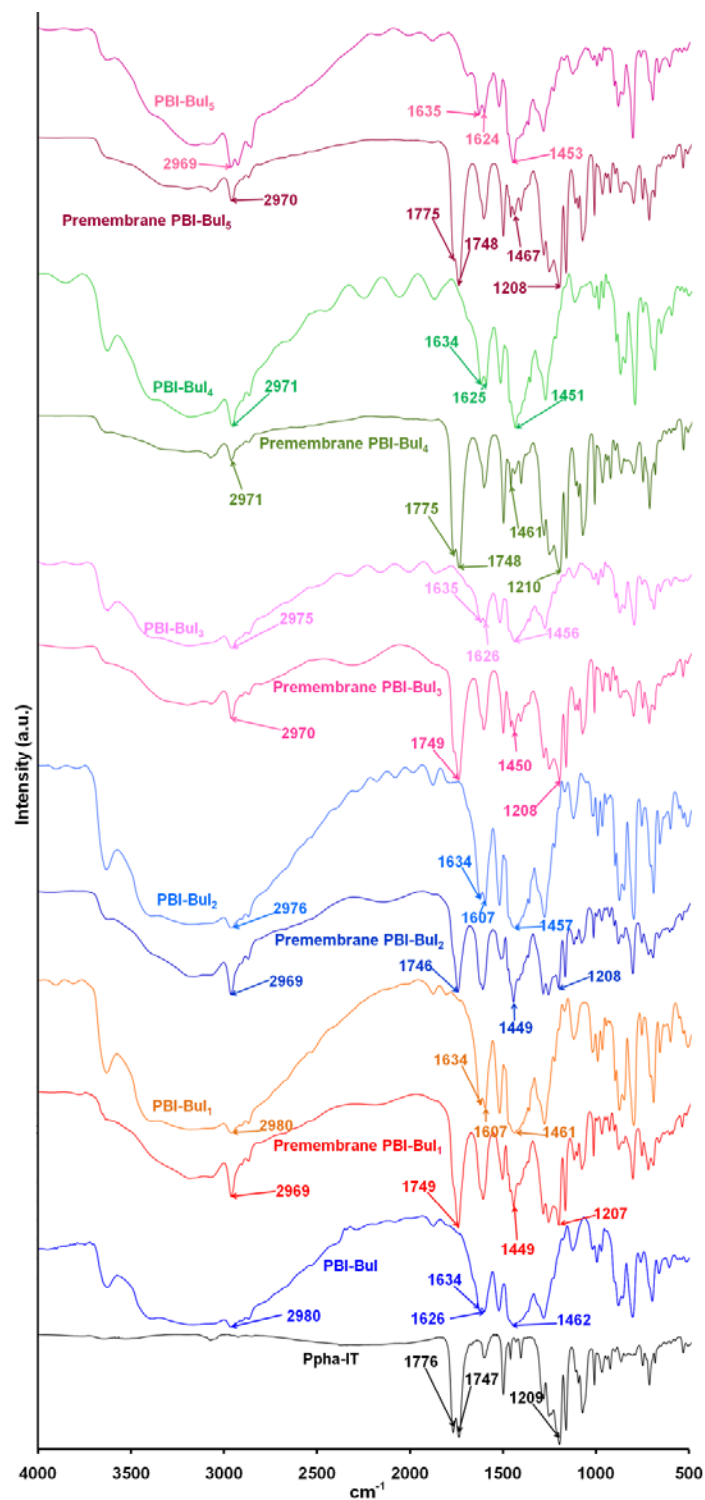
Fig. 4.1b. FT-IR spectra of PBI-BuI, Ppha-IT, premembrane PBI-BuI$_1$, premembrane PBI-BuI$_2$, premembrane PBI-BuI$_3$ premembrane PBI-BuI$_4$, premembrane PBI-BuI$_5$ and dried PDMs based on them

The PBI-I$_4$ and PBI-I$_5$ premembranes containing 60 and 75 % of Ppha-IT could not be analyzed for FT-IR, due to their brittle nature. IR spectra of PBI-BuI based premembranes showed merging of signals at 1776 and 1747 cm^{-1} to a single band at ~1760 cm^{-1}, for all the compositions. They showed a variation in intensity and shapes of bands in the region of 1286-1211 cm^{-1} (Fig. 4.1b). The bands at ~1634 and 1626 cm^{-1} related to C=C and C=N stretching of PBI-BuI were merged to a single band at ~1614 cm^{-1} in these premembranes. This broadening of signal and shifting in band position could be due to closely mixed molecular chains of both the polymers. It would give rise to strong intermolecular interactions and change molecular environment, resulting in broadening of signals and shifting of band positions. Shifting of IR bands for miscible PBI and polyarylate blend is reported earlier [Chung (1990a), Chung (1990b)]. The shifting and broadening of IR bands is reported as a sign of miscible formation for different polymer blends, e.g. polypropylene-polybutylene terephthalate, sodium alginate-hydroxypropyl methyl cellulose [Sun (2009), Swami (2009)].

TGA of PBI based premembranes showed a gradual increase in char yield with decrease in Ppha-IT content of the film (Fig. 4.2). TGA spectra of PBI-I and PBI-BuI based membranes showed a linear increase in weight loss at 550 °C (taken as reference) from PBI to Ppha-IT with increase in porogen content (Fig. 4.3). Increase in the stability of Ppha-IT could be due to the intermolecular interactions between blend components, which would arise from their molecular level compatibility. A linear increase in weight loss at 550 °C with the increase in polyarylate (Ardel or Durel) content of PBI-polyarylate blend has been reported as a sign of molecular level compatibility [Chung (1990a)].

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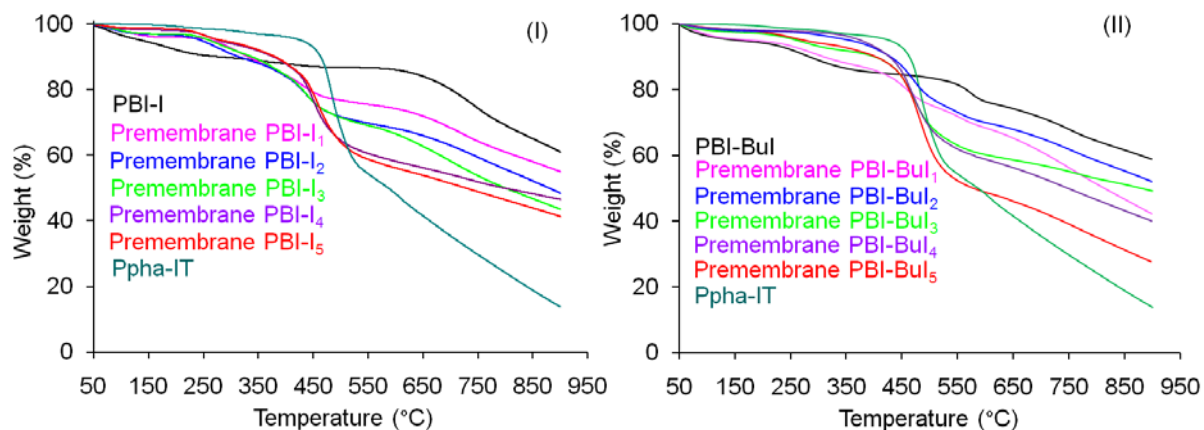
Fig. 4.2. Variation in TGA spectra with composition of the membranes of PBI, Ppha-IT and PBI + Ppha-IT (25, 35, 50, 60 or 75 %) based premembranes, where (I): with PBI-I as base material and (II): PBI-BuI as base material
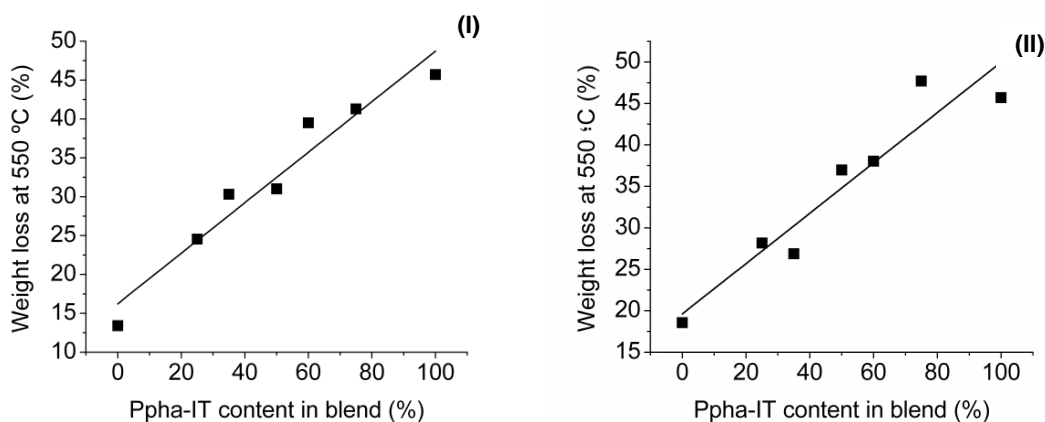
Fig. 4.3. Variation in weight loss at 550 °C during TGA analysis of PBI, Ppha-IT and PBI + Ppha-IT (25, 35, 50, 60 or 75 %) based premembranes, where (I): PBI-I as base material and (II): PBI-BuI as base material

