ABSTRACT

SOLVENT RESISTANT MICROPOROUS/NANOPOROUS POLYMERIC HOLLOW FIBER AND FLAT FILM MEMBRANES AND THEIR APPLICATIONS

by
Praveen B Kosaraju

The separation and purification of organic-solvent-based process streams may be carried out by membrane processes such as nanofiltration/ultrafiltration/microfiltration and membrane solvent extraction. Lack of solvent stability and chemical stability of most commercially available membranes is limiting the utilization of the above mentioned membrane technologies. This dissertation was primarily focused on developing solvent resistant hollow fiber and flat film membranes for separation and purification of organic-solvent-based process streams.

Available porous polymeric supports (Polypropylene (PP), Polyethersulfone (PES) and Nylon) suitable for the required solvent-stable applications were chosen first and then the supports were modified to satisfy the requirements for the applications. Membrane modification techniques employed were interfacial polymerization (IP) and poly(ethyleneimine) (PEI) self crosslinking. Thin film composite (TFC) nanofiltration and ultrafiltration membranes were fabricated on PES, Nylon and hydrophilized PP support membranes. Before carrying out IP, PP was hydrophilized by pre-wetting with acetone and treating with hot chromic acid solution. The introduced procedure of "modified IP" involved wetting next with the aqueous monomer solution followed by the organic monomer solution. Nanofiltration membranes were characterized using solutes, safranin O (MW 351) and brilliant blue R (MW 826) dyes in methanol; ultrafiltration

membranes were characterized with a 70% alcoholic solution of zein (MW 35,000). These membranes were also studied for long term solvent stability in ethanol and toluene. The membrane based on PP was first hydrophilized by the techniques of "modified IP" and PEI self crosslinking. For possible applications in microfiltration of aqueous systems, these hydrophilized membranes were characterized by the water permeation rate. Crosslinking of PEI was implemented on the lumen side of the Nylon hollow fibers to reduce the pore size; then, their performance in membrane solvent back extraction was studied. Extraction of phenol from MIBK into an aqueous caustic solution was studied as a model system for reactive back extraction; extraction of acetic acid from MIBK into water was studied as a model system for nonreactive back extraction. Hollow fibers of PES were coated on the lumen side by IP. The IP layer was again coated with silicone to make the IP coating impervious to water. The coated PES fibers were then tested for heat transfer performance. All modified membranes were also characterized using scanning electron microscopy.

Thin film composite nanofiltration and ultrafiltration membranes were successfully fabricated on PP and PES hollow fiber supports; high rejections of solutes and high solvent fluxes were achieved in UF and NF membranes. However, only the PP-based TFC membranes retained their characteristics after solvent exposure for the studied period of time. Permanent hydrophilization of PP was achieved by the "modified IP" procedure. Reduced pores on the lumen side of Nylon hollow fibers provided stable aqueous-organic interface for solute transport in membrane solvent back extraction; the coating improved the extraction performance of the membranes. Better heat transfer performance was achieved in the coated PES hollow fibers when compared with the non-porous PP hollow fibers.

SOLVENT RESISTANT MICROPOROUS/NANOPOROUS POLYMERIC HOLLOW FIBER AND FLAT FILM MEMBRANES AND THEIR APPLICATIONS

by
Praveen B. Kosaraju

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

Otto H. York Department of Chemical Engineering

January 2007

APPROVAL PAGE

SOLVENT RESISTANT MICROPOROUS/NANOPOROUS POLYMERIC HOLLOW FIBER AND FLAT FILM MEMBRANES AND THEIR APPLICATIONS

Praveen b Kosaraju

Dr. Kamalesh K. Sirkar, Dissertation Advisor Date
Distinguished Professor of Chemical Engineering, NJIT

Dr. Marino Xanthos, Committee Member Date
Professor of Chemical Engineering, NJIT

Dr. Somenath Mitra, Committee Member Date
Professor of Chemistry and Environmental Science, NJIT

Dr. Jing Wu, Committee Member Date
Assistant Professor of Chemical Engineering, NJIT

Dr. Michael Jaffe, Committee Member Date
Research Professor of Biomedical Engineering, NJIT

BIOGRAPHICAL SKETCH

Author: Praveen B Kosaraju

Degree: Doctor of Philosophy

Date: January 2007

Undergraduate and Graduate Education:

- Doctor of Philosophy in Chemical Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2007
- Master of Science in Chemical Engineering,
  New Jersey Institute of Technology, Newark, NJ, 2002
- Bachelor of Science in Chemical Engineering,
  Bangalore University, Bangalore, India, 1999

Major: Chemical Engineering

Presentations and Publications:

Kosaraju, P. B.; Korikov, A. P.; Sirkar, K. K., Interfacially polymerized thin film composite membranes based on microporous polypropylene hollow fibers. AIChE Annual Meeting, San Francisco, CA, Nov 14, 2006.

Kosaraju, P. B.; Sirkar, K. K., Novel solvent resistant hydrophilic hollow fiber membranes for membrane solvent back extraction. AIChE Annual Meeting, San Francisco, CA, Nov 13, 2006.

Kosaraju, P. B.; Korikov, A. P.; Sirkar, K. K., Interfacially polymerized thin film composite membranes based on microporous polypropylene flat films and hollow fibers. NAMS Annual Meeting, Chicago, IL, May 17, 2006.

Kosaraju, P. B.; Sirkar, K. K., Novel solvent resistant hydrophilic hollow fiber membranes for membrane solvent back extraction. Poster session: NAMS Annual Meeting, Chicago, IL, May 15, 2006.

Kosaraju, P. B.; Sirkar, K. K., Novel solvent resistant hydrophilic hollow fiber membranes for membrane solvent back extraction. AIChE Annual Meeting, Cincinnati, OH, Nov 3, 2005.

Kosaraju, P. B.; Kovvali, A. S.; Korikov, A. P.; Sirkar, K. K., Hollow fiber membrane contactor based CO_2 absorption-stripping using novel solvents and membranes. NAMS Annual Meeting, Providence, RI, June 14, 2005.

Kosaraju, P. B.; Sirkar, K. K., Novel solvent-resistant hydrophilic hollow fiber membranes for efficient membrane solvent back extraction. J. Membr. Sci. (accepted for publication). This paper was selected for the AIChE separations division graduate student award in the area of extraction.

Korikov, A. P.; Kosaraju, P. B.; Sirkar, K. K., Interfacially polymerized hydrophilic microporous thin film composite membranes on porous polypropylene hollow fibers and flat films. J. Membr. Sci. 2006, 279, 588-600.

Kosaraju, P. B.; Kovvali, A. S.; Korikov, A. P.; Sirkar, K. K., Hollow fiber membrane contactor based CO_2 absorption-stripping using novel solvents and membranes. Ind. Eng. Chem. Res. 2005, 44, 1250-1258.

Kosaraju, P. B.; Sirkar, K. K., Interfacially polymerized thin film composite membranes on microporous polypropylene support for solvent resistant nanofiltration. (manuscript in preparation).

To my beloved family and friends for their love, support and encouragement

ACKNOWLEDGMENT

First and foremost, I would like to thank my advisor, Dr. Kamalesh K Sirkar for introducing me to this exciting area of membrane science and technology and providing me with most valuable guidance and heartfelt support all through my graduate education. He has always been a source of encouragement and knowledge. His perseverance, sincerity and hardworking qualities will always serve as an inspiration to me.

I would like to thank Dr. Marino Xanthos, Dr. Somenath Mitra, Dr. Jing Wu and Dr. Michael Jaffe, who were kind enough to actively participate in my dissertation committee, providing constructive criticisms and valuable suggestions at all stages of this work. I would also like to thank Dr. Reginald Tomkins and Dr. Basil Baltzis for their help and guidance throughout my studies at NJIT.

I express my deep gratitude to Center for Membrane Technologies at NJIT, which provided me with an opportunity and platform for fulfilling my dreams and desire to reach my goals. I would like to thank Dr. Baoan Li and Dr. Liming Song for testing the heat transfer performance of the fabricated membrane modules. A special thanks goes to Dr. Alexander Korikov for his guidance and involvement in successfully achieving the hydrophilization of flat polypropylene supports. I would also like to thank all members of the research group for their help and guidance in carrying out the research. Jin U Ha's help with FT-IR is also acknowledged herewith.

Finally, no words are enough to acknowledge the constant support and encouragement of my family, especially my parents. Thank you. Lastly, a special note of thanks goes to all my friends who stood with me at all times. I cherish their friendships.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

Chapter **Page**

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF SYMBOLS

A_m	mass transfer area of the hollow fiber modules, cm^2
C_{aq}	concentration of solute in aqueous phase, mol/cm^3
C_{feed}	concentration of solute in the feed solution, g/ cm^3
C_{org}	concentration of solute in organic phase, mol/cm^3
$C_{permeate}$	concentration of solute in the permeate, g/ cm^3
C_p	specific heat, J/(kg K)
ΔC_{LM}	logarithmic mean concentration difference, mol/cm^3, equation (2.3b)
d_i	inner diameter of a hollow fiber, cm
d_o	outer diameter of a hollow fiber, cm
d_{lm}	logarithmic mean diameter of a hollow fiber, cm
D_{Ao}, D_{Aw}	diffusion coefficient of solute in organic, aqueous phase, cm^2/s
D_h	hydraulic diameter of the shell side of hollow fiber module, cm
k_{mo}, k_{mw}	membrane transfer coefficient when membrane is filled up with organic phase, aqueous phase, cm/s
k_o	organic phase film transfer coefficient, cm/s
k_w	aqueous phase film transfer coefficient, cm/s
K_o	overall mass transfer coefficient based on organic phase, cm/s
L	length of hollow fiber module, cm
m	distribution coefficient of solute between organic and aqueous phase, $(\text{gmol/cm}^3)\big\vert_{\text{org}} / (\text{gmol/cm}^3)\big\vert_{aq}$
$\dot{m}$	mass flow rate, kg/s

LIST OF SYMBOLS
(Continued)

N_{Gz}	Graetz number, $\pi d_i N_{\mathrm{Re}-t} N_{Sc-t}/4L$
$N_{\mathrm{Re}-t}, N_{\mathrm{Re}-s}$	tube-side and shell-side Reynolds numbers, $d_i v/\eta_o$, $D_h v_e/\eta_w$
N_{Sc-t}, N_{Sc-s}	tube-side and shell-side Schmidt numbers, η_o/D_{Ao}, η_w/D_{Aw}
N_{Sh-t}, N_{Sh-s}	Sherwood number, $k_o d_i/D_{Ao}$, $k_w D_h/D_{Aw}$
ΔP	transmembrane pressure, kPa
ΔP_b	breakthrough pressure, kPa
Q	rate of heat transfer, W
Q_{aq}	aqueous phase flow rate, cm^3/s
Q_{org}	organic phase flow rate, cm^3/s
r_i	inner radius of hollow fiber, cm
r	radial location in a hollow fiber, cm
r_+	r/r_i
R	percentage rejection of solute, %
t	thickness of membrane, cm
T_s	shell side temperature, K
T_t	tube side temperature, K
ΔT	temperature difference, K
ΔT_{lm}	logarithmic mean temperature difference, K
U	overall heat-transfer coefficient, $W/(m^2K)$
v	velocity, cm/s
v_e	velocity based on empty shell side cross-sectional area, cm/s

LIST OF SYMBOLS
(Continued)

Greek letters

ϕ	packing fraction of shell side of hollow fiber modules
ε_m	porosity of membrane
τ_m	membrane tortuosity
η_o, η_w	kinematic viscosity of MIBK, water, cm^2/s

CHAPTER 1

INTRODUCTION

In separation and purification activities pursued in chemical, petrochemical, pharmaceutical, biotechnology, textile, food and beverage industries, a variety of organic-solvent-based process streams are encountered. The separation and purification of such solutions may be carried out by nanofiltration/ultrafiltration/microfiltration membranes. [1-16] Lack of solvent stability and the chemical stability of most commercially available membranes is limiting the utilization of membrane technologies in the above mentioned industries. Currently available membranes that are claimed to be solvent resistant are generally too expensive; others are not truly solvent resistant.[4, 14, 17, 18] Similarly, solvent resistant hydrophilic membranes with the required pores sizes for membrane solvent back extraction are not available.[19]

1.1 Membrane Processes, Membranes and their Preparation

The pressure-driven membrane processes of interest in this study are nanofiltration, ultrafiltration and microfiltration. Driven by the applied pressure gradient, the solvent permeates in these processes through the membrane and the solutes will be rejected. As we go from microfiltration, through ultrafiltration and nanofiltration, the size of the solutes diminishes; consequently the pore sizes in the membrane must be smaller. As the pore sizes in the membrane become smaller, the applied pressures have to be increased to achieve reasonable solvent permeation rates. The pore sizes of the membranes and the applied pressure ranges of microfiltration, nanofiltration and ultrafiltration are presented in Table 1.1.