SEM analysis of the PBI (PBI-I and PBI-BuI) based premembranes showed plane surface without any abnormal structures or phase separation (Fig. 4.4). This indicated miscibility between the blend components, which results in the formation of homogeneous film. The compatible blends of PBI with Torlon® or poly(styrene sulfonic acid) showing homogeneous plane surface without any phase separation are reported, earlier [Wang (2007b), Acar (2010)].
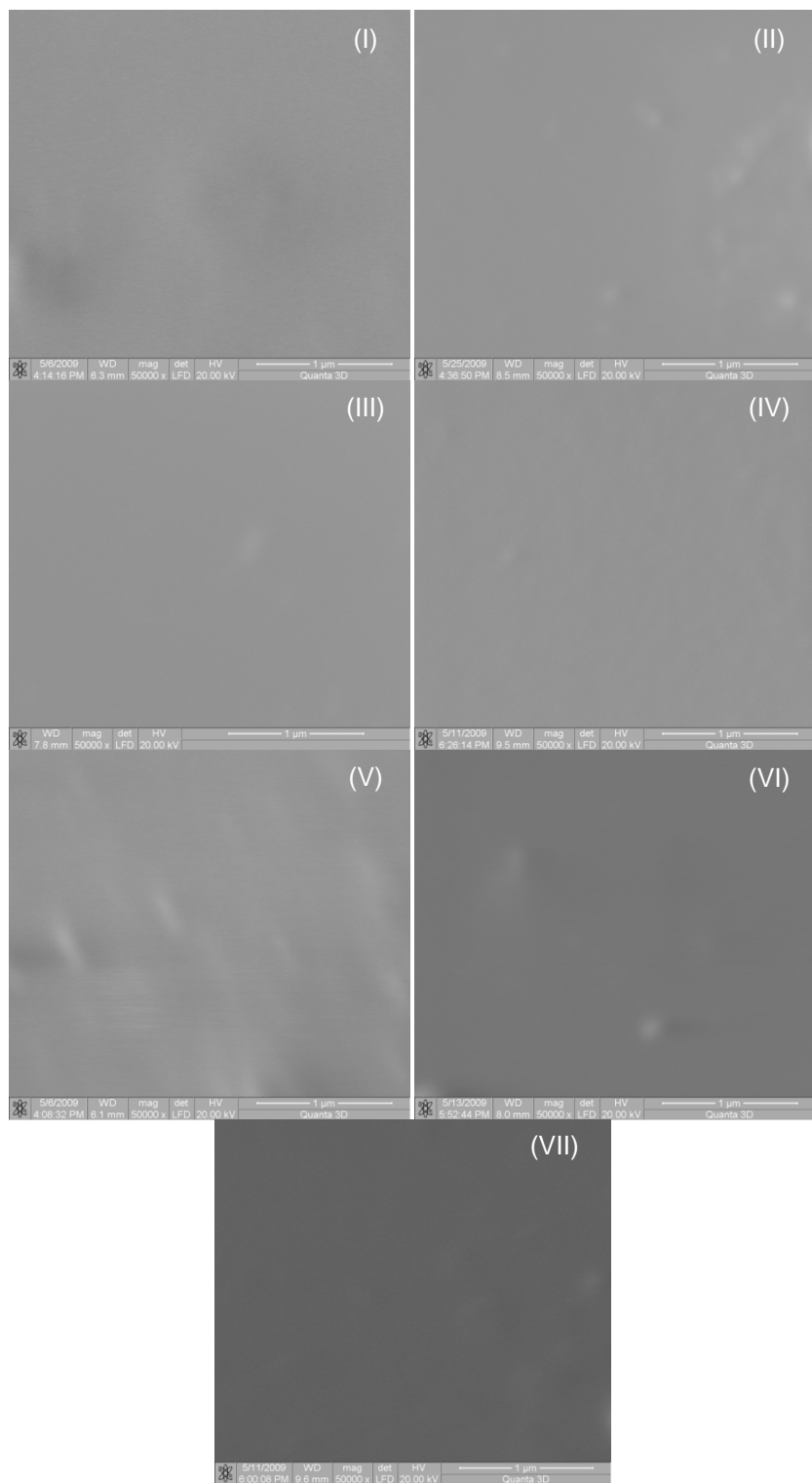
Fig. 4.4a. SEM images of PBI-I based membranes, where (I): PBI-I, (II): premembrane PBI-I$_1$, (III): premembrane PBI-I$_2$, (IV): premembrane PBI-I$_3$, (V): premembrane PBI-I$_4$, (VI): premembrane PBI-I$_5$, (VII): Ppha-IT
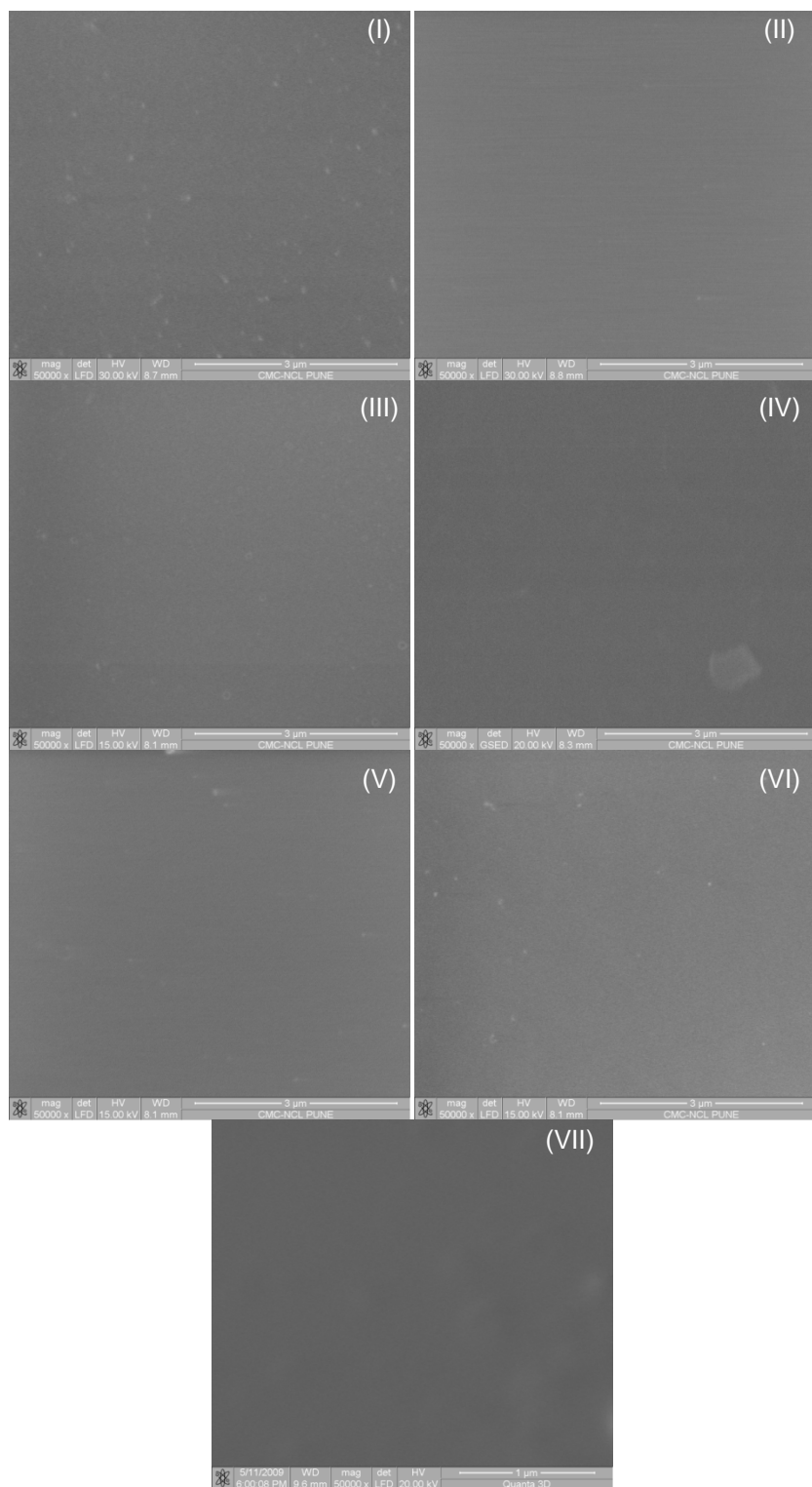
Fig. 4.4b. SEM Images of PBI-BuI based membranes, where (I): PBI-BuI, (II): premembrane PBI-BuI$_1$, (III): premembrane PBI-BuI$_2$, (IV): premembrane PBI-BuI$_3$, (V): premembrane PBI-BuI$_4$, (VI): premembrane PBI-BuI$_5$, (VII): Ppha-IT

WAXD pattern of PBI-I based blend premembranes showed single peak maxima for all compositions (Fig. 4.5). Their *d*-spacing was increased exponentially from PBI-I to Ppha-IT, with increase in the Ppha-IT content (Fig. 4.6).
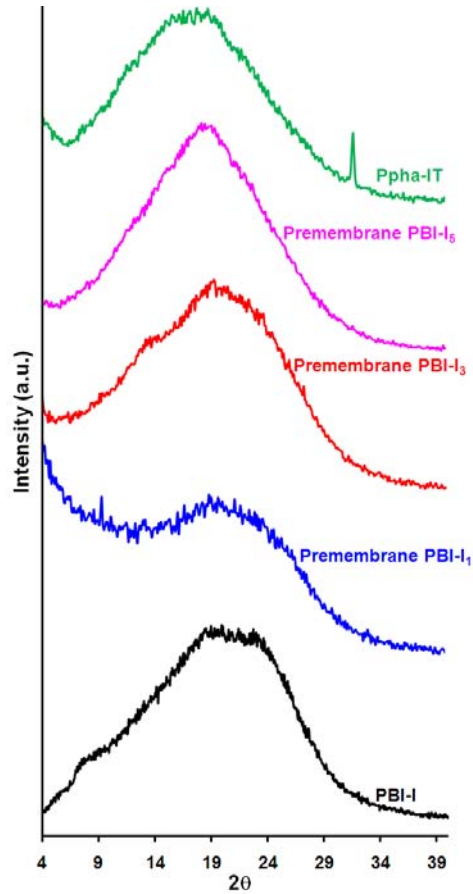
Fig. 4.5. Variation in XRD spectra with membrane composition from PBI-I to Ppha-IT
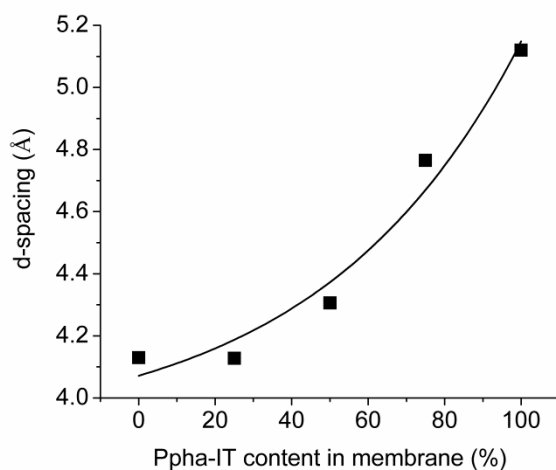
Fig. 4.6. Effect of Ppha-IT and PBI-I content on the d-spacing of membranes

This occurrence of single amorphous hollow rather than separate peaks for different domains could be ascribed to the orientation in X-ray pattern, which arises from the molecular level miscibility of blend components. Orientation in the X-ray pattern is reported for the blend of high molecular weight polyethylene and nylon 12 after addition of compatibilizer maleic anhydride [Sato (2005)]. All these characters (IR, SEM, TGA and WAXD) indicated towards formation of compatible blend between PBI (PBI-I/PBI-BuI) and Ppha-IT for all the compositions (Ppha-IT content = 25, 35, 50, 60 and 75 %).

4.3.4. *Formation of PDM by leaching of Ppha-IT*

4.3.4.1. *Alkali degradation of Ppha-IT*

For preparation of PDMs, the degradation and leaching of Ppha-IT from premembranes was necessary. Hence, we investigated the hydrolysis and degradation of Ppha-IT in dense membrane form to find the favorable conditions for its leaching from premembranes. These membranes were stable in water at 60 °C, without any reduction in weight for 8 days. Hence further investigations were carried out using aq. NaOH. The Ppha-IT membranes showed an increase in weight reduction with increase in NaOH concentration as, $1 < 2.5 < 5$ %, at 60 °C (Fig. 4.7).
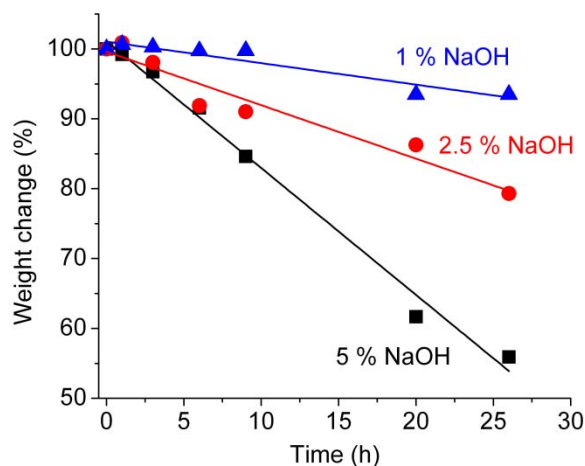
Fig. 4.7. Effect of concentration of aq. NaOH on the degradation of Ppha-IT, at 60 °C

At higher alkali concentration the frequency of OH⁻ attack on polyester would increase. It would lead to higher chain scission resulting in the sodium salts of phenolphthalein and dicarboxylic acids. They would dissolve in the alkali solution used for hydrolysis, resulting in higher rate of Ppha-IT degradation. An increase in polyester degradation with increase in the alkali concentration is reported in literature [Dave (1987), Jung (2006)]. The weight of Ppha-IT membranes was reduced by ~45 % within 26 h, in contact with 5 % NaOH solution. These conditions (5 % NaOH at 60 °C) were used for degradation and leaching of Ppha-IT from premembrane matrix to form PDMs.

4.3.4.2. *Leaching of Ppha-IT from PBI based premembrane*

Hydrolysis of Ppha-IT and leaching of degradation products from the premembranes showed increase in weight loss and volume reduction with increase in premembrane porogen content, till PBI-I$_3$ premembrane (with 50 % Ppha-IT) or PBI-BuI$_4$ premembrane (60 % Ppha-IT content) (Table 4.1). The reduction in weight after NaOH treatment and water wash was lower than premembrane Ppha-IT content (Table 4.1). This reduction in weight was due to the removal of porogen from the premembrane. The difference between weight loss and premembrane Ppha-IT content could be due to the loss of sorbed water in thus formed PDMs. The PBI is known to sorb large quantities of water [Kumbharkar (2009)].

Table 4.1. Leaching of PBI based premembranes using 5 % aq. NaOH at 60 ºC

Premembrane composition	PDM designation	Leaching analysis (% reduction)				Porosity of PDM (%)
		Wet condition		Dry condition		
		Weight	Volume	Weight	Volume	
PBI-I (75 %) + Ppha-IT (25 %)	PBI-I$_1$	11.3	6.7	37.0	29.1	37.6
PBI-I (65 %) + Ppha-IT (35 %)	PBI-I$_2$	21.0	18.4	48.4	44.5	43.8
PBI-I (50 %) + Ppha-IT (50 %)	PBI-I$_3$	31.1	31.0	59.6	60.0	54.4
PBI-BuI (75 %) + Ppha-IT (25 %)	PBI-BuI$_1$	-1.4	-2.2	27.0	19.7	33.4
PBI-BuI (65 %) + Ppha-IT (35 %)	PBI-BuI$_2$	10.7	3.4	36.2	31.4	31.9
PBI-BuI (50 %) + Ppha-IT (50 %)	PBI-BuI$_3$	19.8	8.6	49.7	40.3	42.4
PBI-BuI (40 %) + Ppha-IT (60 %)	PBI-BuI$_4$	24.4	14.3	60.3	52.0	50.7
PBI-BuI (25 %) + Ppha-IT (75 %)	PBI-BuI$_5$	36.4	21.9	72.6	36.2	58.2

As seen from Table 4.1, the volume of membrane was reduced during the hydrolysis and leaching of porogen. This reduction in volume could be due to the rearrangement in PBI matrix during hydrolysis and leaching of porogen. Removal of porogen from membrane would result in the formation of pores equivalent to their molecular size. A uniformly dispersed porogen in the membrane bulk would generate a large free volume in the polymer matrix, after it has been leached out. Assuming a total free volume of few percent in the form of discrete pores, the corresponding internal surfaces would be several hundred m^2/cm^3 of the membrane [Baniel (1990)]. A possibility of rearrangement in the membrane matrix during the leaching of porogen by chemical degradation is reported [Baniel (1990)]. This is happening in the present case only when the membranes are dried. This rearrangement would result in a reduction in membrane volume. A contraction of polysulfone based membranes during the leaching of porogen by chemical degradation is reported in literature [Baniel (1990)].

The PDMs PBI-BuI$_4$ and PBI-BuI$_5$ showed an opaque structure. It could be due to the incomplete leaching and presence of residual degradation products in the membrane matrix. Higher premembrane Ppha-IT content (60 and 75 %) would result in very large surface porosity during initial stages of leaching. This would result in unstable

structure and lead to the collapse of pores or rearrangement in the membrane matrix. It would affect further leaching of the degradation products, resulting in their incomplete leaching. Leaching of Ppha-IT from PBI-I$_4$ and PBI-I$_5$ premembranes (containing 60 and 75 % porogen) content could not be studied, due to unstable membranes which were cracked during leaching analysis.

4.3.4.3. *PDMs characterization*

Drying of the PBI (PBI-I and PBI-BuI) based PDMs at 100 °C under vacuum showed a total weight loss almost equal to their premembrane porogen content (Table 4.1). This indicated a complete removal of Ppha-IT from the membranes. The reduction in weight from wet to dried membranes is attributable to the loss of water from the PDMs. Drying of these PDMs also showed a reduction in volume. The reduction in volume from premembrane to dry PDM was almost equal to its porogen content. It could be due to rearrangement in membrane during the drying of formed PDM. In wet condition, water in these PDMs is hold due to H-bonding interactions, originated by host PBI matrix. Loss of this water during drying of the PDMs result in membrane matrix similar to the dense membrane. This can be called as an ultimate rearrangement. According to Baniel et. al. ultimate rearrangement would eliminate the pores completely and result in dense membrane formation [Baniel (1990)]. This formation of nearly dense membrane like structure was supported by mechanical properties of dried PDMs of PBI-I. They showed mechanical properties similar to the base polymer (PBI-I) (Young's modulus = 31.7 and 22.9 MPa; while breaking stress = 122.7 and 111.4 MPa, respectively). The higher mechanical stability of dried PDMs could be due to the leaching of low molecular weight PBI in alkaline solution (5 % aq. NaOH) during the hydrolysis of Ppha-IT. This could be seen from the higher reduction in weight and volume than their premembranes Ppha-IT content, after leaching of porogen and drying of PDMs (Table 4.1). The PBI-I dense membranes on treatment with 5 % aq. NaOH at 60 °C showed 5 % reduction in weight, which could be due to the leaching of PBI. Such leaching could be anticipated, as PBI is known to dissolve in ethanolic NaOH solution [Li (2009)]. SEM images of the formed PDMs showed a plane surface structure without

any surface porosity (Fig. 4.8). This can be a sign of formation of PDMs with molecular level porosity rather than any distinct voids.
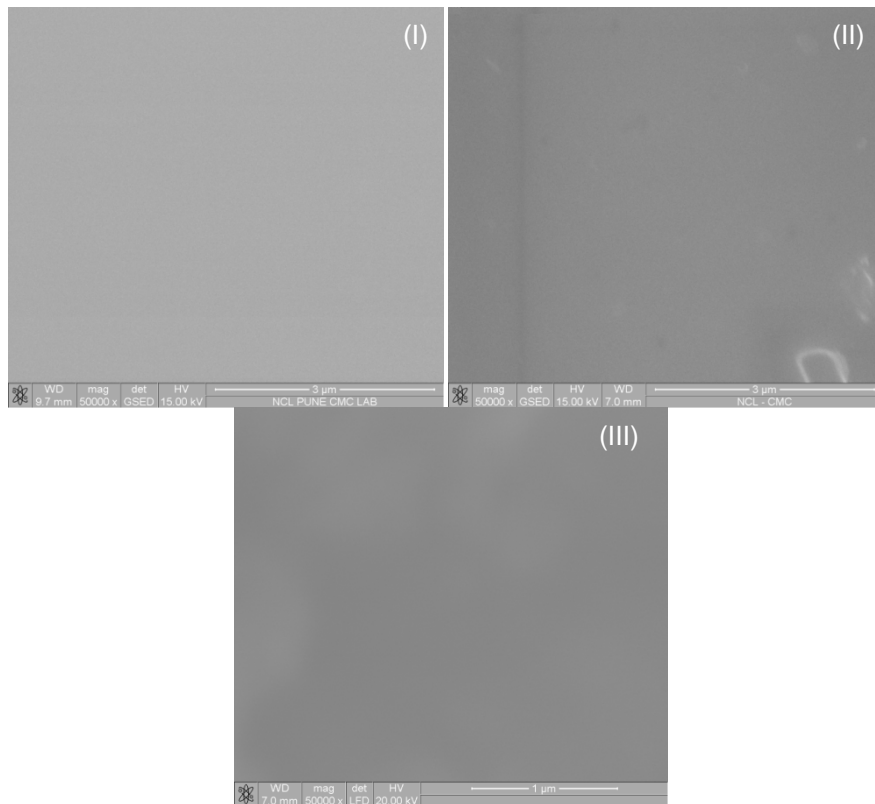
Fig. 4.8a. SEM images of PBI-I based PDMs; (I): PBI-I$_1$, (II): PBI-I$_2$, (III): PBI-I$_3$
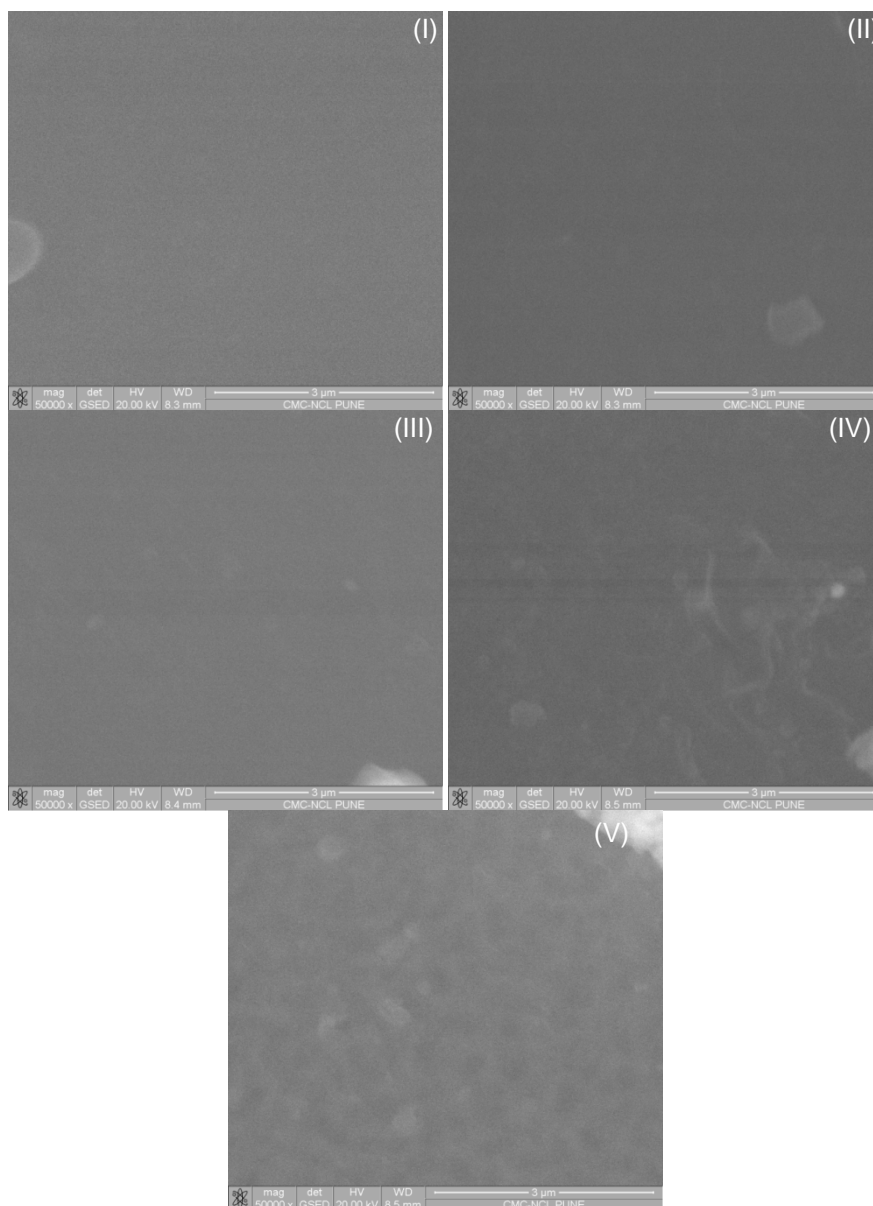
Fig. 4.8b. SEM images of PBI-BuI based PDMs, where the premembranes composition varies as (I): PBI-BuI$_1$, (II): PBI-BuI$_2$, (III): PBI-BuI$_3$, (IV): PBI-BuI$_4$, (V): PBI-BuI$_5$

The comparison of FT-IR spectra of dried PDMs with base PBIs showed complete removal of porogen (Ppha-IT), till 50 % premembrane Ppha-IT content (Fig. 4.1). The IR Band at ~1746 cm^{-1} related to ester group of Ppha-IT seen prominently in premembranes was eliminated completely after leaching and IR spectra of dried PDMs was matched to base PBI. Complete removal of Ppha-IT could be due to its hydrolysis in contact with NaOH and removal of degradation products. Hydrolysis products of

polyester (Ppha-IT) being phenolphthalein and aromatic dicarboxylic acid possess capability of instantaneous salt formation with aq. NaOH used for degradation. These salts were water soluble and smaller in size as compared with Ppha-IT. Hence they can be easily leached out in the surrounding solution leaving molecular level pores, which would provide a passage for further transport of NaOH and degradation of Ppha-IT from the bulk of membrane. Additionally, sorption of aqueous alkali by PBI is well reported in literature [Xing (2000), Hou (2008)]. It would ensure removal of Ppha-IT from the bulk of membrane. The FT-IR spectra of PBI-BuI$_4$ and PBI-BuI$_5$ PDMs showed small band at ~1705 cm^{-1} (Fig. 4.1). It could be due to residual degradation product in the PDM matrix.