Table 1.1 Membrane Pore Size and Applied Pressure Range for Microfiltration, Ultrafiltration and Nanofiltration

Membrane process	Pore sizes (nm)	Pressure range (bar)
Microfiltration	50 to 10,000	0.1 to 2
Ultrafiltration	1 to 150	1 to 5
Nanofiltration	< 2	5 to 20

Membranes are classified based on different criteria; classification of membranes according to the morphology is relevant to this study. Membranes are primarily classified as symmetric and asymmetric membranes based on the membrane morphology. Figure 1.1 illustrates this classification along with the morphology of different membranes. Pore dimensions of symmetric membranes will be uniform throughout the cross section of the membrane. Thickness of symmetric membranes range roughly from 10 to 200 μm. Resistance to mass transfer is determined by the membrane thickness and a decrease in membrane resistance will result in an increased permeation rate. Asymmetric membranes consist of a very dense top layer or skin having a thickness of 0.1 to 0.5 μm supported on a porous sublayer of about 50 to 150 μm thickness. The skin or the selective layer in the asymmetric membrane largely controls the membrane properties; hence asymmetric membranes have the advantage of high permeation rates resulting from the thin selective layers.[20]

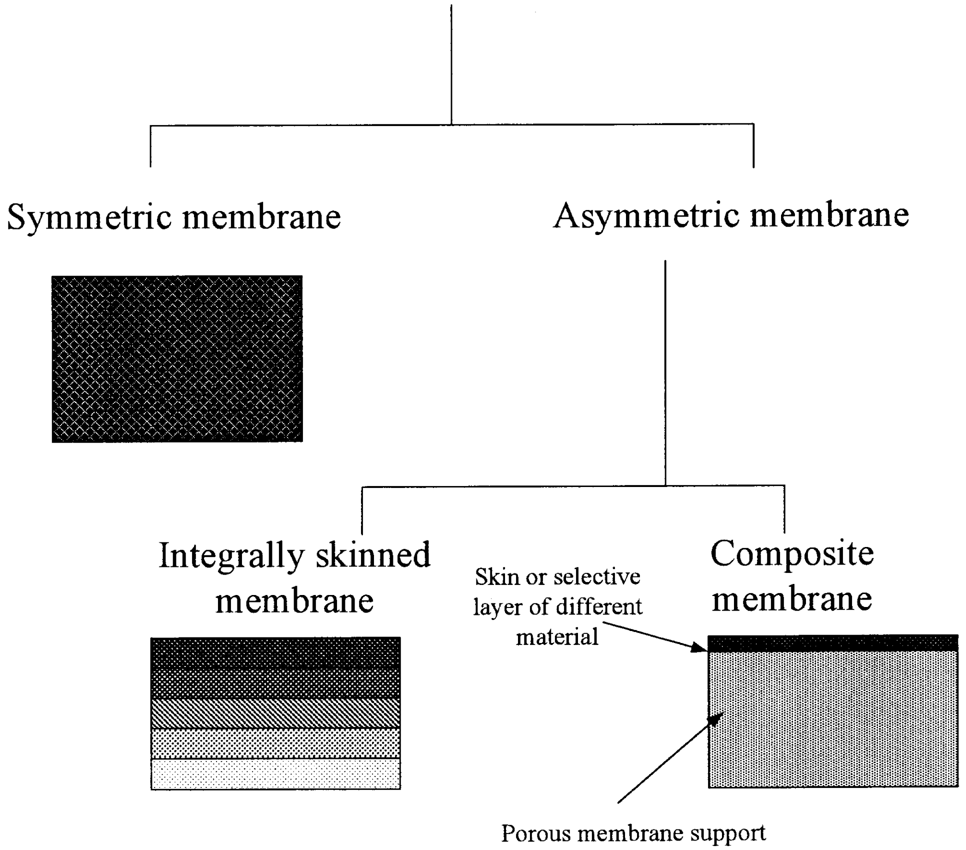

Figure 1.1 Classification of membranes based on membrane morphology.

Table 1.2 summarizes commonly employed manufacturing methods for synthetic membranes as well as the membrane materials commonly used.[20, 21] Pores of microfiltration membranes are larger; therefore symmetric membranes having large-sized pores are good enough to generate higher fluxes required in microfiltration. It is not necessary to employ asymmetric membranes to generate higher fluxes in microfiltration. Hence microfiltration membranes are in general symmetric membranes. Techniques for fabrication of symmetric membranes are sintering, stretching, track-etching and phase inversion. Among these techniques, phase inversion can produce ultrafiltration as well as dense membranes; the rest of the techniques can only produce membranes with pores in the microfiltration range. Symmetric membranes prepared from hydrophobic materials such as polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF) and PP are often used for microfiltration. These materials exhibit good chemical and thermal stability, but water can not wet these membranes spontaneously because of their hydrophobicity. Therefore, these membranes have to be prewetted (usually by ethanol) when used with aqueous solutions.

Table 1.2 Membrane Manufacturing Methods and Membrane Materials

Process	Materials
Phase inversion by solvent evaporation	Cellulose acetate (CA), polyamide
Phase inversion by temperature change	Polypropylene, polyamide (PA)
Phase inversion by precipitant addition	Polysulfone (PS), polyethersulfone (PES)
Stretching sheets of partially crystalline polymers	Polytetrafluroethylene(PTFE), Polypropylene(PP)
Track-etching	Polycarbonates (PC), polyester
Interfacial polymerization	Selective layer: polyamide

Asymmetric membranes can be further classified as integrally skinned membranes and composite membranes. The selective layer and the support are made up of the same material in integrally skinned membranes. Integrally skinned asymmetric membranes are generally fabricated by the technique of phase inversion. In phase inversion, a polymer solution is transformed in a controlled manner from a liquid state to a solid state. By controlling the initial stage of phase transition, the membrane morphology can be controlled. Symmetric, asymmetric, porous and nonporous membranes can be prepared by the technique of phase inversion.

In composite membranes, the selective layer originates from a membrane material different from the support. Most composite membranes are thin film composite (TFC) membranes; “thin film” refers to a thin selective layer on the support. The major advantage of TFC membranes is that the selective layer and the support can be optimized individually to achieve the desired membrane properties with respect to selectivity, permeation rates, and chemical and thermal stability. Dip-coating, interfacial polymerization and plasma polymerization are a few of the established methods for fabrication of thin film composite membranes.[20] Dip-coating makes membranes with a very dense skin; composite membranes prepared by dip coating are used for reverse osmosis, gas separation and pervaporation. Another method of applying a very thin dense layer upon a porous support is via plasma polymerization. Plasma is obtained by the ionization of a gas by means of an electrical discharge at high frequencies and precipitated on the support membrane surface. The structure of the resulting polymer is generally difficult to control. Coating the lumen side of the hollow fibers via plasma polymerization is difficult to achieve. The technique used in the current study for fabrication of TFC membranes is interfacial polymerization (IP). More details about this technique are provided in Section 1.5.1.

1.2 Solvent Stable Membranes for Different Membrane Applications

Membrane processes such as microfiltration, ultrafiltration, nanofiltration and membrane solvent back extraction demand solvent stable membranes when the processes involve organic solvents. These membrane processes and the solvent stability of the membranes for organic solvents will be discussed in this section.

1.2.1 Solvent Resistant Nanofiltration/Ultrafiltration Membranes

Nanofiltration has gained a lot of attention because of its low operation and maintenance costs.[22] Nanofiltration is well established for aqueous systems whereas it is still under development for non-aqueous systems mainly due to lack of appropriate solvent resistant nanofiltration membranes.[4, 14] The applications of solvent resistant nanofiltration membranes (SRNF) are however rapidly increasing. These include: materials recovery from fermentation broth or whey, dyeing industry, separation of active pharmaceutical compounds (antibiotics), residual reactants or solvents in pharmaceutical synthesis, separation of homogeneous catalysts from organic solutions, separation of mineral oil from organic solvents, separation of free fatty acids from vegetable oil and separation of light hydrocarbon solvents from lube filtrates.[1-10, 14, 22-25] Polymeric membranes after contact with an organic solvent may suffer from swelling or dissolution/disintegration of membranes or relaxation of polymer chains due to plasticization in solvent. This results in a loss of membrane characteristics. Commercially available SRNF membranes have been explored for a number of applications and their solvent stability was studied.[4, 14] It was reported that the membranes claimed to be solvent resistant failed in the long run.[14] A number of novel SRNF membranes are also under development.[4, 12, 13, 26]

Nanofiltration membranes are generally fabricated by the method of making composite membranes.[27, 28] Thin film composite (TFC) membranes via interfacial polymerization is the most effective method as these membranes provide high fluxes over other nanofiltration membranes.[22] In TFC by IP, reactive monomers are dissolved in two immiscible phases and the polymerization of the reactive monomers takes place on the surface of the porous support membrane. The benefit of TFC by IP is that the membrane properties can be controlled by optimizing the characteristics of the selective layer and support. The selective layer can be optimized for solute rejection and solvent flux by controlling the coating conditions and characteristics of the reactive monomers.[29] The microporous support can be selectively chosen for porosity, strength and solvent resistance. The support membranes generally used are ultrafiltration membranes of polysulfone or polyethersulfone; these supports have limited stability for organic solvents. They can not handle aromatic hydrocarbons, ketones, ethers and esters.[17, 18, 21] Hence the TFC fabricated from these supports can not be utilized for solvent resistant nanofiltration applications.