Variation in weight and volume during the drying of PDMs was utilized in the calculation of porosity (%) of PDMs. Formed PDMs showed an increase in the porosity till PDMs based on premembranes containing 50 % porogen (PBI-I$_3$ and PBI-BuI$_3$). The (%) porosity of these PDMs was almost same to their premembrane Ppha-IT content. Such an increase in the porosity with increase in porogen content for PBI based PDMs is reported earlier [Wang (2012)]. The porosity of PDMs based on premembranes containing higher Ppha-IT (60 and 75 %) was smaller than their porogen content (Table 4.1). This could be due to the residual degradation products present in membrane matrix. This variation in (%) porosity of PDMs with premembrane Ppha-IT content would have an effect on transport properties.

4.3.5. *Lactic acid sorption: Effect of membrane structure, concentration and temperature*

The PBI-I$_3$ PDMs showed higher sorption of lactic acid than dense membranes of base (PBI-I), at all the temperature (30 and 40 °C) and initial bath concentration (1-12 %, w/v) conditions (Fig. 4.9).
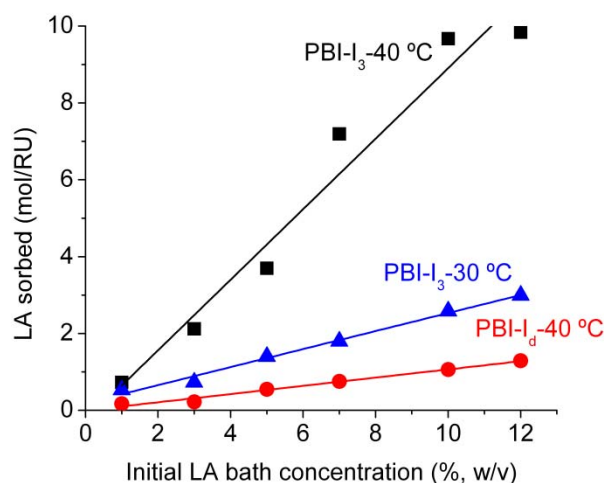
Fig. 4.9. Variation in sorption of LA in PBI based dense[a] at 40 °C and PBI-I$_3$ membranes at 30 and 40 ºC [[a]: Chapter 3]

At 30 °C, the acid uptake was increased by 3.53 to 3.36 times; while at 40 °C, the increase in sorption was 9.76 and 7.29 times at 1 and 12 % initial bath concentration, respectively. This higher acid uptake in PDMs (PBI-I$_3$) than dense membranes could be due to molecular level pore present in the membrane. This open structure would offer higher sorption of water and lactic acid molecules inside the membrane bulk, than in the case of PBI-I dense membranes. Additionally, acid sorbed on the PBI by interaction would be in equilibrium with the acid and water from the pores of PDMs. This would enhance the overall acid uptake in membrane matrix. Higher acid uptake in PBI based PDMs as compared to their dense membranes is reported, earlier [Mecerreyes (2004), Shen (2011), Wang (2012)].

These membranes showed a linear increase in the acid uptake with increase in bath concentration, at both the temperatures (Fig. 4.9). Since the formed PDMs contains molecular level porosity, the acid sorption in these membranes takes place by interaction with base PBI. The increase in bath concentrations would increase the interactions and hence the acid sorption. An increase in sorption of lactic acid with bath concentration was observed for PBI earlier [Chapter 3]. Such an increase in sorption of different acids in PBI with bath concentration was seen earlier [Kumbharkar (2009)].

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As seen from Fig. 4.9, higher lactic acid sorption was seen in PBI-I$_3$ PDMs at 40 °C than 30 °C. These membranes showed 3.13-3.14 times higher sorption of lactic acid, with increase in temperature from 30 to 40 °C. As discussed above, these membranes contain molecular level porosity. The increase in temperature would facilitate the entry of acid into bulk of membrane matrix, resulting in high acid uptake by interaction with base PBI from membrane matrix. Such an increase in lactic acid sorption with temperature was observed in PBI based dense membranes also [Chapter 3].

4.3.6. *Transport of non-acidic solutes*

Formed PBI based PDMs were analyzed for the transport of NaCl and glucose, individually. Glucose was taken as a representative of carbohydrate molecules (used as feed for the production of carboxylic acid by fermentation); while NaCl was taken as a representative of inorganic minerals and salts present in the fermentation broth. The concentration of glucose in the feed was 10 % (w/v); while it was 0.1 % (w/v) for NaCl. Water was used as a stripping solvent. No transport for either of these molecules could be detected on the permeate side after a continuous circulation of respective feed solutions for more than 72 h using PBI-I membranes. This inability of transport of nonacidic solutes could be explained on the basis of membrane properties. These PDMs contained pores with confined boundary layer rather than interconnected pores. Hence, transport of these molecules cannot occur by diffusion through pores. For the transport to occur by solution-diffusion mechanism sorption of solutes has to take place in the membrane matrix. No such sorption of glucose or NaCl was observed in PBI, as discussed in earlier publication [Chapter 3]. Thus, diffusion and permeability of these molecules through PBI based membranes could not be detected. These observations have important practical significance and assure the purity of transported acid.

PBI-I$_3$ PDMs were investigated for the transport of NaOH (1 N) also, using water as a stripping agent. The concentration of NaOH on the stripping side was increased with time (Fig. 4.10).
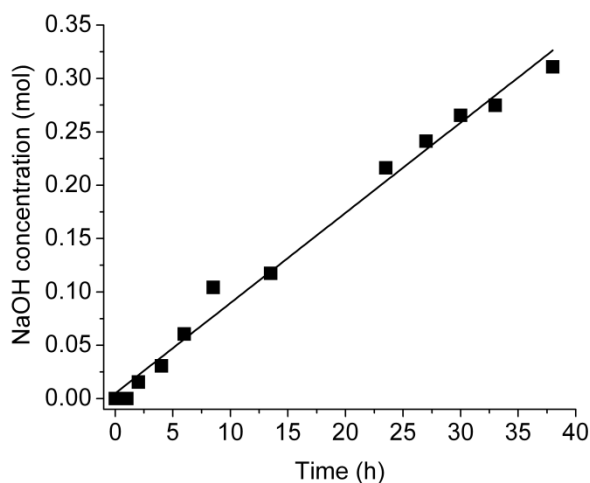
Fig. 4.10. Increase in NaOH concentration on the stripping side during its transport through PBI-I$_3$; with 1 M NaOH as feed solution and water as stripping agent at 40 °C

Flux and permeability of NaOH through these membranes was found to be 34.34 g/m^2.h and 8.23 × 10^{-12} m^2/s, respectively. The sorption of aq. alkali in PBI is known in literature [Xing (2000), Hou (2008)]. This sorption of NaOH in PBI in combination with easy migration across the PDMs due to presence of pores would result in its transport across these membranes.

4.3.7. *Acid transport analysis*

A solution containing equal amount of acid and glucose was used as a feed in the following experiments. Though PBI based PDMs does not allow glucose to permeate, there was a need to evaluate the effect of acid being present as a co-solute on glucose transport. During several experiments performed as given below, no glucose was detected on the permeate side. We continued to use glucose in the feed as a marker to conform membrane integrity. Due to the transport of NaOH across these PDMs, we used water as a stripping agent mostly, except in case of transport analysis through wet and dried membranes. Also, the water was a preferable stripping agent as the transported acid could be used in further application after suitable concentration.

4.3.7.1. Effect PDM drying on lactic acid transport

PBI-BuI$_3$ membranes were investigated for the transport of lactic acid (10 %, w/v) in wet and vacuum dried (at 100 °C) condition. With water as a stripping agent, these membranes showed appreciable permeability for acid in wet condition; while it was nil after drying (Table 4.2).

Table 4.2. Effect of drying on the transport of lactic acid through the PBI-BuI$_3$ membranes (feed solution: 10 % lactic acid + 10 % glucose, temperature: 40 ºC)

Membrane	Stripping agent	Flux (g/m^2.h)	Permeability (m^2/sec)
Wet membrane	Water	30	4.6×10^{-12}
	Aq. NaOH	62.6	3.78×10^{-11}
Vacuum dried membrane	Water	NT	-
	Aq. NaOH	13.1	1.59×10^{-12}

Transport of acid in wet PDMs could be due to the presence of pores in the membranes, which lead to high acid uptake as seen in section 4.3.5. This acid would present as bound as well as free acid. Presence of pores would also lead to easy migration of sorbed acid through the PDM. This would result in high acid transport and availability of free acid on the permeate side, which could be leached by water used as the stripping agent. It resulted in transport of lactic acid even with water as stripping agent in these PDMs. Leaching of free acid from PBI based membranes by suitable solvent is reported earlier [Li (2004b), Li (2004c), Leykin (2010)]. Drying of PDMs would lead to rearrangement in membrane to the extent of nearly dense membrane formation (Section 4.3.4.3). It would reduce acid uptake and increase the resistance for its migration across the membrane. This would result in nil transport for lactic acid with water as a stripping agent. A nil transport for lactic acid through PBI based dense membranes was observed at 10 % feed concentration and 40 °C [Chapter 3].

Further the transport of lactic acid (10 %, w/v) through wet and dried PBI-BuI$_3$ PDMs was investigated using aq. NaOH as stripping agent. As seen from Table 4.2, wet PDMs showed 23.8 times higher permeability for lactic acid as compared to dried

membranes. Lower transport in case of dried membranes could be due to the collapse of pores and rearrangement in the membrane, as discussed above. It would reduce acid uptake and increase the resistance for its transport through the membranes, resulting in lower acid transport. The lactic acid permeability through dried PBI-BuI$_3$ PDMs was almost equal to its permeability through PBI-BuI dense membranes (15.9×10^{-13} and 18.5×10^{-13} m^2/sec [Chapter 3], respectively). This is due to rearrangement in PDMs during drying, upto formation of dense membrane as discussed above.

4.3.7.2. *Effect of premembrane composition on lactic acid transport*

Three PDMs *viz*., PBI-BuI$_1$, PBI-BuI$_3$ and PBI-BuI$_5$ based on premembranes containing 25, 50 and 75 % of Ppha-IT were investigated for the transport of lactic acid (10 %, w/v). The acid permeability was increased from PBI-BuI$_1$ to PBI-BuI$_3$ (0.7×10^{-12} and 4.6×10^{-12}m^2/sec, respectively) (Table 4.3).

Table 4.3. Effect of premembrane (PBI-BuI + Ppha-IT) composition on the transport of lactic acid through PDM (feed solution: 10 % LA + 10 % glucose, temperature: 40 ºC, stripping agent: water)

Membrane	Flux(g/m^2.h)	Permeability(m^2/sec)
PBI-BuI$_1$	7.5	0.7×10^{-12}
PBI-BuI$_3$	30	4.6×10^{-12}
PBI-BuI$_5$	11.8	1.3×10^{-12}

This could be due to the increase in porosity (%) from PBI-BuI$_1$ to PBI-BuI$_3$ (33.4 to 42.4, respectively) (Table 4.1).Higher porosity in PBI-BuI$_3$ would provide open structure, leading to higher acid sorption and reduction in the resistance for its transport across membrane. It would result in higher acid permeability. The acid permeability was reduced to 1.3×10^{-12} m^2/sec for the PBI-BuI$_5$ PDMs (Table 4.3). It could be due to incomplete leaching of degradation products from the membrane at this premembrane composition, as discussed in section 4.3.4.2. Presence of these residual degradation products might reduce the acid uptake and increase the resistance for its transport across the membrane. It would reduce the acid permeability from PBI-BuI$_3$ to PBI-BuI$_5$.