Organic solvents are being increasingly used in extraction, purification and processing of pharmaceuticals, food and flavor compounds.[11-13] Ultrafiltration would be the method of choice for separating the desired compounds and for recycling the solvents if solvent stable ultrafiltration membranes can be employed. Most ultrafiltration membranes are manufactured by the phase inversion process. During the membrane fabrication by the process of phase inversion, the polymers are dissolved in organic solvents. Hence, the membranes are likely to swell or dissolve in the organic solvents during the usage leading to the changes in solvent flux or solute rejection.[17, 18] As the stability of the polymer increases, it generally becomes more difficult to process the polymer into a membrane. Stability and processability of the polymer oppose each other.[20]

Shukla and Cheryan[17] screened a number of ultrafiltration membranes for solvent stability and tested some of the membranes claimed to be solvent resistant for stability in aqueous ethanol solution. Out of a number of ultrafiltration membranes tested, cellulose and polysulfone-based membranes failed in a few weeks of solvent exposure. Although polyacrylonitrile-based membranes appeared to have the longest stability periods among the tested membranes, their performance declined slowly with time.[17] This clearly indicates the need for solvent stable membranes for ultrafiltration. Limitations of some of the commercially available ultrafiltration membranes are listed in Table 1.3.[20, 21]

Table 1.3 Limitations of Commercial Ultrafiltration Membranes

Membrane	Limitations
Cellulose acetate	Narrow temperature range ($T_{max} = 30°C$) Narrow pH range (3 to 6) Highly susceptible to microbial attack
Polysulfone, Polyethersulfone	Poor stability for aromatic hydrocarbons, ketones, ethers and esters Low pressure limits (100 psig (790 kPa) for flat sheets and 25 psig (274 kPa) for hollow fibers)
Regenerated cellulose	Is stable to only alcohols
Polyvinylidene fluoride	Hydrophilized PVDF cannot withstand caustic conditions

1.2.2 Solvent Resistant Hydrophilic Microfiltration Membranes

Hydrophobic materials such as PTFE, PVDF and PP are often used for microfiltration; they can withstand wide pH ranges, and exhibit good chemical and thermal stability. But their use in aqueous systems such as water purification/recovery in beverage industry, pulp and paper, and food processing industry has been limited because of their high hydrophobicity.[15] Water can not wet these membranes spontaneously because of their hydrophobicity. These membranes have to be prewetted (usually by ethanol) when used with aqueous solutions. Their use in biotechnology and food industries is also limited because of the biofouling that results from the hydrophobic nature of these membranes.[16]

Microfiltration membranes from PTFE may be prepared by sintering and stretching whereas PVDF membranes are made by phase inversion. Microporous membranes can be formed from polyolefins such as polypropylene and polyethylene by the thermally induced phase separation (TIPS) process or high melt stretch extrusion process.[15, 20] Out of these membrane materials and membranes, polypropylene or polyethylene base materials are of low cost and the membrane fabrication processes for PP or PE are well established. PP membranes possess many desirable properties such as high void volumes, well controlled porosities, usable over wide pH ranges and high chemical stability.[15] Because of these reasons, the polypropylene or polyethylene membranes are very attractive. Hydrophilizing such an inexpensive membrane from PP or PE would allow the use of membrane microfiltration technologies in food, beverage, biotechnology, pulp and paper industries and water purification/recovery systems.[15, 16] Although hydrophilic PVDF membranes are commercially available, they can not sustain alkaline conditions and hence cleaning of the membranes is problematic.

1.2.3 Solvent Resistant Hydrophilic Membranes for Membrane Solvent Back Extraction

Nondispersive membrane solvent extraction is being extensively used and studied for a number of applications including extraction of metals, pollutants and pharmaceutical products.[19, 30-43] Large-scale industrial installations exist.[35, 36] Membrane solvent extraction (MSE) is generally followed by membrane solvent back extraction (MSBE) for regeneration of organic solvents contaminated with metals and pollutants from the feed stream.[19, 44-47] Membrane solvent extraction as well as membrane solvent back extraction have the following wellknown advantages: dispersion-free operation eliminates emulsion formation, phase entrainment and the separation of aqueous and organic phases after achieving the required separation; no limitation on the phase flow rate ratio and density differences; highly compact devices. Additional advantages are discussed in the literature.[39-42]

In MES/MSBE, two immiscible phases (the aqueous phase and the organic phase) will be flowing on either side of the membrane and membrane pores will be filled with one of the phases. Hydrophobic membrane pores can only be filled with aqueous phase whereas the hydrophilic membrane pores can be filled either with aqueous phase or the organic phase. When the phase that fills the membrane pores is maintained at an equal or lower pressure than the other phase, the aqueous-organic phase interface will be immobilized at each pore mouth. One or more solutes can be transferred between the two immiscible phases through the immobilized interface. Schematic of the immobilization of the aqueous-organic interface at the pore mouth of the hydrophilic membrane with aqueous phase filled pores is shown in Figure 1.2.

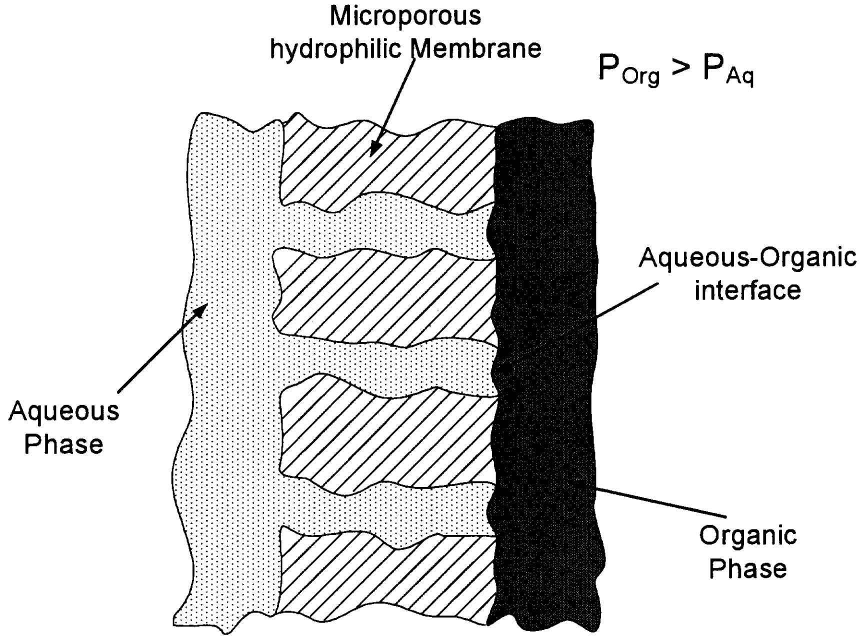

Figure 1.2 Schematic of the immobilization of the aqueous-organic interface at the pore mouth of the hydrophilic membrane with aqueous phase filled pores.

In MSE/MSBE, the overall mass transfer rate of solute is controlled in general by the boundary layer resistances on both sides of the membrane and the membrane resistance; the membrane resistance appears due to the liquid phase occupying the membrane pores.[41] Membrane-based solvent extraction introduces this additional resistance of the membrane phase to the solute mass transfer processes. Membrane resistance is reduced if the solute prefers the phase in the membrane pores.[19, 41-43] In back extraction, the solute should prefer the aqueous phase. Therefore, it is necessary to have a hydrophilic membrane with the aqueous phase in the pores. It is well known in the literature.[19, 41, 42] One can achieve it by employing hydrophilic membranes; however such membranes have to be resistant to organic solvents. Hydrophobic membrane pores can be filled only with the organic phase and are advantageous only for membrane solvent extraction. On the other hand, pores of the hydrophilic membranes can be filled either with the organic phase or with the aqueous phase and nondispersive operation can be carried out as long as the correct phase pressures are maintained.[31] Hence, hydrophilic membrane modules can be used for efficient solvent extraction as well as solvent back extraction. Porous hydrophilic membrane modules are potentially advantageous in that a single kind of membrane module (hydrophilic) can be used for both solvent extraction and solvent back extraction.[19, 31, 41]

Basu et al.[19] have studied membrane solvent back extraction of phenol from MIBK by aqueous caustic solution employing flat porous films of hydrophilic Nylon 6 and Celgard polypropylene hydrophobic membranes. Higher overall mass transfer coefficients were observed in Nylon-based hydrophilic membranes over polypropylene hydrophobic membranes since the membrane pores were filled with the aqueous solution in Nylon-based hydrophilic membranes.[19] Lin and Juang[46] have studied extraction and back extraction of metallic cations and anions in hydrophobic hollow fiber membranes modules; organic phase was in the membrane pores for the back extraction. They reported that extraction was governed mostly by aqueous-layer diffusion, whereas back-extraction was governed by membrane diffusion and organic-layer diffusion. Very similar results were reported by Ortiz et al.[47] for simultaneous extraction and back extraction of chromium(VI) carried out using hydrophobic fibers. D'Elia et al.[42] concluded that extraction in hollow fibers will be the fastest when the fibers are wetted by the fluid in which the solute is more soluble. These results indicate the existence of considerable additional membrane resistance in MSBE when hydrophobic membranes are employed. These studies support the earlier argument of using hydrophilic membranes to reduce the membrane resistance and suggest the use of solvent resistant hydrophilic membranes for efficient membrane solvent back extraction.

In addition to hydrophilicity and solvent-resistant nature of the membranes for MSBE, it is critical to have optimum pore sizes as it influences the breakthrough pressure. Some immiscible aqueous-organic phase systems such as water-n-butanol and water- methyl isobutyl ketone (MIBK) have lower interfacial tensions; some solutes to be extracted behave as surfactants and reduce the interfacial tension of the immiscible phase systems.[41] Membranes with small pore sizes are required for such systems as the breakthrough pressure, ΔP_b, is proportional to the interfacial tension and inversely proportional to the pore size:

$$\Delta P_b = \frac{2\gamma\cos\theta}{r} \tag{1.1}$$

Here γ is the interfacial tension, r is the pore radius and θ is the contact angle. Microfiltration membranes offer relatively low mass transfer resistance to solute transport, but usually have low breakthrough pressures.[48] Low breakthrough pressures create problems of phase dispersion even at reasonable transmembrane pressure differences and affect operational stability.

For example, Basu et al.[19] reported that when porous hydrophilic hollow fibers (Nylon 6) were used with the water-MIBK system and the organic phase was passed through the lumen side, nondispersive operation could not be carried out above 3.5 kPa pressure difference between the phases. Larger pores on the inner surface (ID) of the porous Nylon fibers could not provide stable immobilized aqueous-organic interface even at low transmembrane pressures. In contrast to microporous solvent-resistant membranes, employment of solvent-resistant nanofiltration membranes will increase the breakthrough pressures; however the overall mass transfer coefficients will be drastically reduced especially if nonporous membranes are used.[48, 49] Hence, one has to employ solvent-resistant hydrophilic membranes with optimum pore sizes that would provide a higher breakthrough pressure and lower membrane mass transfer resistance for successful utilization of membrane technology in solvent back extraction. Ultrafiltration membranes of membrane materials such as polysulfone and polyethersulfone do not tolerate organic solvents well. The nature of the thick skin of these asymmetric membranes offers high resistance to solute mass transfer. Hydrophilic solvent resistant membranes having the desired properties are not available.

1.2.4 Thin Film Composite Membranes for Heat Transfer Applications

Plastic heat exchangers are of increasing interest for lower temperature applications because of their better chemical resistance and fouling characteristics.[50, 51] Polymers are less expensive; their densities are much lower resulting in lower construction, transportation and installation costs of the heat transfer modules.[52, 53] Polymeric hollow fiber membrane modules also provide much higher surface area per unit volume ratios compared with shell and tube heat exchangers. However, thermal conductivities of polymer materials are 100 to 300 times lower than that of metals.[51] For the polymers to compete with the performance of the metals, one has to use polymers of very thin walls.[54]

Polypropylene-based solid nonporous hollow fibers of 77.5 μm wall thickness were explored by Zarkadas and Sirkar[54] and superior heat transfer performance was reported. Heat transfer performance of the solid polymeric hollow fibers can be further improved by moving from solid nonporous membranes to porous asymmetric membranes having an impervious coating.[51] Therefore, membrane modification for heat transfer is another interesting application where the available asymmetric microporous membranes can be modified to enhance heat transfer performance of the polymeric hollow fibers.

1.3 Approach

Available polymeric supports suitable for the required solvent-stable applications are chosen first and then the supports are modified to satisfy the application requirements. Coating the membrane surface and/or pores to satisfy the specific requirement is referred to as membrane modification. Hydrophobic supports chosen were polypropylene (PP) microfiltration hollow fibers and flat film membranes. Hydrophilic supports chosen were Nylon-based microfiltration hollow fiber membranes and polyethersulfone (PES) ultrafiltration hollow fiber membranes.

Thin film composite nanofiltration and ultrafiltration membranes based on hydrophilized polyolefinic membrane supports such as polypropylene were fabricated to fulfill the need for solvent stable membranes for many applications in nonaqueous systems. Relatively inexpensive hydrophilic supports from polymers such as Nylon and PES were also coated with a solvent stable coating to meet the requirements for increasing number of applications of solvent-stable membranes in nonaqueous systems as well as applications. Since the selective layer will determine the membrane separation characteristics in TFC membranes, solvent stable coating on PES may provide stable performance in organic solvent systems.

Hollow fiber membrane modules were coated on the lumen side to reduce the pore sizes so that the reduced pores will provide stable aqueous-organic interface for solute transport. For heat transfer applications, the hollow fibers modules were coated on the lumen side with an impervious coating. The lumen side was further coated with a hydrophobic layer to make the first layer of coating impervious to water.

Coating the inner diameter of hollow fiber membranes was the principal objective in this study rather than coating of flat films because of the well known advantages of hollow fiber membranes over flat films. However, flat membranes are suitable for many applications in spiral wound form; therefore flat polypropylene membranes were also coated to study their potential applications in nanofiltration. In addition to nanofiltration applications, hydrophilization of flat hydrophobic polypropylene membranes was studied as it is convenient to work with flat films rather than hollow fiber membrane modules which have to be fabricated from hollow fibers.

Membrane modification techniques primarily employed were interfacial polymerization, “modified IP” and self crosslinking of poly(ethyleneimine) (PEI). These techniques are discussed in detail in Section 1.5. Coating techniques studied and the supports chosen for different membrane separation applications are listed in Table 1.4.

1.4 Support Membranes

Polypropylene (PP) is a very attractive material as a support for forming a thin film composite membrane due to its high durability and resistance to chemicals, pH variations and a substantially wide range of solvents.[15] The PP hollow fiber and flat film membranes used in this study are from Celgard Inc. (Charlotte, NC). Celgard Inc. developed the technology of making microporous PP membranes by melt stretch extrusion. Celgard PP membranes (both flat and hollow fiber) are probably the highest quality microporous PP membranes available. They are symmetric membranes with elliptical pores; the average pore size is 0.042 μm by 0.117 μm (short axis and long axis, respectively) with the membrane thickness equal to 25 μm and volume porosities ranging from 30% to 40% as reported.[55, 56] The elliptical pore structure of Celgard 2400 PP flat film membranes is provided in Figure 1.3. The hollow fiber membranes, Celgard X-10 and Celgard X-20, also have a similar pore structure; Celgard X-10 PP hollow fiber membranes are available with a smaller inner diameter of 240 μm whereas X-20 PP fibers are available with a larger inner diameter of 400 μm. Using microfiltration membranes rather than the ultrafiltration membranes as a support would increase the solvent flux of TFC membranes[57] and hence can be operated at lower pressures to achieve reasonable fluxes. Since polypropylene is hydrophobic, the polypropylene support has to be hydrophilized to fabricate a TFC membrane.

Table 1.4 Membrane Modification Techniques and the Supports Used for Different Membrane Applications

Support	Applications			
	Ultrafiltration/ Nanofiltration	Microfiltration	Solvent extraction	Heat transfer
PP (HF*, FS**)	IP (HF, FS)	"Modified IP", PEI crosslinking (FS)	"Modified IP" (FS)	-
PES (HF)	IP	-	-	IP followed by silicone coating
Nylon (HF)	IP	-	IP, PEI crosslinking	

* Hollow fiber membranes
** Flat sheet membranes

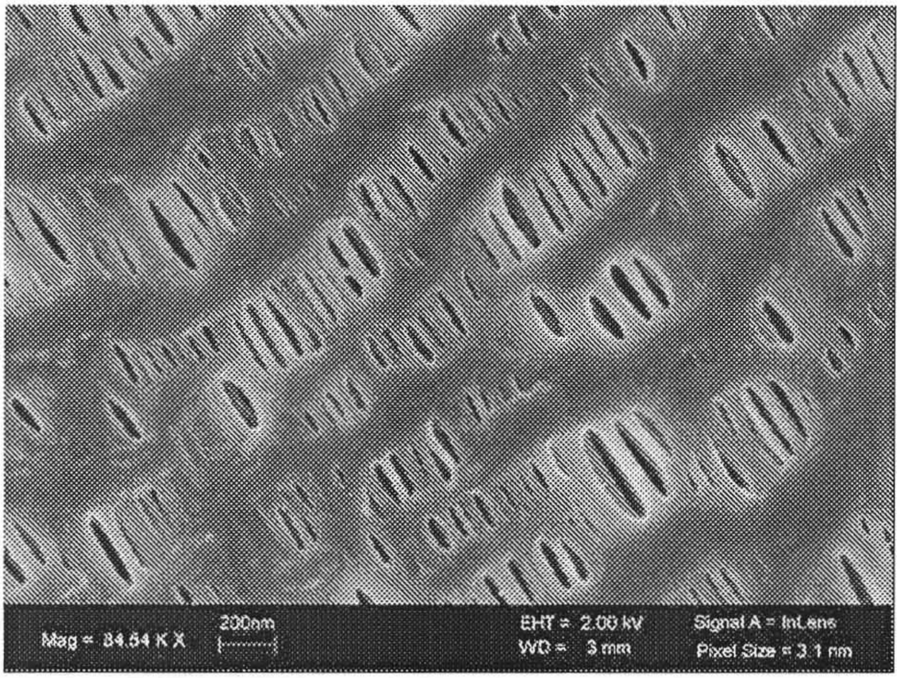

Figure 1.3 Pore structure of Celgard PP flat film membranes.

The hollow fiber membranes of PES used were ultrafiltration membranes with 70 kD molecular weight cut off.[58] These fibers were supplied by Membrana Inc. (Wuppertal, Germany), under the trade name UltraPES. They are partially hydrophilic and asymmetric membranes having a skin on both the ID (inner diameter) and the OD (outer diameter) of the fiber. Cross section of the PES membrane is shown in Figure 1.4.

Nylon hollow fiber membranes used were asymmetric microfiltration membranes. They are hydrophilic membranes from ENKA America Inc. (Ashville, NC). Scanning electron microscopy-based (SEM) pictures of ID and the OD of Nylon hollow fiber membranes are shown in Figure 1.5 and Figure 1.6, respectively. Table 1.5 provides characteristics of PP, PES and Nylon support membranes.

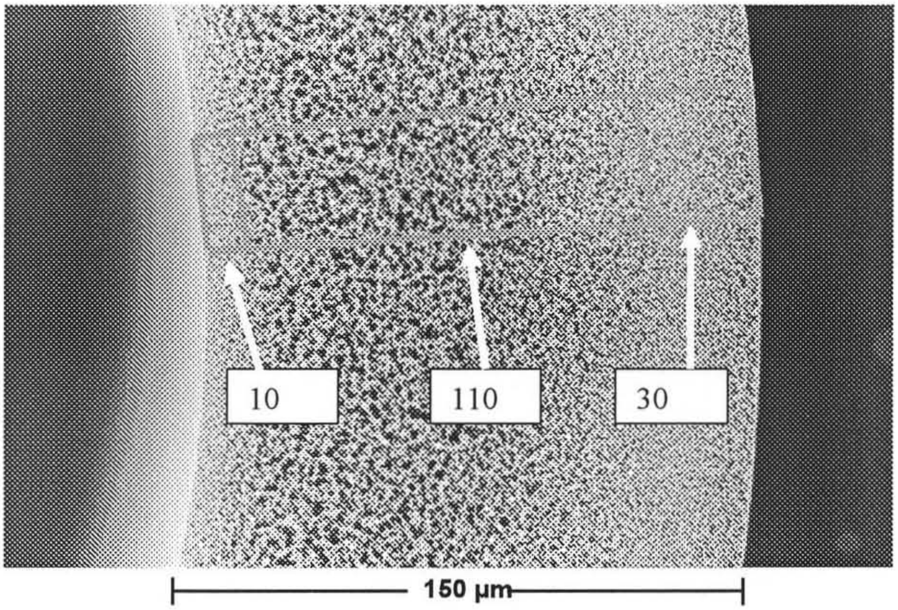

Figure 1.4 Cross section of PES membrane.[58]

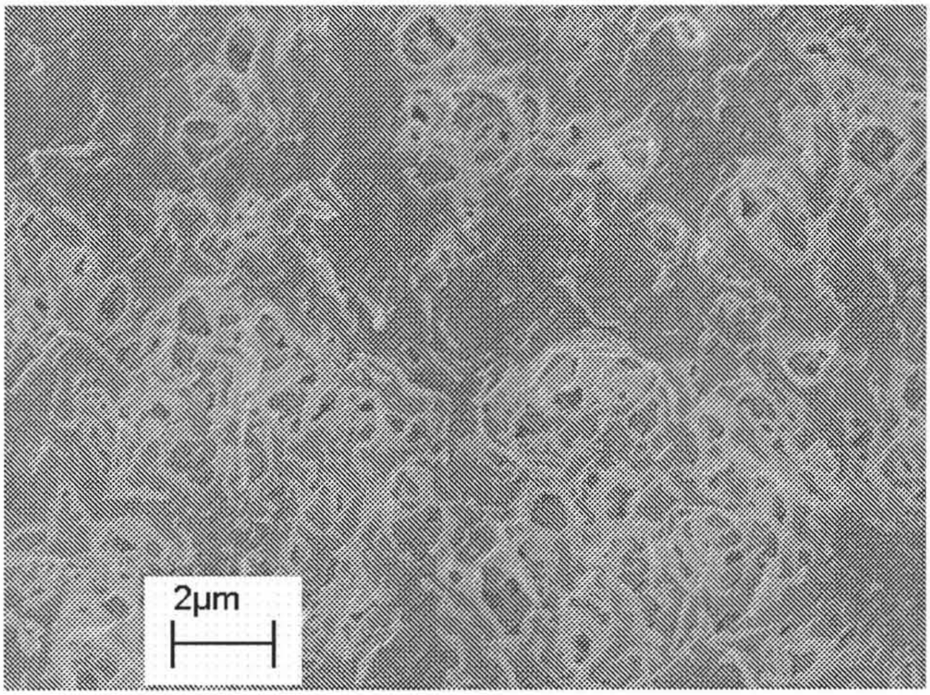

Figure 1.5 ID of Nylon hydrophilic hollow fiber membrane.

Table 1.5 Characteristics of the Porous Support Membranes

Support membrane	Membrane material	Membrane geometry	Hydrophilicity/ hydrophobicity of the membrane	ID, µm	Wall thickness, µm	Porosity	Pore size
Calgard 2400	Polypropylene	flat film	Hydrophobic	-	25	0.37	0.117 µm x 0.042 µm
Celgard X-10	Polypropylene	Hollow fiber	Hydrophobic	240	25	0.3	0.117 µm x 0.042 µm
Celgard X-20	Polypropylene	Hollow fiber	Hydrophobic	400	25	0.4	0.117 µm x 0.042 µm
Nylon 6	Nylon 6	Hollow fiber	Hydrophilic	600	200	0.75	0.2 to 1 µm
UltraPES	Polyethersulfone	Hollow fiber	Partially hydrophilic	700	150	0.68	*MWCO:70 kD

*MWCO-Molecular weight cut off

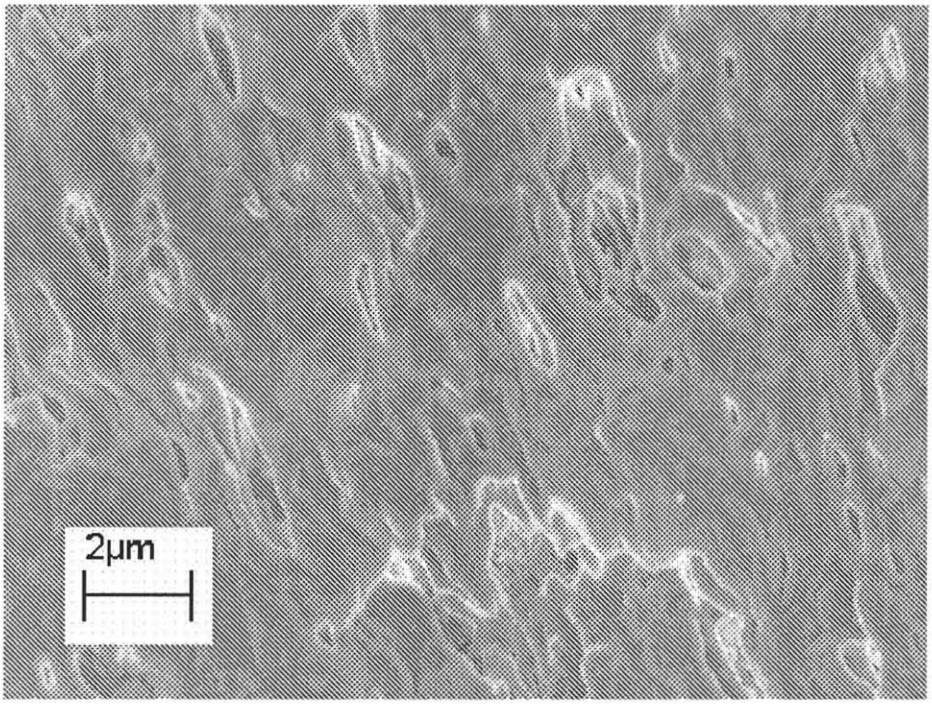

Figure 1.6 OD of Nylon hydrophilic hollow fiber membrane.