4.3.7.3. Effect of temperature on lactic acid transport

PBI-I_3 PDMs showed a linear increase in the permeability of lactic acid (10 %, w/v) with increase in the temperature (Fig. 4.11).
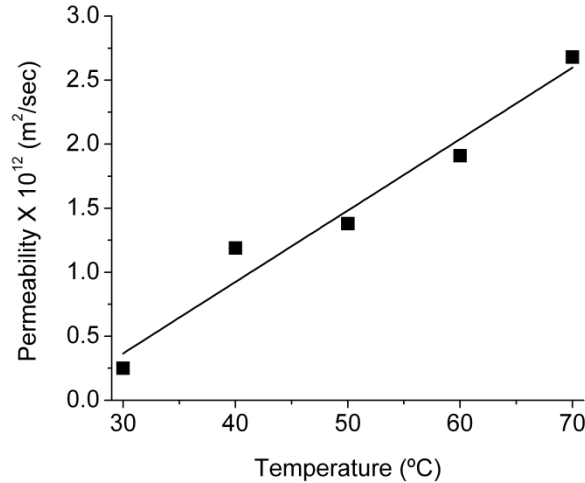
Fig. 4.11. Effect of temperature on transport of lactic acid (10 %) through PBI-I_3, with water as a stripping agent

With increase in temperature from 30 to 70 ℃, acid permeability was increased by 10.7 times ($2.5 \times 10^{-13}$to 2.68×10^{-12} m^2/s). This could be attributed to the increase in acid sorption with temperature. These membranes showed more than three times increase in the sorption of lactic acid, with increase in temperature from 30 to 40 ℃ (Section 4.3.5). Such increase in acid uptake with temperature would result in higher concentration gradient; the driving force for transport of acid across the membrane. At the same time increase in temperature would assist the diffusion of acid through the membrane. It would ultimately lead to increase in acid permeability. Such increase in lactic acid permeability with temperature was observed in PBI based dense membranes, also [Chapter 3].

4.3.7.4. Effect of feed concentration on lactic acid transport

PBI-I_3 PDMs were investigated for the transport of lactic acid at varying feed concentrations. They showed an increase in acid flux (1 to 6.4 g/m^2.h) but reduction in

its permeability (1.91 $\times 10^{-12}$ to 1.19 $\times 10^{-12}$ m^2/sec) with increase in feed concentration from 1 to 10 % (Table 4.4).

Table 4.4. Effect of feed concentration on transport of LA through the PBI-I$_3$ membranes (temperature: 40 ºC, stripping agent: water, feed solution: equal concentration of acid and glucose)

Concentration (%, w/v)	Flux (g/m^2 h)	Permeability (m^2/sec)
1	1.0	1.91×10^{-12}
3	2.1	1.45×10^{-12}
4	2.85	0.85×10^{-12}
5	2.24	0.73×10^{-12}
6	1.61	0.45×10^{-12}
7	4.8	1.31×10^{-12}
10	6.4	1.19×10^{-12}

Increase in flux could be due to the increase in acid sorption with feed concentration. These PDMs showed 5.6 times increase in sorption of lactic acid with increase in bath concentration from 1 to 10 % (Fig. 4.9). It would result in higher concentration gradient (driving force), enhancing overall flux across these membranes. Though flux was increased from 1 to 6.4 g/m^2.h, corresponding increase in feed concentration was higher (1 to 10 %, respectively) (Table 4.4), which resulted in lower permeability. This could be due to nature of the membranes, which contains molecular level porosity. Hence acid transport through these PDMs was dependent upon its sorption. Though the resistance for the transport of acid through the membrane is reduced, it has a role in determining overall permeability.

4.3.7.5. Transport of various organic acids through PBI-I$_3$ PDMs

The transport of other organic acids (succinic acid, fumaric acid, malic acid, maleic acid, acetic acid) was investigated through PBI-I$_3$ PDMs, to check applicability of the method for their separation. Permeabilities of these acid sat 1 % (w/v) feed

concentration were increased in the series as, succinic acid < fumaric acid < malic acid < lactic acid < maleic acid < acetic acid (Table 4.5).

Table 4.5. Transport of various organic acids through PBI-I$_3$ membranes (feed solution: 1 % acid + 1 % glucose, temperature: 40 ºC, stripping agent: water)

Acid in feed	Flux of acid (g/m^2.h)	Flux of glucose (g/m^2.h)	Permeability of acid (m^2/sec)
Acetic acid	17.27	0	9.12×10^{-12}
Maleic acid	4.88	0	2.01×10^{-12}
Fumaric acid	5.75	0	0.88×10^{-12}
Succinic acid	3.15	0	0.86×10^{-12}
Malic acid	4.03	0	1.24×10^{-12}
Lactic acid	1.0	0	1.91×10^{-12}

This variation in permeabilities could be due to the difference in acid properties. They would affect the interactions between acid and PBI used as a base material for PDM formation. As seen from the discussion till now, acid transport through these PDMs is dependent upon its sorption by interaction with base PBI. These interactions could affect migration of acid across the membrane and leaching by stripping agent, also. Different properties of acid which could influence its transport through PBI based PDMs are; its acidity or pK$_a$, molecular size, presence of more than one carboxylic group (−COOH), presence of interactive groups (e.g. −OH group in case of lactic acid, amine functionality for amino acid, etc.), presence of other functional groups (such as sulfonic acid, NO$_2$, halogen, etc.), hydrophilicity, etc. All these properties will have their own effect on acid-PBI interactions, in turn sorption and permeation of acid across the formed PDMs to a large extent.

During the investigation for transport of citric acid (10 %, w/v), PBI-I$_3$ membranes showed a flux of 0.28 g/m^2.h and permeability of 1.32×10^{-13} m^2/s with water as stripping agent. This could be due to the presence of pores in these membranes, similar to transport of lactic acid through these membranes in these conditions (Section

). The permeability of citric acid through these PDMs was lower than lactic acid, similar to its permeation through PBI based dense membranes [Chapter 3].

4.4.   Conclusions

PBI based porogen derived membranes (PDMs) were prepared with aromatic polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen to improve acid transport properties. The porogen was removed by hydrolysis and leaching of degradation product by using aq. NaOH. Formed PDMs contained molecular level porosity (since no voids could be detected by electron spectroscopic techniques). These porosity could have been extended till the length of the polymer chain. There was no direct/indirect proof for any porosity through the membrane. Transport of acids through these PDMs was dependent upon various factors as; properties of PBI, properties of acid, properties of stripping agent, sorption of acid in the membrane, premembrane composition, post treatment after formation of PDM and operational parameters like temperature, feed acid concentration, etc. These PDMs showed excellent transport for various organic acids with water as a stripping agent. Most importantly, they showed practically infinite selectivity for the transport of acid over non-acidic solutes. Use of water as a stripping agent and excellent selectivity profile would allow use of transported acid in the further processes after suitable concentration. With water as a stripping agent, it could reduce multiple steps required for acid separation by conventional method during their biotechnological synthesis. It could eliminate requirement of pH maintenance, waste generation and disposal issues with the conventional method and lead to large economical and ecological benefits.

Considering the possible benefits of this process for the separation of acids from non-acidic co-solutes we thought to apply the method for separation of inorganic acids. Hence, we investigated the transport of different inorganic acid, through the PBI based membranes and the effects of various parameters (PBI structure, acid properties, feed concentration and membrane structure) on the same.

Chapter 5

Application of chemodialysis for the transport of inorganic acid through polybenzimidazole based membranes

5.1.   Introduction

During our earlier investigations for the transport of organic acids by chemodialysis, polybenzimidazole (PBI) based membranes showed appreciable transport for organic acids with practically infinite selectivity over non-acidic co-solutes [Chapter 3]. The acid permeability could be enhanced by preparing porogen derived membranes (PDMs) with aromatic polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen. These membranes showed appreciable transport for acids even with water as stripping agent, while nil transport for inorganic salt (NaCl) and organic molecules (glucose) was maintained [Chapter 4]. While with the use of water as stripping agent; the recovered acid could be used in further applications after suitable concentration. Inspiring from these results, it was thought to extend the method of chemodialysis for the separation of inorganic acids from non-acidic co-solutes.

In this study, the transport of various inorganic acids (*viz.*, HCl, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$) having wide industrial applicability was investigated through PBI based membranes. Four PBIs (*viz.*, PBI-I, PBI-BuI, PBI-Py and PBI-HFA) synthesized by polymerizing a tetramine, *3,3'*-diaminobenzidine (DAB) with either isophthalic acid (IPA), *5-tert*-butylisophthalic acid (BuI), *2,6*-pyridinedicarboxylic acid (Py) or *4,4'*-(hexafluoroisopropyledene)bis(benzoic acid) (HFA) were investigated for acid transport properties. Stability of these PBIs in contact with acid and base solution was analyzed in the view of long term applicability. Initially the PBI-I based dense membranes were evaluated for the sorption of various acids. Effects of various parameters such as, PBI structure, acid properties, feed concentration and stripping agent (aq. NaOH and water) on acid transport were investigated. PBI-I based PDMs prepared with Ppha-IT as a porogen were analyzed for the transport of different acid to investigate the effect of membrane structure on transport properties.

5.2. Experimental

5.2.1. Materials

3,3'-diaminobenzidine (DAB), isophthalic acid (IPA), *5-tert-*butylisophthalic acid (BuI), *4,4'-*(hexafluoroisopropyledene)bis(benzoic acid) (HFA), *2,6-*pyridinedicarboxylic acid (Py), isophthaloyl chloride (IPC), terephthaloyl dichloride (TPC) and benzyltriethylammonium chloride (BTEAC) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, ca. 84 % as P_2O_5) was procured from Alfa Aesar. Phenolphthalein was procured from Loba Chemie. *D*-Glucose was procured from Qualigens Fine Chemicals. Dichloromethane (DCM), *N,N*-dimethyl acetamide (DMAc), hexane, ethanol, acetone, chloroform, *1,1,2,2-*tetrachloroethane (TCE), acids (HCl, HNO_3, H_2SO_4 and H_3PO_4), bases (NaOH and $NaHCO_3$), NaCl, *3,5-*dinitrosalicylic acid (DNSA) and $CaCl_2$ (GR/extrapure grade) were obtained from Merck. Recrystalization of IPC, TPC (using hexane) and phenolphthalein (using ethanol) was done prior to use; while other chemicals were used without further purification.

5.2.2. Polymer synthesis

Three polybenzimidazoles (PBIs) (*viz.*, PBI-I, PBI-BuI and PBI-Py) were synthesized as discussed in Chapter 3. The PBI-HFA based on DAB and HFA was synthesized by solution polycondensation in PPA as reported earlier [Kumbharkar (2009)]. Typically, a three-neck round bottom flask equipped with a mechanical stirrer, N_2 inlet and an outlet fitted with $CaCl_2$ guard tube was charged with 2400 g of PPA and heated to 120 °C under constant flow of N_2. A 80 g (0.3738 mol) of DAB was added with continuous stirring. The temperature was raised to 140 °C and an equimolar quantity of HFA was added. The temperature was slowly increased to 170 °C and maintained for 5 h. It was further raised to 200 °C and maintained for 6 h. Obtained reaction mixture was poured into stirred water to precipitate PBI-HFA polymer. It was crushed and sequentially washed with water, $NaHCO_3$ solution and water; till the filtrate was neutral to pH. Obtained PBI was dried at 100 °C under vacuum for a week. It was purified by dissolving in DMAc at 120 °C followed by centrifugation at 2800 rpm (2 h) and precipitation in stirred water. The precipitated polymer was dried at 100 °C under vacuum for a week. Structure and abbreviations of monomers and PBI-HFA are given in Scheme 5.1.
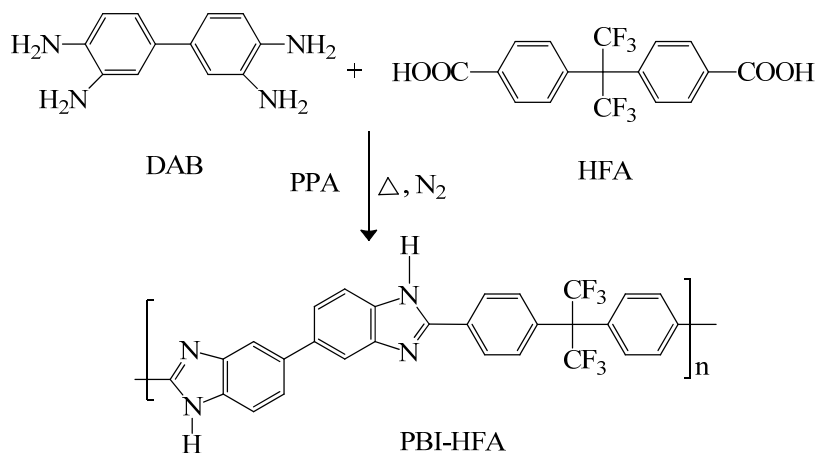
Scheme 5.1. Structure and abbreviations of monomers and PBI-HFA

The polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) was synthesized by interfacial polycondensation using Na-salt of phenolphthalein and equimolar quantity of IPC and TPC with BTEAC as phase transfer agent, as discussed in Chapter 4.