1.5 Coating Techniques

1.5.1 Interfacial Polymerization

Interfacial polymerization is a method of polymerization by polycondensation at relatively low temperatures. Reactive reagents or monomers are dissolved in two immiscible phases. When the two immiscible phases having reactants are brought into contact, formation of the polymer takes place at the interface of two immiscible liquids; hence it is called interfacial polymerization. The two immiscible phases used in general are an aqueous phase and an organic phase. A compound containing active hydrogen in the functional group (e.g., amine, phenol) is used as the aqueous phase monomer. An acid halide is used as the other reactive monomer in the organic phase. Coating the support membranes with poyamide is the objective in this study; polyamides can be synthesized from aliphatic or aromatic diacid halides with aliphatic and alicyclic diamines. The terms "diacid halide" and "diamine" are used in the thesis to refer to organic phase and aqueous phase monomers although multiacid halides and multiamines are also used as monomers. Polymerization at the interface of the organic solvent containing diacid halide and aqueous solution of diamine is shown in Figure 1.7. The Polycondensation reaction between an aqueous solution of 1,6-hexanediamine and an organic solution of sebacoyl chloride in organic solvent in the presence a base is given below:

$$H_2N\text{-}(CH_2)_6\text{-}NH_2 + Cl\text{-}CO\text{-}(CH_2)_8\text{-}CO\text{-}Cl \longrightarrow$$

$$H\text{-}(NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_8\text{-}CO\text{-})_n\text{-}Cl + HCl \qquad (1.2)$$

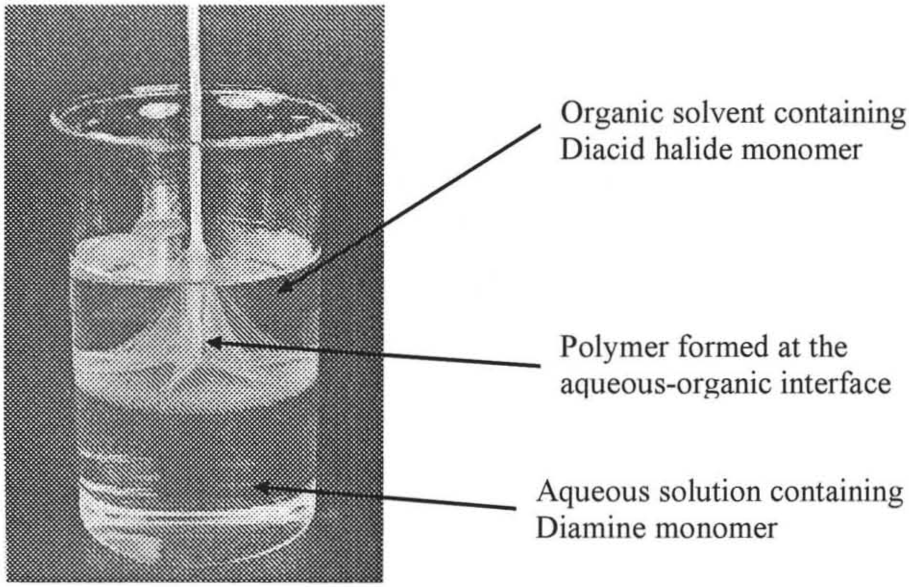

Figure 1.7 Polymerization at the interface of immiscible phases having reactive monomers.[59]

Membrane modification by the technique of interfacial polymerization is widely used for the fabrication of thin film composite membranes for reverse osmosis (RO) and less often for nanofiltration.[20, 29] The porous support membrane is impregnated with one monomer-containing solution; then, another monomer-containing solution is brought into contact with the other solution in the pores. The support will get coated at the interface of the aqueous and organic monomer solutions. Acid acceptor is not necessary during the course of interfacial polymerization for fabrication of TFC membranes.[60] Thin film composite membranes for reverse osmosis (RO) by the technique of interfacial polymerization was first successfully fabricated by Cadotte et al..[61] They used PEI and toluene diisocyanate as monomers to generate polyurea; PEI and isophthaloyl chloride to generate polyamide. Later, the technique was improved and optimized for higher water fluxes, high salt rejections, membrane stability and durability. Almost all commercially available RO membranes are now manufactured by the technique of interfacial polymerization.

The primary difference between the current work with the well established technique of fabricating RO membranes is using a microporous hydrophobic support (polypropylene) instead of a porous hydrophilic or a very mildly hydrophobic support. Supports currently used for IP are mostly polysulfone (PS) or polyethersulfone (PES). For example, there are a series of commercial thin film composite (TFC) membranes based on PS, for example, FT30 Filmtec membrane[62] and NS-100[63] or PES based, for example, NF50 M10 Capfil membrane.[64] The TFC membranes for RO by the technique of IP are flat sheet membranes and only a limited number of studies were carried out in literature on fabrication of thin film composite membranes in the hollow fiber form by interfacial polymerization.[65, 66] Advantages of hollow fiber membranes over flat sheets membranes are discussed in Section 1.7.

The course of interfacial polymerization depends on the nature of the monomers, the monomer concentrations, the reaction kinetics and the nature of the organic phase. Diacid halides have very little solubility in water and diamines can easily partition into organic solvents. It is generally known that the aqueous phase monomer partitions into the organic phase and hence the polymerization takes place in the organic phase. It has been proved for polyamides that polymerization takes place in the organic solvent.[59] When the immiscible phases having reactive monomers are brought into contact, the first batch of diamine molecules partitioned into the organic phase meets the acid halide and presumably is acylated to a large extent at both ends. The next batch of diamine molecules diffused/partitioned into the organic phase, finds a layer of acid halide-terminated oligomers and diacid halide molecules. A schematic of this process is shown in Figure 1.8. During this process, the concentration and size of oligomers increase and ultimately but quickly a polymer is formed. Diamine molecules will now have to diffuse through this polymer to meet acid chloride molecules. But, the polymer hinders/prevents further diffusion of diamine molecules into the organic phase: the polymerization becomes selfinhibitive. As the concentration of the polymer increases, the interchain contacts increase until a contact network is formed and the polymer precipitates.[59] In other words, the polymer network freezes during the precipitation and forms a membrane structure.[67]

Polymer precipitation time depends on the polymer-solvent interactions and hence the properties of the coating layer such as thickness and porosity depend on the organic solvent used. The order of interactions of polyamide 6-10 with the solvents is as follows: Cyclohexane < Xylene < CCl_4 < $CHCl_3$. With higher polymer-solvent interactions, precipitation takes place slowly and thickest film will be formed.[59] For example, thickest films would be formed in chloroform and the thinnest in cyclohexane. Hexane or xylene is generally used as a solvent for dichloride monomer for fabrication of TFC membranes by IP.[60, 68] Here, xylene is used as organic solvent for dichloride monomer throughout the IP-based coating studies.

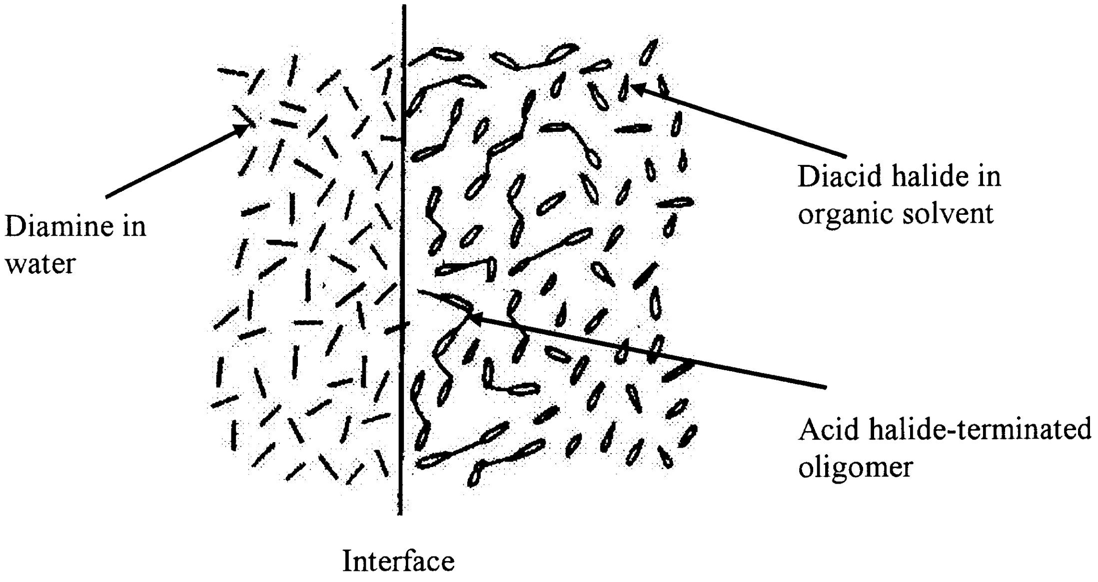

Figure 1.8 Schematic of the course of polymerization in the organic phase.[59]

The characteristics of the polyamide coating depends greatly on the properties of the the monomers such as their partition coefficients, functional groups and molecular weights.[29, 60, 67, 69] During the polymerization, aqueous monomer has to partition into the organic phase and diffuse through the nascent polymer network. If the molecular weight of the aqueous monomer is high, it diffuses slowly into the reactive zone and hence the coated film will be thin.[59] The coating would be thick if a low molecular weight aqueous monomer is used instead of a high molecular weight monomer in the aqueous monomer. The number of functional groups of the aqueous/organic monomers affects the surface morphology of the coating. For example, when a monomer having three functional groups is used, the polymer grows in a three dimensional network and the roughness of the coating will be high. It was also observed that aromatic amine monomers lead to a high surface roughness of the coating compared with the aliphatic monomers.[29] For the given reactive monomer system, a change in the concentrations of the monomers alters the pore size of the coating and a change in the reaction times alters the thickness of the coating. Higher concentration and high reaction times produces a thick coating with smaller pore sizes.[70] There are a variety of monomer systems generally used for IP. Following reactive monomer systems were used in this thesis:

- 1,6-hexanediamine - Sebacoyl chloride
- Poly(ethyleneimine) - Isophthaloyl dichloride
- 1,3-Phenylenediamine - Trimesoic acid trichloride.