5.2.3. *Membrane preparation*

Dense membranes of synthesized PBIs were prepared by solution casting method, using their 2 % (w/v) polymer solution in DMAc, as detailed in Chapter 3. These membranes were casted in various batches with varying thickness, at different times. PBI-I based porogen derived membrane (PDM, PBI-I_3) was prepared from premembranes containing 50 % (w/w) Ppha-IT, with the detail procedure described earlier [Chapter 4]. They were preserved in water till further use.

5.2.4. *Physical property analysis*

Inherent viscosity of synthesized PBIs was determined using their 0.2 g/dL solutions in concentrated H_2SO_4, at 35 °C. The intrinsic viscosity of Ppha-IT was measured using its solutions in TCE, as described in Chapter 4. The thin films of PBI-HFA were analyzed by Fourier transfer infrared (FT-IR) spectra, thermogravimetric analysis and wide angle X-ray diffraction (WAXD) spectra as given in detail earlier [Chapter 3]. Stability of PBI based membranes in contact with acids and bases was assessed by keeping their samples (3 × 3 cm^2) in 10 M H_2SO_4, 6 M HNO_3 and 2.5 M NaOH solutions and the visual observations on membrane integrity were noted.

5.2.5. Sorption Studies

The synthesized PBIs were studied for the sorption of acid (*viz.*, HCl, HNO$_3$, H$_2$SO$_4$ or H$_3$PO$_4$), at 1 N bath concentration and 40 ($\pm$ 0.1) °C, as discussed in detail earlier [Chapter 3]. After attaining equilibrium the acid uptake and swelling ratio were calculated and given in Table 5.1.

5.2.6. Acid transport

PBI based membranes were investigated for the transport of various acids, as per the procedure discussed in Chapter 3. The transport of HNO$_3$ through PBI-I dense membrane was investigated at varying feed concentrations of 1, 4 and 6 N. For the other acids (HCl, H$_2$SO$_4$ and H$_3$PO$_4$) and membranes, the transport was measured at 1 N feed concentration. Their flux and permeability values are given in Table 5.2-5.4 and Fig. 5.2.

5.3. Results and discussion

5.3.1. Selection of polybenzimidazole

PBI membranes were used in the inorganic acid transport investigations, as they showed practically infinite selectivity for the transport of organic acid over non-acidic co-solutes during our earlier investigations [Chapter 3]. Four PBIs (*viz.*, PBI-I, PBI-BuI, PBI-Py and PBI-HFA) were chosen in these investigations due to the variations in structural and physical properties. Three PBIs (*viz.*, PBI-I, PBI-BuI and PBI-Py) were taken from earlier investigations, which showed appreciable transport of organic acid [Chapter 3]. PBI-HFA synthesized using *4,4'-* (hexafluoroisopropyledene)bis(benzoic acid) containing bulky and polar hexafluoro group was chosen as the fourth polymer. Presence of this group would affect the interactions between PBI and acid molecules, varying its sorption and transport properties. Presence of this group in PBI-HFA, led to several times enhancement in gas permeability as compared to PBI-I [Kumbharkar (2006)]. Hence we thought that, PBI-HFA would be an interesting candidate for acid transport investigations.

5.3.2. Polymer synthesis and physical characteristics

The PBIs (*viz.*, PBI-I, PBI-BuI, PBI-Py and PBI-HFA) synthesized and obtained polymer were purified by reprecipitation as detailed in Section 5.2.2, which was necessary to obtain soluble polymer, as reported earlier [Chapter 3]. Inherent viscosities of the formed PBIs (PBI-I, PBI-BuI, PBI-Py and PBI-HFA) were found to

be 1.2, 1.15, 0.9 and 1.35 dL/g, respectively. Inherent viscosity of Ppha-IT was 1.24 dL/g.

Formation of PBIs was confirmed by comparing their IR, TGA and WAXD pattern of with the same PBI as reported earlier [Kumbharkar (2009)]. The IR spectra and other properties of PBI-I, PBI-BuI and PBI-Py were similar to our earlier publications [Kumbharkar (2009)] and conforms the formation of respective PBIs as discussed in Chapter 3.

IR spectra of PBI-HFA showed a typical broad band at 2368-3718 cm^{-1} (PBI-HFA), similar to other PBIs as shown in Fig. 5.1. They were attributed to the hydrogen bonding N-H/N and non-hydrogen bonded N-H stretching of PBI, as reported earlier. Also a match for other bands, *viz.*, small band responsible for C-H stretching (3080 cm^{-1}); characteristic band for imidazole C=C and C=N in the range of 1450-1650 cm^{-1} and bands in fingerprint region (in-plane C-H deformations at 1090-1230 cm^{-1}, typical benzene ring bands at ~1011 and ~980 cm^{-1}; while out-of-plane deformations of substituted benzene rings at 900-800 cm^{-1}) conformed the formation of PBI-HFA.
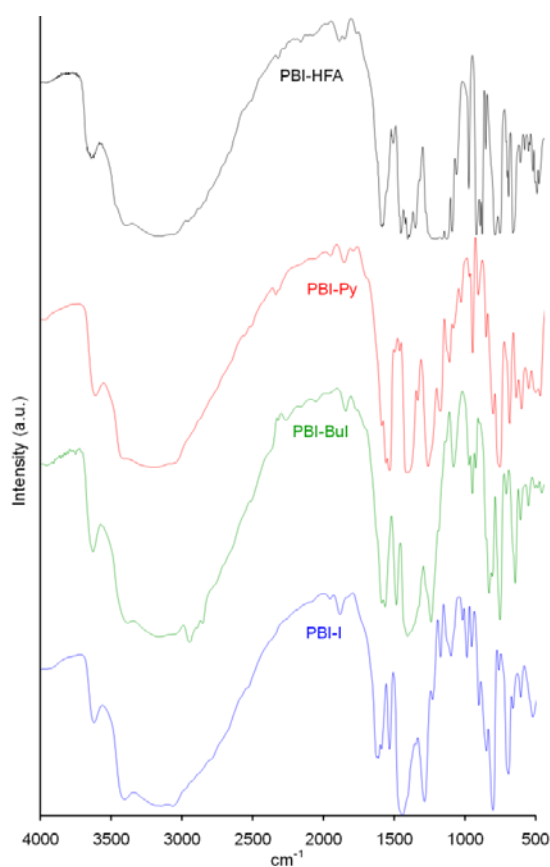
Fig. 5.1. FT-IR spectra of the synthesized PBIs

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This was further substantiated by its initial decomposition temperature as, 550 °C; similar to earlier report. Similarly, WAXD pattern and d_{sp} (3.98 Å) were also found to be almost identical as that of earlier work. All these properties were similar to our earlier publications [Kumbharkar (2009)] and conforms the formation of PBI-HFA. The physical properties of polyester (Ppha-IT) were found to be similar, as detailed in Chapter 4.

5.3.3. *Membrane preparation*

PBI based dense membranes and composite premembranes were prepared by solution casting followed by treatment with water and under vacuum as described in section 5.2.2. This water treatment and vacuum drying after membrane formation was necessary to ensure the complete removal of DMAc used as solvent for membrane casting. The porogen derived membranes (PDM) PBI-I$_3$ were prepared with PBI-I as base material containing Ppha-IT (50 %, w/w) as a porogen in premembrane, to enhance acid transport rate. This particular composition was chosen as PDMs based on the same showed higher transport rate for organic acids, during our earlier investigations [Chapter 4]. Moreover, during our earlier investigations, the PBI based PDMs were found to be transporting acid molecules only; rejecting non-acidic co-solutes, like salt (NaCl) or organic molecules (glucose) [Chapter 4]. This selectivity would insure the purity of transported acid during its separation from spent liquors of various industries, which contain various co-solutes of inorganic or organic in nature depending upon process conditions [Schwartz (2000), Kladnig (2003), Kim (2006), Van Der Merwe (2010)]. The presence these impurities would restrict the use of separated acid in further processes.

5.3.4. *Stability of PBI towards strong acids and bases*

PBI based membranes were immersed in either 10 M H$_2$SO$_4$, 6 M HNO$_3$ or 2.5 M NaOH solutions, at ambient temperature. They were found to be stable for more than a month in above solutions without any visual change or damage to membrane. Only a greenish tinge was developed in PBI-I based membranes treated with H$_2$SO$_4$. The original light brown color of these samples was regained back after immersing these samples in water for 3 days. These membranes retain integrity and no physical change or damage was observed for them. These observations were in accordance with the excellent chemical stability of PBI towards various acids and bases, as reported in the literature [Xing (2000), Hou (2008), Li (2009)]. Present

investigations were performed for the longer duration. The retained integrity of membranes for this duration indicated that PBI based membranes could be used in the continuous acid separation or recovery applications for longer durations. Additionally, stability of PBI in the presence of base solution indicated that an alkali solution can be used as a stripping agent for acid transport investigations depending upon process requirements.

5.3.5. *Acid sorption in PBI-I*

The dense membranes of PBI-I showed an increase in the sorption of different acids in the sequence of $H_3PO_4 < H_2SO_4 < HNO_3 < HCl$, at 1 N bath concentration (Table 5.1).

Table 5.1. Sorption of inorganic acids in PBI-I; temperature: 40 °C

Acid (1N)	Acid uptake (mol/RU)	Weight uptake (%)	Swelling ratio (%)
HCl	1.604	50.0	12.59
HNO_3	1.595	56.7	14.65
H_2SO_4	1.007	67.1	14.55
H_3PO_4	0.981	73.7	19.03

This variation in the sorption of acids is anticipated from the bath concentration. Though 1 N bath concentration is taken for the investigations its concentration in molar basis would vary as $HCl = HNO_3$ (1 M) > H_2SO_4 (0.5 M) > H_3PO_4 (0.33 M). This increase in bath concentration would increase sorption of acid by interaction. An increase in the sorption of acid with bath concentration was observed for organic acids also [Chapter 3]. Increase in acid uptake with bath concentration is reported in literature [Kumbharkar (2009), Leykin (2010)]. Marginal lower sorption for HNO_3 (1.595 mol/RU) than HCl (1.604 mol/RU) might be due to the variation in interaction because of difference in pK_a (-1.4 and -7, respectively [Smith (2007)]). It would vary the interaction between acid and PBI resulting higher uptake for HCl. Sorption of acid in PBI by acid-base type interactions is well reported [Chanda (1985), Glipa (1997), Fontanella (1998), Bouchet (1999), Li (2004b), Li (2004c), Kumbharkar (2009), Leykin (2010)].

Though the molar bath concentration was lower for H_2SO_4 (0.5 M) and H_3PO_4 (0.33 M), they showed strong acid uptake (1.007 and 0.981 mol/RU, respectively). This could be due to presence of higher acidic protons (pK_a of $H_2SO_4 =$

-3.0, 1.96 and H_3PO_4 = 1.7, 6.5 and 12.1 [Teichert (1999), Csermely (1985)]), which could interact with multiple interaction sites and results in higher acid uptake. This could be seen from the weight uptake of the membranes, which increased in the sequence of, $HCl < HNO_3 < H_2SO_4 < H_3PO_4$ (Table 5.1). Similar variation was observed in the swelling of the membranes as, $HCl < HNO_3 \cong H_2SO_4 < H_3PO_4$. The increase in interactions would reduce the interchain hydrogen bonding in PBI and lead to higher swelling of the membranes. It would lead to higher sorption of water as secondary molecule. An increase in weight due to sorption of acid and water was observed during the sorption of organic acids also [Chapter 3]. Higher sorption of H_3PO_4 due to more H-bonding arising from its tribasic nature is reported [Kumbharkar (2009)].

5.3.6. *Transport investigations*

5.3.6.1. *Transport of different acids through PBI-I*

Transport of different acids through PBI-I based membranes showed an increase in the permeability in the sequence of, $H_3PO_4 < HNO_3 < HCl < H_2SO_4$ for both (water and aq. NaOH) as stripping agent (Table 5.2).

Table 5.2. Effect of acid properties and stripping agent on the transport of inorganic acid through PBI-I based membranes; temperature: 40 ºC

Feed solution (1 N)	Flux (g/m^2.h)	Permeability (m^2/sec)
A) With NaOH solution (0.24 N) as the stripping agent		
H_2SO_4	48.3	6.07×10^{-11}
HNO_3	24.5	0.60×10^{-11}
HCl	19.4	0.80×10^{-11}
H_3PO_4	7.12	0.28×10^{-11}
B) With water as the stripping agent		
H_2SO_4	23.3	2.52×10^{-11}
HNO_3	20.8	0.43×10^{-11}
HCl	16.1	0.67×10^{-11}
H_3PO_4	3.27	0.10×10^{-11}

This increase in permeability could be attributed to the variation in acid properties. Increase in the permeability from H_3PO_4 to HCl was in accordance with

their sorption in membrane, which was increased in the order of $H_3PO_4 < H_2SO_4 <$ $HNO_3 < HCl$ (Table 5.1). It would result in higher acid permeability. Such, higher permeability of acid due to their higher sorption in PBI was observed for organic acids earlier [Chapter 3]. The higher permeability of H_2SO_4 could be due to multiple interactions arising from di-basic nature of H_2SO_4. Due to which, H_2SO_4 could lead to bonding with the basic sites on adjacent PBI chains. It would assist the transport of sorbed acid in the direction of concentration gradient resulting in higher permeability. A large effect of acid properties on the transport of organic acids through PBI based membranes was observed during our earlier investigations also [Chapter 4].

The permeabilities were higher with aq. NaOH than with water as a stripping agent for all the acids (Table 5.2). Higher acid permeability with aq. NaOH as a stripping agent was due to its basic nature. The acid molecules are sorbed in the PBI membranes as bonded with basic N and unbound or free [Li (2004b)]. The desorption of acid from PBI based membranes would take place by two ways; (i) leaching of free acid by suitable solvent (water) and (ii) leaching of bonded acid by overcoming the interactions with PBI using solution of strong alkali as a stripping agent [Chapter 3]. Water could leach only the free acid while aq. NaOH would be able to leach both free as well as bonded acid molecules, resulting higher permeability. Additionally, use of aq. NaOH as a stripping agent would convert the transported acid to its Na-salt; maintaining the concentration of acid on permeate side to practically zero. Hence at any given time, the concentration gradient across the membranes would be same as feed acid concentration. While with water as a stripping agent, acid is recovered in its acidic form. This would reduce the concentration gradient to the difference between acid concentrations on both sides. It would result in the lower acid permeability with water as a stripping agent.

Though the transport rate is high using NaOH as a stripping agent, its major draw-back is that it would convert acid to its salt. Hence, transported acid needs further treatment to convert it back to the acidic form; which may not be economically advisable. Use of water as the stripping agent would allow recovery of acid in its acidic form, till the equilibrium is reached on both side solutions. Thus it has a limitation that all the acid may not be transported and the transport rate would be lower. So, the stripping agent needs to be selected depending upon the process requirements and economic considerations.

5.3.6.2. Transport of HNO$_3$ through various PBIs

The permeability of HNO$_3$ through different PBIs was increased in the order of PBI-BuI < PBI-HFA < PBI-I < PBI-Py, for both water and aq. NaOH as the stripping agents (Table 5.3).

Table 5.3. Effect of PBI properties on the transport rate of HNO$_3$; temperature: 40 °C, feed solution: 1 N acid

Feed solution (1 N)	Flux (g/m^2.h)	Permeability (m^2/sec)
A) With NaOH solution (0.24 N) as the stripping agent		
PBI-I	24.5	0.60×10^{-11}
PBI-BuI	12.72	0.27×10^{-11}
PBI-Py	22.05	1.13×10^{-11}
PBI-HFA	19.47	0.37×10^{-11}
B) With water as the stripping agent		
PBI-I	20.8	0.43×10^{-11}
PBI-BuI	12.68	0.25×10^{-11}
PBI-Py	21.40	1.01×10^{-11}
PBI-HFA	18.64	0.36×10^{-11}

This variation in HNO$_3$ permeability could be due to the difference in the physical properties of these PBIs. The increase in permeability as, PBI-BuI < PBI-I < PBI-Py could be attributed to increase in their 'N' density (15.38, 18.18 and 22.65 %, respectively). This increase in 'N' density of PBI would facilitate the interactions and sorption of acid in the membrane. It would increase the concentration gradient, driving force for migration of acid across the membrane and result in higher acid permeability. Similar increase in the lactic acid permeability with increase in its sorption in different PBIs was observed during our earlier work [Chapter 3]. Though PBI-HFA has lowest 'N' density (10.49 %) in the series; it showed intermediate permeability for HNO$_3$ between PBI-I and PBI-BuI. It could be due to higher free volume in PBI-HFA. The free volume these PBIs varies in the order as, PBI-I < PBI-Py < PBI-BuI < PHI-HFA (0.3036, 0.3226, 0.3393 and 0.3605 cm^3/cm^3, respectively). This open structure in PBI-HFA would assist in the sorption and migration of acid across the membrane, resulting in higher permeability than PBI-BuI. A variation in

sorption and permeability of lactic acid with PBI structure was observed during our earlier work [Chapter 3].

5.3.6.3. *Variation in HNO₃ transport with feed concentration*

The investigations of transport of HNO_3 through PBI-I based membranes showed a linear increase in permeability (from 0.6005×10^{-11} to 1.522×10^{-11} m^2/sec) with increase in feed concentrations (from 1 to 6 N) (Fig. 5.2).
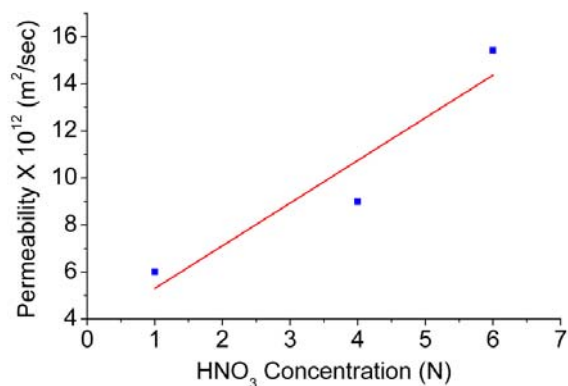
Fig. 5.2. Variation in transport of HNO₃ with feed solution concentration through PBI-I based membranes; stripping agent: aq. NaOH

Increase in HNO_3 feed concentration would increase its sorption in the membrane matrix, which would result in higher permeability. An increase in the sorption of acid in PBI, with increase in bath concentration is well reported earlier [Kumbharkar (2009), Leykin (2010)].

5.3.6.4. *Effect of membrane morphology*

The porogen derived membranes (PDMs) PBI-I₃ were investigated for the transport of different acids (*viz.*, HCl, HNO₃ and H₂SO₄) at 1 N feed concentration. They showed a large increase in the permeability of these acids (2.7 for H₂SO₄ times to 12.2 times for HCl) as compared to PBI-I dense membranes (Table 5.4).

Table 5.4. Transport of inorganic acid through PDMs (PBI-I$_3$), stripping agent: water, temperature: 40 ºC, feed solution: 1 N Acid

Acid	Flux (g/m^2.h)	Permeability (m^2/sec)	Permeability - dense membrane (m^2/sec)	Permeability increase (dense to PDM)
H$_2$SO$_4$	319.47	6.76×10^{-11}	2.52×10^{-11}	2.7
HNO$_3$	333.93	5.27×10^{-11}	0.43×10^{-11}	12.2
HCl	240.4	7.57×10^{-11}	0.67×10^{-11}	11.0

This increase in acid permeability could be attributed to the presence of pores in the PDM, formed during hydrolysis and leaching of porogen (Ppha-IT). It would lead to higher acid uptake and reduce the resistance for migration of sorbed acids across these membranes. This would lead to an increase in acid permeability. Such an increase in the organic acid permeability through the PDMs as compared to PBI-I dense membrane was observed earlier [Chapter 2].

The extent of increase in permeability was found to be varying in the series as H$_2$SO$_4$ < HCl < HNO$_3$ (2.7, 11 and 12.2 times, respectively) (Table 5.4). This trend was apposite to their dense membrane permeabilities and could be due to the properties of acids. The transport of acid through these PDMs was depended upon its sorption by interaction with PBI and followed by migration across the membrane, as they contain molecular level porosity [Chapter 4]. These pores in the PDMs would assist to enhance the acid sorption and permeation properties. It resulted in 11 and 12.2 times increase in the permeability for HCl and HNO$_3$, respectively. Enhancement in the permeability was lower for H$_2$SO$_4$ (2.7 times) as compared to other two acids. This could be due to its high permeability through PBI-I dense membranes though it has lower sorption than HCl and HNO$_3$. This high permeability was due to its di-basic nature, which leads to multiple interactions assist its migration though the membrane as discussed above (Section 5.3.6.1). The presence of pores in PDMs would reduce these interactions and result in lower increase in the permeability.

This increase in permeability by the formation of PDMs would help to make chemodialysis (CD), an economically viable option for the separation of acid.

5.4.   Conclusions

The transport of inorganic acids was investigated through PBI based membranes by Chemodialysis (CD), for their separation from non-acidic co-solutes. PBI based membranes showed acceptable permeability for various acids. Preparation of porogen derived membranes (PDMs) with PBI as base led to a large increase in acid transport rate. These membranes showed 2.7 (for H_2SO_4) to 12.2 (for HNO_3) times increase in the permeability of various acids, while maintaining practically infinite selectivity over non-acidic co-solutes. Excellent selectivity and appreciable permeabilities with water as a stripping agent makes this method suitable for the practical acid separation application. It works with concentration gradient as a driving force. It requires energy only for the circulation of solution on feed and stripping sides and thus is highly energy efficient. Use of water as the stripping agent would allow recycle of acid, after suitable treatment for concentration. This would lead to effective utilization of acids and have ability hand over the cost benefit to industry. Most importantly it would addresses environmental concern; where need for acid neutralization and disposal is eliminated. It could make this process an economically and ecologically attractive option for separation of inorganic acids.

Chapter 6

Conclusions

We proposed and demonstrated a method of chemodialysis (CD) for the separation of acids from non-acidic solutes. It uses polymeric membranes possessing chemically active functional groups, which can sorb acid molecules by interaction. Sorption of acid is followed by its transport across the membrane by concentration gradient as a driving force. Transported acid molecules are leached by suitable stripping agent (water or base solution) from permeate side of the membrane.