A variety of monomers (aliphatic, aromatic, bifunctional, trifunctional, multifunctional, low molecular weight and high molecular weight) were selectively chosen to study the effects of monomer properties on the coating characteristics. Out of the aqueous monomers used, poly(ethyleneimine) and 1,6-hexanediamine are aliphatic, and 1,3-phenylenediamine is aromatic. Poly(ethyleneimine) used is a high molecular weight (MW 50,000) compound and the rest of the aqueous monomers are low molecular weight compounds. Isophthaloyl dichloride (IPD) and trimesoic acid trichloride are aromatic, and sebacoyl chloride is aliphatic. Isophthalyol chloride is a bifunctional compound and trimesoyl chloride is a trifunctional compound. These reactive monomer systems are widely used and the properties of the polyamide coating are well studied in the literature.[29]

Coating by IP can be carried out by impregnating the porous membrane support with aqueous monomer-containing solution followed by contacting with organic monomer-containing solution or vice versa. Impregnating the membrane support first with organic solution is also possible when hydrophilized PP membrane is used as a support. However, hydrophilized groups on the PP support are likely to get inverted when contacted with an organic solution.[71] The effects of such a possibility of inversion of the hydrophilized groups were explored and an appropriate coating procedure was developed.

1.5.2 Modified Interfacial Polymerization

The pore interior of PP microfiltration membranes was coated with polyamide by the "modified IP" procedure. The objective in this case was to modify and hydrophilize the internal pore structure rather than form an additional layer on the PP membrane surface. The "modified IP" procedure was as follows. The diamine was dried onto the membrane internal surface from a mixture of water and ethanol. The deposited diamine was reacted with diacid halide monomer to coat the pore interior with the polyamide. This "modified IP" procedure was first developed to increase the shrink resistance of wool fibers by coating with polyamide.[72] Dickson et al.[15] studied hydrophilization of PP internal structure by a "modified IP" technique. In the current study, the pore interior of PP was first prehydrophilized by prewetting with acetone, followed by chromic acid treatment (Section 1.6). The "modified IP" procedure was then carried out. Hydrophilization of the PP pore interior prior to carrying out "modified IP" will facilitate uniform deposition of the amine on the surface of the pore and helps uniform hydrophilization. These membranes were tested for possible applications in membrane solvent back extraction and microfiltration.

1.5.3 PEI Self-Crosslinking

Commercial PEI is obtained by ring opening polymerization of ethyleneimine and has a substantial degree of branching and a ratio of primary:secondary:tertiary amines as 3:4:3. Figure 1.9 provides the structure of PEI. Poly(ethyleneimine) was previously used as a multifunctional amine for preparation of NS-100 RO membrane.[63] This polymer is available in the molecular weight range between 600 and 70,000;[73] however best results for preparation of RO membranes were obtained with a MW of 10,000–60,000.[63] This polyfunctional amine possesses a high free energy of adhesion of 191 J/mol[73] that allows its use in a variety of applications such as adhesives, flocculating agents, ion exchange resins, absorbents, etc. It was also used for surface treatment of polymers, including PP with preliminary surface modification by air corona discharge.[74] Internal crosslinking of PEI takes place via ammonia elimination from adjacent amino groups at a temperature of 110°C (Figure 1.9).[61] In this thesis, PEI was coated on the surface of the inner diameter of Nylon hollow fibers for possible applications in membranes solvent back extraction and ultrafiltration. PEI insolubilization was also carried out on the surface and inside the pores of porous polypropylene flat membranes to hydrophilize the polypropylene hydrophobic support for possible use as microfiltration membranes in aqueous systems.

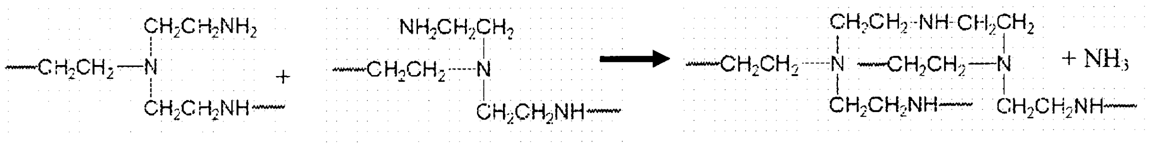

Figure 1.9 Structure and self-crosslinking of poly(ethyleneimine).

1.6 Hydrophilization of the Hydrophobic Support

Polypropylene is a hydrophobic polymer having a contact angle with water of 116 degrees in the case of isotactic PP.[73] An IP procedure can be carried out by impregnating the microporous hydrophobic support with an organic solution of diacyl chloride first followed by a subsequent contact with an aqueous amine reactant.[75] However, it is better to first make PP hydrophilic, for example, by surface oxidation and then soak the support in an aqueous solution of an amine reactant (diamine or polymeric amine) and subsequently contact with an organic solution of diisocyanate or diacyl chloride. Such surface pretreatment procedure may increase wettability with aqueous amine solution; but more importantly it will provide better adhesion between the coating and the support in the already formed composite membrane.[76-78]

The most widely used PP is isotactic, which is semi-crystalline, as for example in the Celgard series;[79] therefore, the kinetics of oxidation of the crystalline and amorphous regions are likely to be different. Further, the amorphous regions of PP have a tendency to flip their oxidized groups towards the membrane interior while drying or changing the media to hydrophobic.[71] The fact that PP is not wettable by strong aqueous-based oxidants like chromic acid, potassium persulfate etc., can increase the non-uniformity of the membrane surface modification resulting in poor quality of the selective layer of a thin film composite membrane. Therefore, a strategy to provide better contact between an oxidant and the treated surface might improve the uniformity of modification.

The surface of PP flat films and the surface of the inside diameter of PP hollow fibers were modified in this study by chemical surface oxidation. Techniques like UV activation are incapable of altering the inside surface of hollow fibers; plasma-based approach used for modification of surfaces of membranes[16] and polymers[74] is also difficult for the hollow fiber surface on the lumen side. Porous polypropylene support was prewetted with acetone prior to hydrophilizing the support by treating with chromic acid solution to improve the hydrophilization of the pore mouth and the pore interior. This was followed by interfacial polymerization to form a thin coating on the polypropylene support. When hydrophilic porous supports made out of PES and Nylon were used for the fabrication of thin film composite membranes by interfacial polymerization, the hydrophilization step was not necessary.

By creating polar groups on the support surface, one can substantially improve adhesion between the support and the selective layer containing polar groups itself. Using an organic liquid such as acetone to wet the pores of polypropylene before treatment with an oxidizer (chromic acid) is beneficial: first, acetone is miscible with water; second, it is hard to oxidize because it is a ketone. It is an aprotic solvent but if it is present in small amounts it should not substantially reduce the oxidizing properties of the oxidizer. In such a case the very edge of the membrane pore is supposedly getting hydrophilized as well as the between-pore polymer part of the membrane surface. If the coated layer is attached close to the membrane pore edge, it might be beneficial in terms of better attachment of the selective layer to the support.

1.7 Coating Hollow Fiber Membranes

Hollow fiber modules provide a much higher surface area to volume ratio than spiral wound modules; this pre-treatment is also less demanding than that for the spiral wound modules.[66] Hence TFC membranes in hollow fiber configuration were fabricated rather than flat sheet membranes. Having the selective skin on the lumen side of the hollow fibers will minimize the problems of concentration polarization and fouling.[65] Coating on the lumen side is also advantageous as fiber surface abrasion will damage the coating if the coating is on the OD. On the other hand, a selective skin on the OD would allow the hollow fibers to withstand higher pressures. If a microfiltration membrane is used as a support instead of an ultrafiltration membrane, higher fluxes can be achieved at lower pressures. This reduces the need for operating the hollow fibers at higher pressures in the inside-out configuration.

Coating by IP on hollow fibers differs from coating on flat films because of the primary differences in geometry, and handling of the membranes and solution flow. Individual fibers can be coated only on the outer surface (OD); it is also difficult to handle long individual fibers. The coating process by IP on individual fibers also lacks reproducibility when carried out in bench scale. For these reasons, leak-proof hollow fiber membrane modules were fabricated first using microporous PP hollow fibers potted in a module; the coating by IP was next carried out on the inside surface (ID) of the hollow fibers. It is to be noted that coating on the OD of the fibers in the module is not a good option because the coating could make the neighboring fibers stick to one another unless other steps are taken.

For coating on the ID of the hollow fibers, the monomer-containing solution has to be passed through the lumen side of the fibers. On the other hand, for coating flat film membranes, the whole flat membrane can be dipped at once in the monomer-containing solution. This flow behavior of the monomers during the coating process in hollow fibers can influence the characteristics of the thin film. The degree of removal of the excess monomers from the lumen side of the fibers also plays an important role because of the dependence of the coating characteristics on the amount of monomers left on the surface of the support.[65, 66] Further because the ID of the hollow fibers used in this work is relatively small (240μm for PP X-10, 400 μm for PP X-20 fibers, 600 μm for Nylon and 700 μm for PES), it is very critical to remove the excess monomers uniformly from the lumen side of all the fibers in the membrane module without complete or partial elimination of the monomer solution coated on the support.

The self crosslinking of PEI takes place via heat treatment at 110 °C. Heat treatment of the coating by IP and "modified IP" techniques is also a necessary step and helps to complete the polymerization process, remove the organic solvent and insolubilize the unreacted monomers.[61, 67, 69] Removing the organic solvent in IP also plays a substantial role in improving adhesion between the support and the selective layer: decreasing actual inter-atomic distances increases adhesion which is based on weak attraction forces. Thus, heat treatment influences the final morphology of the coating to some extent and hence affects the coating characteristics.

The following are the controlling factors in coating on the ID of the PP fibers:

1) Hydrophilization of the fibers (when PP is used as support);
2) Nature of the monomers and the reaction times;
3) Removing the excess monomers from the lumen side;
4) Heat treatment technique.

It is apparent that only an appropriate combination of all of the above mentioned parameters of the IP process using appropriate techniques will lead to the desired, nondefective coating in the ID of hydrophobic hollow fibers. Hydrophilization of the PP hollow fibers was discussed in Section 1.6. One of the monomer solutions will be first deposited on the lumen side of the hollow fibers. Another monomer solution will be then passed from one side to the other side of the fiber. The second monomer starts reacting as soon as the monomer solution enters the hollow fiber and the monomer concentration will decrease as it flows in the hollow fiber to the other end. This concentration gradient along the length of the module could lead to the nonuniform coating. This nonuniformity can be reduced to some extent by carefully choosing the monomers. Using a high molecular weight polyamine monomer such as poly(ethyleneimine) will reduce the chances of nonuniformity in the coating as poly(ethyleneimine) will have a low mobility to the reaction zone.

Excess monomer solutions from the lumen side will be removed by passing air at a low flow rate and low pressure. High flow rates of air will remove the deposited monomers from the lumen side resulting in defects in the coating. At the same time, using very low rates of air may not remove the excess monomers from the lumen side uniformly. Therefore, the flow rate of air to remove the excess monomer solutions will have to be optimized for defect-free coating. As mentioned earlier, it is important to heat treat the coating and different heat treatment techniques explored are the following: passing hot water through the lumen side of the fibers, passing hot air through the fiber and placing the module in an oven. Again, it is very critical not to damage the film during the heat treatment as the nascent coating will be fragile. There is a possibility of detachment of the coating from the support during the flow involved in the heat treating process (especially when PP hollow fibers are used as a support).

1.8 Membrane Modification, Characterization and their Applications

Modified membranes were tested in the respective applications such as microfiltration, ultrafiltration, nanofiltration, membrane solvent back extraction and heat transfer. In addition to the characterization of the coated membranes by testing them for the applications that the coated membranes are intended for, they were characterized using scanning electron microscopy. Membrane modification techniques and the supports used for different membrane applications are provided in Table 1.4.

1.8.1 Ultrafiltration/Nanofiltration

Polypropylene hollow fiber membranes of the types Celgard X-10 and X-20, and hollow fiber membranes of PES were coated on the lumen side by interfacial polymerization. Membranes coated with the objective of making ultrafiltration membranes were tested and characterized by ultrafiltration of an ethanol-soluble protein, zein. Zein is a corn protein having a MW of 35,000 and belongs to prolamins. It is insoluble in both pure water and alcohol, but soluble in 70-80% alcohol solutions. The approximate size of the zein molecule having a MW 24,000 in 70 vol% ethanol in water is 13 nm*2.8 nm.[80] Zein molecule used in the study will be slightly bigger in size, since the molecular weight of zein used was 35,000. This particular system (zein in 70% ethanol in water) was chosen because zein is an inexpensive protein; analysis of zein is relatively simple. Solvent stability of commercially available ultrafiltration membranes with zein in alcoholic solutions was studied by Shukla and Cheryan.[17] This allows a comparison of the solvent stability of the fabricated membranes with the information available in the literature. Polypropylene hollow fiber membranes coated by IP with the objective of making nanofiltration membranes were characterized by rejection of appropriate solutes (e.g., safranin O (MW 351) and brilliant blue R (MW 826) dyes) in methanol. Solvent stability of the coated ultrafiltration membranes was tested with ethanol. Solvent stability of coated nanofiltration membranes was tested with toluene.

Factors that control the coated membrane characteristics like coating thickness and pore size of the coating, would ultimately determine/dictate the solvent flux and solute rejection behavior. These behaviors are expected to be controlled by the monomer concentrations, reaction time, mode of heat treating the coating, and the extent of hydrophilization when a hydrophobic support is used. The effect of these controlling factors on the coating characteristics were studied.

1.8.2 Microfiltration

The feasibility of hydrophilizing microporous polypropylene flat film membranes without effectively reducing its pore size was studied by the coating techniques of “modified IP” and PEI crosslinking. Water flux through the modified membranes was measured to study the hydrophilicty of the membranes. Changes in hydrophilic coating characteristics with membrane conditioning by organic solvents and with repeated drying of the membranes were also studied.

1.8.3 Membrane Solvent Back Extraction

It is evident from Section 1.2.3 that one has to employ hydrophilic solvent resistant membranes for efficient membrane solvent back extraction. Polypropylene microporous membrane is hydrophobic and membrane solvent back extraction can be carried out in PP microporous membranes if they can be hydrophilized. Therefore, PP flat film membranes were hydrophilized by the procedures described in the Section 1.5.2 and feasibility of using such a modified membrane for MSBE was studied.

Available solvent-resistant hydrophilic microporous hollow fiber membranes (e.g., Nylon) having large pore sizes cannot withstand higher breakthrough pressures; hydrophilic nanofiltration hollow fiber membranes do not provide higher values of overall mass transfer coefficients. Therefore, porous hydrophilic Nylon hollow fibers were coated on the internal diameter (ID) to optimize the pore sizes required for efficient MSBE. The coating technique primarily employed to reduce the pore size of nylon hollow fibers is PEI crosslinking. The possibility of employing Nylon hollow fibers coated by IP was also explored for membrane solvent back extraction. Hollow fibers were coated on the ID rather than on the outer surface (OD) for the following reasons. Unless the shell side flow is designed properly, it is preferable to pass the solution that has to be treated (organic phase in the case of MSBE) through the lumen side rather than the shell side to prevent channeling and bypassing. This will lead to lower mass transfer coefficient, but it will be easily characterizable. When the organic phase is passed through the lumen side, most of the mass transfer resistance will be in lumen side in reactive MSBE and quantification is easier as mass transfer correlations for lumen side are more reliable than those for the shell side. The goal was to coat only on the ID rather than the entire pore to minimize the increase in membrane resistance with coating. The objective was to make a thin film composite membrane since it would provide high solute mass transfer rates compared to the asymmetric membranes.

Coated membranes were studied for nondispersive operation at higher organic phase pressures in the lumen side and back extraction (non-reactive and reactive extraction) of solute from organic solvent into the aqueous phase. Breakthrough pressure studies were carried out in noncoated and coated membranes using the water-MIBK system with or without caustic in the water phase. Back extraction of phenol from MIBK was used as a model system for reactive extraction. Back extraction of acetic acid from MIBK into water was studied as a model system for non-reactive back extraction. Mass transfer rates of acetic acid and phenol from organic phase to the aqueous phase were studied before and after the coating. Back extraction of acetic acid and phenol from MIBK was also studied in the widely used hydrophobic polypropylene porous hollow fiber membranes to compare the performance of water-filled pores vs. the organic-filled pores, characteristic of hydrophobic membranes.

1.8.4 Hollow Fiber Membranes for Heat Transfer

Membranes of PES which have an asymmetric pore structure were chosen as the support for fabrication of TFC membranes for heat transfer. The lumen side of the fibers was coated with a polyamide via IP. The reactive monomer systems used are 1,6-hexanediamine-sebacoyl chloride, poly(ethyleneimine)-isophthaloyl dichloride and 1,3-phenylenediamine-trimesoic acid trichloride. Since the objective here was to make the coating impervious, high monomer concentrations (0.5 to 2 wt%) and high reaction times (2 to 20 minutes) were used to develop a thick coating.

The polyamide coating is hydrophilic and if these coated membranes are used with water or aqueous systems, there is a possibility of water permeating through the coating at high transmembrane pressures. Therefore, the coating was further made impervious to water by applying a layer of a hydrophobic coating of silicone on the polyamide coated layer. Silicone coating to increase the hydrophobicity of the coating was studied by Kistler and Cussler.[81] During heat transfer applications, the pores of the support will be filled by one solution; this solution will be separated from the other solution by two layers of coating (polyamide coating and silicone coating). Heat transfer between the two streams takes place through the coating layers. Coated membranes were tested for leakage of water at low pressures and the heat transfer performance was studied in collaboration with other investigators in the laboratory. Overall heat transfer coefficient in the coated hollow fiber module was calculated and compared with the values on solid PP hollow fibers.

CHAPTER 2

EXPERIMENTAL

2.1 Membranes, Chemicals and Instruments

2.1.1 Membranes

Support membranes used in the study are as follows:

- Celgard 2400 polypropylene flat film membrane (Celgard, Charlotte, NC)
- Celgard X-10 and X-20 hollow fibers (Celgard, Charlotte, NC)
- Nylon 6 hydrophilic hollow fiber (ENKA America Inc., Ashville, NC)
- UltraPES hollow fibers (Membrana, Wuppertal, Germany)

Characteristics of these membranes are provided in Table 1.5.

2.1.2 Chemicals

N_2 high purity (Welco CGI, Newark, NJ); sebacoyl chloride - 99% purity, 1,6-hexanediamine - 98% purity, iso-phthaloyl dichloride - 99% purity, potassium dichromate - 99% purity ACS reagent, ethanol absolute - 99.5% purity ACS reagent, methyl isobutyl ketone - certified ACS grade, sodium hydroxide, acetic acid - glacial, 4-aminoantipyrine, potassium ferricyanide, sodium tetraborate decahydrate, brilliant blue R - dye content 90%, phenol, 1,3-phenylenediamine - 99+% purity (Sigma-Aldrich, St. Louis, MO); sulphuric acid - 95.7% purity, acetone - 99% purity (Acros Organics); poly(ethyleneimine) aqueous solution of 50 wt.% with polymer-average M.W. between 50,000-60,000 (Fisher Scientific, Suwanee, GA); Zein protein (Freeman Industries, Tuckahoe, NY); methanol, xylene, toluene, safranin O -dye content 95% (Fisher, Fair Lawn, NJ); 184 silicone elastomer base, 184 silicone elastomer curing agent (Dow

Corning, Midland, MI); C-4 resin, D activator (Beacon Chemicals, Mt.Vernon, NY); RTV 118 translucent silicone rubber adhesive sealant (General Electric, Waterford, NY); Loctite M-21HP medical device epoxy adhesive (Hysol, CT); water deionized by Barnstead 5023 (Barnstead, Dubuque, Iowa).

2.1.3 Instruments

- UV-VIS Spectrophotometer (Model U-2000, Hitachi, Danbury, CT)
- Scanning electron microscope (Model Leo 1530)
- Interfacial tensiometer (Model K8, Kruss, Hamburg, Germany)
- FT-IR Spectrometer (Spectrum One, PerkinElmer Instruments, Wellesley, MA)
- Liquid pump controller (Model 7553-50, Masterflex, Barrington, IL)
- Pump head (Model 7518-60, Masterflex, Barrington, IL)

2.2 Handling of the Membranes

Two different geometries of the membranes used in the study are flat film membranes and hollow fiber membranes. Flat film and hollow fiber membranes have to be handled differently; handling of these two types of membranes is described below.

2.2.1 Handling of Flat Film Membranes

To pass different solutions through the flat membranes during the coating process, an apparatus (Figure 2.1) consisting of a glass porous support and a reservoir was used. The membrane was clamped between the porous support and the reservoir. Vacuum was applied through the porous support to pull the solutions (monomer solutions/water/chromic acid solution) through the membrane. Solvent permeation studies for characterization of the modified flat film membranes was carried out in a flat membrane cell (Figure 2.2) having 7 cm^2 membrane area. The flat film membrane was supported on a porous polypropylene support (membrane holder for Model 8400 from Millipore, Billerica, MA). The solvent was pressurized from the top side of the membrane using a pressure vessel filled with a solvent and a nitrogen cylinder. Permeate was collected from the other side (supported side) of the membrane and the permeation rate of the solvent was measured.

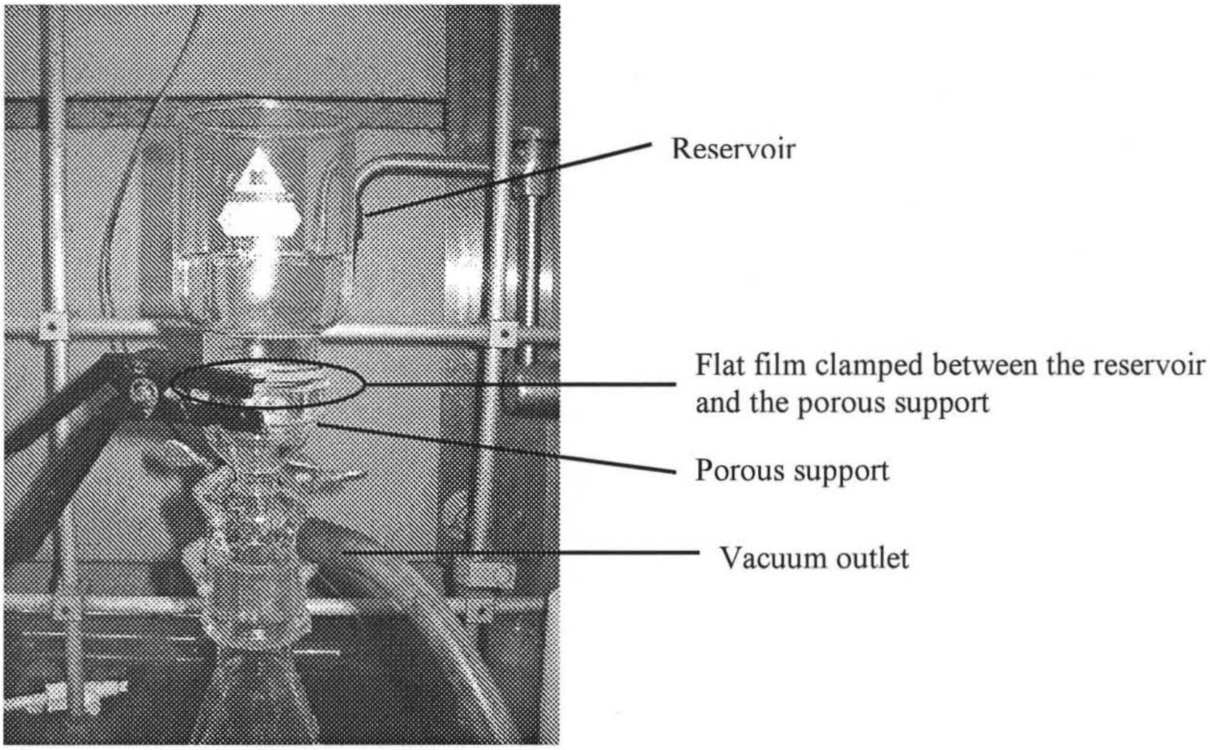

Figure 2.1 Setup for passing different solutions through the flat film membranes in the coating process.