During the investigations for selection of membrane material, the thin film composite (TFC) membranes based on aminated silicon rubber (ASR) and polyethyleneimine (PEI) were the quick choice based on material characteristics. They showed either nil or low transport for lactic acid depending upon the nature of stripping agent (aqueous or organic solution and its basicity) used. Transport of acid through these membranes was accompanied by co-transport of glucose, with unacceptably low acid/glucose selectivity. The stability of these membranes was also low, as conveyed by the lowering in gas selectivity after the acid permeation experiments and observed transport of triethyl amine (used as a stripping agent) to the feed side. This was attributable to chain flexibility associated with these polymers.

As an alternative to this, we changed the material type from rubbery to glassy. A polybenzimidazole (PBI) was chosen as a membrane material, which his known for high inorganic acid sorption. This membrane showed appreciable transport for different acids. It also exhibited excellent selectivity (practically infinite) for the transport of acid over non-acidic co-solutes (inorganic and organic in nature). This selectivity was attributed to the selective sorption of only acid molecules (by acid-base type interactions) and not the neutral ones (glucose and NaCl). The transported acid is subsequently leached by suitable stripping agent (water or base). The membrane showed excellent stability in acid or base environment, as anticipated based on the properties of this type of polymers known in the literature.

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As conveyed by the results summarized in Chapter 3, acid sorption as well as transport in PBIs was found to be strongly dependent upon nature of PBI, stripping agent, nature of transporting solute (acid) and process parameters like feed concentration and temperature. The acid uptake is also affected by the variation in PBI structure. The incorporation of *tert*-butyl resulted higher free volume in PBI-BuI. It led to high sorption and transport of lactic acid, as compared PBI-I. Also the introduction of additional basic nitrogen through pyridine dicarboxylic acid led to the increase in acid uptake and transport in comparison to PBI-I. The sorption of acid was increased with the increase in bath concentration, as anticipated. The same phenomenon is observed with increase in temperature.

Though high obtained selectivity of acid over non-acidic solutes using these PBI based membranes looks to be an attractive option, need of alkali solution as a stripping agent was a draw-back. The transport of organic acids was either low (permeability = 3.3×10^{-13} m^2/sec for acetic acid) or nil (for lactic acid and citric acid), with water as stripping agent. Hence it was thought that, an introduction of molecular level porosity in the membrane matrix would help to overcome the issue. Chapter 4 details investigations with porogen derived membranes (PDMs). They were prepared with PBI as a base material and an aromatic polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen. It was leached by hydrolysis using aq. NaOH followed by water wash.

Formed PBI based PDMs contained molecular level porosity. Due to which the acid uptake in these membranes was dependent upon its sorption by interaction with base PBI. These membranes showed higher permeability of acids as compared to the dense membranes. Most significantly, they showed transport of lactic acid and citric acid even with water as a stripping agent, while still maintaining the high selectivity of acid over non-acidic solutes. Permeability of different organic acids through these PDMs was increased in the order of, succinic acid < fumaric acid < malic acid < lactic acid < maleic acid < acetic acid. Transport of acid through these PDMs was dependent upon properties of PBI used as base material, properties of acid, properties of stripping agent, sorption of acid, premembrane composition, post treatment after formation of PDM and operational parameters like temperature, feed acid concentration. In case of inorganic acids, PBI-I

based PDMs prepared from premembranes containing 50 % Ppha-IT showed 2.7 (for H_2SO_4) to 12.2 (for HNO_3) times increase in the permeabilities, as compared to the dense membrane of base PBI.

The transport of acid through PBI based membranes using water as a stripping agent allows separation or recovery of acid in the acid form itself; owing to which, the transported acids can be utilized directly. It could eliminate environmental issues during the treatment of acid by conventional (neutralization-precipitation) method. It could reduce the multiple stages required for separation of acid by conventional methods. This method works on concentration gradient as a driving force and hence does not require use of pressure, temperature or electrical potential for the transport to occur. Thus it has low energy consumption, with energy required only for the circulation of solutions on either side of the membrane. This would reduce the installation and operational costs, as it does not require any additional gadgets other than pumps. This makes chemodialysis (CD), an attractive alternative for the separation of acids with prospects of multiple economical and environmental benefits. Further work is required to obtain these membranes in a form to ease module preparation; which will address a stage of process scale up.

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"Transport of Acids through Polymeric Membranes"

Synopsis

For the degree of Doctor of Philosophy
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In
Chemical Engineering

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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO THE UNIVERSITY OF MUMBAI FOR THE DEGREE OF DOCTOR OF PHYLOSOPHY (TECHNOLOGY) IN CHEMICAL ENGINEERING

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Significance of the work

Acids are important chemicals used in different industries, e.g. food processing, synthetic chemistry, natural products, inorganic chemicals, steel treatment, surface treatment, metal refining, electronic and glass industry, pigment and chemical production, etc. [Kim (2006), Koltuniewicz (2008)]. Acids can be either organic or inorganic in nature and may be utilized as a reagent or catalyst; they could be product, byproduct or undesirable impurity in various process streams. Their separation and recovery from such streams is an important task. Their use in large quantities can be exemplified by HNO_3 production, which was 55–60 million T/y [Ponce-de-Leon (2000)]; while acetic acids production was reported to be 5.4 million T/y [Sano (1999)]. Production of organic acids from biomass seems to be attractive vis-à-vis their production using petroleum based precursors; though their separation and purification is tedious and lengthy. Separation and purification of the lactic acid during its production by fermentation accounts to ~50 % of the production costs [Wasewar (2004)].

Recovery and reuse of inorganic acids from spent streams can offer multiple benefits. It is reported that ~40 % of the cost can be saved in steel galvanizing plant by acid recycling [Stocks (2005)]. Separation of acids from non-acidic co-solutes is a major task.

A suitable technique for acid separation is required for various purposes such as isolation of acid as a product/byproduct from fermentation broth, quality refinement (e.g. deacidification of fruit juice), inorganic acid recovery, etc.; which would not only have economical benefits but also have environmental impact (e.g. reduction in sludge disposal, lesser ground water contamination, etc.)

Different processes such as neutralization-precipitation, steam stripping, reactive distillation, adsorption, ion-exchange, extraction, reactive extraction, liquid membrane extraction, membrane distillation, nanofiltration, reverse osmosis, pervaporation, diffusion dialysis and electrodialysis are reported for acid treatment. They have their own feasibility, economical and environmental issues. Present thesis is devoted to a new

method of acid separation, named as 'Chemodialysis' using chemically active polymeric membranes which can selectively sorb molecules and transport them based on chemical interactions. The method involves contacting feed solution on feed side of the membrane; while a suitable stripping agent is circulated on permeate side to desorb the acid transported through the membrane. The driving force for this process is concentration gradient. Thus the only energy requirement is for feed and stripping solution circulation and thus can prove highly energy efficient. Additional advantages of membrane based processes (operational simplicity, modular nature, space efficiency and easy scale up, are also applicable to this process.

Aim of this work is to evaluate chemically active membrane materials for transporting some chosen organic / inorganic acids by 'Chemodialysis'. The work done is presented in following 6 chapters.

Chapter 1: (Title: Acid separation: A brief literature survey)

Need of acid treatment (for recovery, separation or disposal) and various methods reported for this purpose with their advantages and limitations are reviewed in beginning of this Chapter. Requirement of a new method of acid separation for few cases, such as acid production by fermentation is emphasized in light of issues and disadvantages of currently practiced processes. A method of Chemodialysis for the separation of acids using polymeric membranes, containing chemically active functional groups is proposed. Basis, methodology of evaluating this approach and anticipated advantages are discussed. This is followed by scope and objectives of the work. This chapter ends with the organization of thesis.

Chapter 2: (Title: Selection of membrane material)

Screening of chosen polymeric membrane materials for the transport of some acids and their separation from non-acidic solutes is given in this chapter. Three polymers containing amine functionality were chosen for membranes preparation and their investigation towards stability and acid transport properties. Aminated silicon rubber (ASR) and polyethyleneimine (PEI) were crosslinked during membrane preparation while one of the member of polybenzimidazole family (PBI-I) were

evaluated. Membranes based on ASR and PEI either showed low transport of lactic acid, accompanied by transport of glucose (co-solute) resulting in very low selectivity of acid over glucose. Moreover, stability of these membranes was weak. Owing to these observations, we decided to work on membrane materials bearing aromatic backbone to impart rigidity (and thus mechanical stability). Polybenzimidazole, known for high inorganic acid sorption was chosen for the purpose. One of the member of PBI family, obtained by polycondensation of *3,3'*-diaminobenzidene and isophthalic acid (PBI-I) showed transport of lactic acid, while transport of non-acidic co-solutes (like, aq. Et$_3$N, inorganic bases, glucose or NaCl) was beyond detection limit. Inspiring from these results, PBI was used as membrane material during further studies.

Chapter 3: (Title: Transport of organic acids through polybenzimidazole based membranes by Chemodialysis)

This chapter deals with the transport of organic acids through chosen variant of PBI family. Effect of operational parameters feed concentration, temperature, acid properties and structure of PBI on sorption and transport of acids through these membranes was investigated. Experimental section details synthesis of various PBIs, evaluation of their physical properties and dense membrane preparation method. Sorption and permeation properties of different acids (*viz*., acetic acid, lactic acid and citric acid) were investigated using dense membranes of these PBIs.

Though PBI based membranes showed poor acid transport using water as a stripping agent, they showed appreciable permeability using aq. alkali as a stripping agent. Transport of acid was found to be dependent upon various factors such as properties of transporting acid, stripping agent used, inherent properties of PBIs used for the membrane preparation and operational parameters (concentration of acid in the feed, stripping agent concentration and operational temperature). Significantly, these membranes showed no transport of non-acidic co-solutes used (NaCl, a representative of inorganic type and glucose as a representative of organic type of solutes). This leads to practically infinite selectivity of the transport of acids over non-acidic co-solutes. This was due to interaction of feed acid with basic PBI, which does not show sorption of nonacidic solute (and thus no transport following solution-diffusion mechanism).

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This method does not require external force for acid transport. The only energy is for solution circulation on feed and permeating sides of the membrane. It does not involve use of any chemicals (except stripping agent). It could be proved to be highly efficient, provided (i) acid could be stripped out as such (without using bases) and (ii) fluxes could be enhanced. With this as a goal, further efforts are given in the next chapter.

Chapter 4: (Title: Chemodialysis: Flux enhancement through PBI based membranes using porogen concept)

Use of base as a stripping agent in chemodialysis resulted in formation of salt of the transporting acid. To obtain acid, further treatment becomes necessary. An introduction of molecular level porosity in the membrane matrix would help to increase the transport rate; which would allow use of water as a stripping agent. Formation of porogen derived membranes (PDMs) was evaluated for this purpose. The chapter begins with introduction of porogen based membrane formation. Basis for selection of polyester, poly(phenolphthalein iso-terephthalate) (Ppha-IT) as a porogen is described. Experimental section details synthesis of Ppha-IT and its degradation using aq. alkali. Formation of PDMs, their physical, acid sorption and transport properties were evaluated subsequently.

Formed PDMs showed substantial increase in acid sorption and transport properties as compared with the dense membranes. Most significantly, these membranes showed good acid transport while using water as the stripping agent and its selectivity over NaCl and glucose was maintained.

Chapter 5: (Title: Application of chemodialysis for the transport of inorganic acids through polybenzimidazole based membranes)

Inorganic acids are a part of feedstock in different chemicals industries. The method of Chemodialysis using PBI based membranes were evaluated for the transport of chosen inorganic acids (HCl, HNO_3, H_2SO_4 and H_3PO_4). Experimental section of this chapter describes investigations of sorption and transport properties of inorganic acids through dense membranes and PDMs based on selected PBIs.

The PBI based dense membranes showed appreciable transport rate for different inorganic acids; depending upon polymer structure, acid properties and stripping agent used. Preparation of PDMs showed large increase (2.7 to 12.2 times) in permeability for various acids, with water as a stripping agent. It would result in economical benefits during the recovery and recycle of acids. This makes the method of 'Chemodialysis' an economically attractive and environmentally benign option for inorganic acid recovery.

Chapter 6: (Title: Conclusions)

The results obtained and conclusions drawn are summarized in this chapter.

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