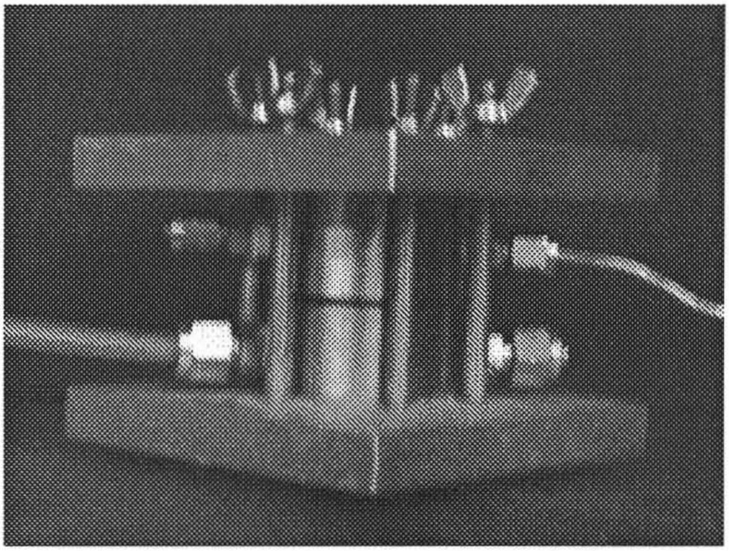

Figure 2.2 Flat film membrane cell.

2.2.2 Handling of Hollow Fiber Membranes

Membrane modules were fabricated first using the hollow fiber support membranes. The assembly of a hollow fiber membrane module is similar to that of a shell-and-tube heat exchanger. A picture of a hollow fiber membrane module is shown in Figure 2.3. Polytetrafluoroethylene (PTFE) tubing was used as the shell for the module. The tubing was fitted with 1/4″ male run tees at both ends. The required number of fibers for the membrane module was bundled together; one end of the bundle was tied with a string. This end was pulled through the bore of the tubing. A leak-free tube sheet was prepared at the two ends of the tubing. The process of making the tube sheet is referred to as potting. The tube sheet held the bundle of fibers in place and prevented the shell side fluid and tube side fluid from mixing.

The regular method of potting the ends of the module is as follows. A two layer potting was used to prepare each tube sheet for a module. A two-component RTV 118 translucent silicone rubber adhesive sealant was applied as the first layer at the end of the each module end fitting. This sealant is highly viscous and hence it does not flow out of the end fittings of the module when applied. After curing for one day, epoxy (C-4: resin; D: activator; weight ratio:4/1) was applied as the second layer through the nearest shell side outlet using a glass dropper; the epoxy was cured for two days. Low viscosity of this epoxy helped its penetration into the spacing between the fibers and provided a leak-proof tube sheet.

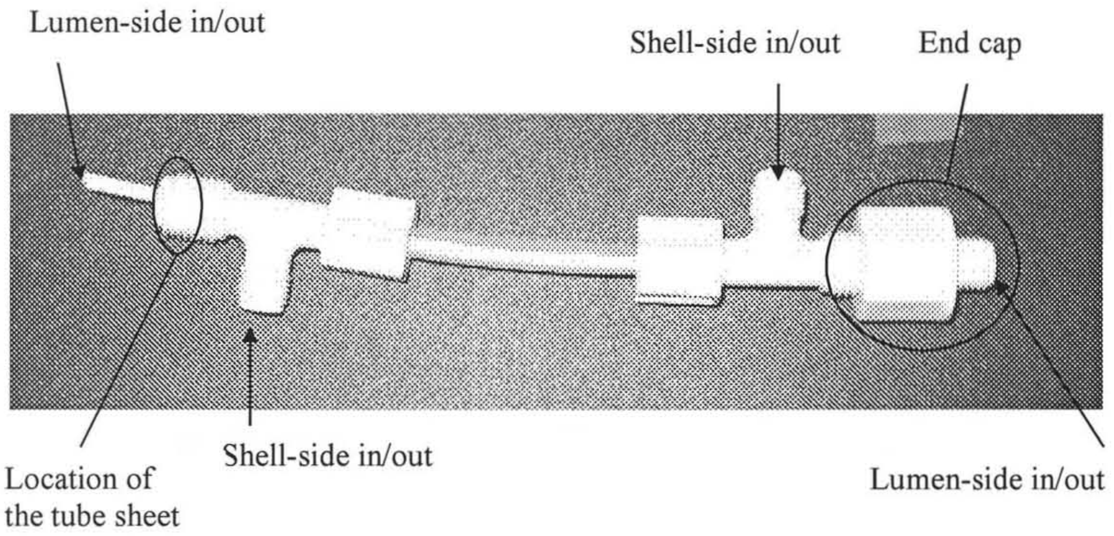

Figure 2.3 Assembly of a hollow fiber membrane module.

The fabricated membrane modules were intended for use with organic solvents; but silicone rubber (sealant) swells in organic solvents. Hence use of the silicone rubber as a first layer for potting was eliminated. The regular epoxy (C-4 resin with activator) is not viscous enough to stand by itself when applied at the end fittings with out the layer of silicone rubber. Therefore, the membrane modules were potted by the following procedure which eliminated the use of silicone rubber. Highly viscous and a solvent stable epoxy (Loctite M-21HP, Medical device epoxy adhesive) was used to make a tube sheet. This epoxy was applied into the end fittings from the module ends and epoxy was forced to go in between the fiber gaps by separating the fibers apart and creating the spacing between the fibers. The inner surfaces of the end fittings were grooved before potting, so that the grooves would anchor the epoxy to the fittings. The effective module length was the length of the PTFE tubing less double the potting thickness (to account for both sides of the potting).

Before using these modules, preliminary tests were carried out. To test for any leakage, the shell side of the module was filled with deionized water. Water pressure was maintained at 40 psig (377 kPa) for about 1 hour. If no water leaked through the potting, the module was considered leak-free. Hollow fiber membrane modules were fabricated with different number of fibers and in different lengths to match the requirements of different applications. Characteristics of these membrane modules are given in Table 2.1.

Membrane modules were fabricated first from hollow fiber membranes; hollow fibers potted in the module were then modified. The experimental setup (Figure 2.4) used for hydrophilization, modification and characterization of the hollow fiber membrane modules consisted of a pump connected to the hollow fiber membrane module to pass the solutions through the lumen side and a valve arranged after the hollow fiber module to control the pressure. A peristaltic pump was used as it facilitated the use of different flow lines using the same pump. Different flow lines were used to pass different solutions so that washing of the lines was not required during the hydrophilization/coating process. For example, flow lines for acetone, chromic acid solution, water, aqueous monomer solution and organic monomer solution were different.

Table 2.1 Characteristics of the Fabricated Hollow Fiber Membrane Modules

Membrane	Module designation	Application	Fiber ID (μm)	Shell ID (cm)	No. of fibers	Length of module (cm)	Surface area* (cm^2)
Celgard X-10	Module A	Nanofiltration/Ultrafiltration	240	0.46	30	15	33.9
Celgard X-20	Module B	Nanofiltration/Ultrafiltration	400	0.46	6	12	9.05
UltraPES	Module C	Nanofiltration/Ultrafiltration	700	0.46	4	12	10.5
Nylon 6	Module D	Nanofiltration/Ultrafiltration	600	0.46	4	12	9.05
Nylon 6	Module E	Membrane solvent back extraction	600	0.46	10	7	13.2
Celgard X-20	Module F	Membrane solvent back extraction	240	0.46	102	18.5	171.9**
UltraPES	Module G	Heat transfer	700	0.46	6	24	31.67

* surface area calculated based on ID
** surface area calculated based on OD

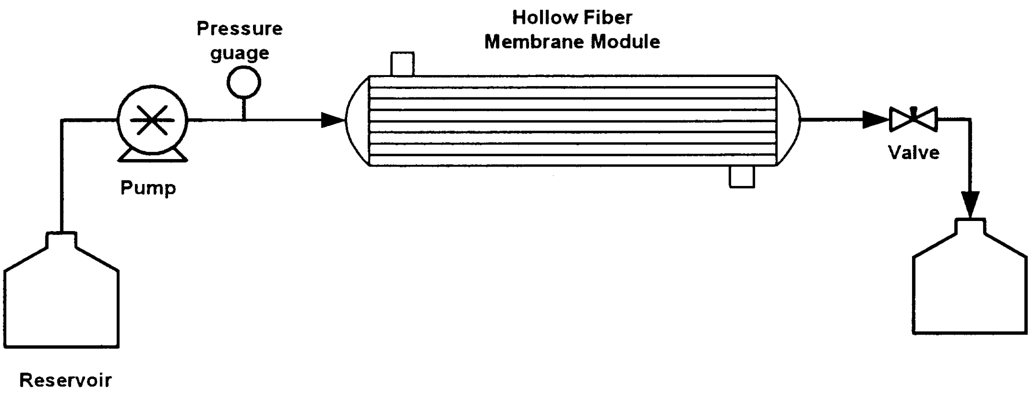

Figure 2.4 Experimental setup for modification of hollow fiber membrane modules (this setup was also used for characterization).

2.3 Membrane Modification

2.3.1 Hydrophilization of PP Hollow Fibers and Flat Films to Carry Out IP

Polypropylene hollow fibers and flat film membranes were hydrophilized by oxidizing with various concentrations of chromic acid solutions. Different concentrations of chromic acid solutions were prepared by slow mixing of $K_2Cr_2O_7$ with H_2O and H_2SO_4 in different proportions in a fume hood. The experimental setup shown in Figure 2.4 was used for hydrophilization of hollow fiber membranes. Pores of the hollow fibers were first wetted with acetone by passing acetone through the lumen side at 2 psig (115 kPa) for 2 minutes. Then excess acetone in the lumen side of the fibers was removed by passing air at a low flow rate followed by continuous circulation of the chromic acid solution at 65°C through the bore of the fibers. Chromic acid was passed at 5 psig (135.8 kPa), so the acetone in the pores was slowly replaced by the chromic acid solution. After carrying out the treatment for 30 min, the used chromic acid solution in the reservoir was replaced with a fresh chromic acid solution of the same concentration and hydrophilization was carried out for another 30 min. Membranes were then washed by passing water through the lumen side at a pressure of 10 psig for 30 minutes. This ensured the complete removal of chromic acid from the lumen and shell side of the module as well as from the pores. Membrane modification by coating followed the washing process.

The flat PP membrane was placed on top of a glass porous support and the reservoir was clamped on top of the membrane (Figure 2.1). The membrane was prewetted with acetone for a couple of minutes before treating it with the chromic acid solution. The reservoir was filled with a hot chromic acid at 65°C and vacuum was pulled from the bottom of the porous support through the membrane. Hydrophilization was carried out for 30 minutes. After half an hour, the solution in the reservoir was replaced with a fresh hot chromic acid solution. The membrane was also turned over so that the other side of the membrane now faces the fresh chromic acid solution. After the hydrophilization, flat films were washed with water for 30 minutes to completely replace the chromic acid in the pores and on the surface of the membrane with water. Coating procedure of the flat films was implemented following the hydrophilization process.

2.3.2 Coating Hollow Fiber Membranes of PP, PES and Nylon in Modules by IP

Membranes can be coated by interfacial polymerization via the following two procedures. Impregnate the membranes with the organic monomer solution followed by contacting with aqueous monomer solution to form a coating: this procedure is referred to as the "reverse procedure". The "regular procedure" involves soaking the membranes first with the aqueous monomer solution followed by contacting with organic monomer solution.

2.3.2.1 Regular Procedure. Polypropylene membrane modules hydrophilized by the procedure described in Section 2.3.1 were modified by the following procedure. On the other hand, PES and Nylon membrane modules were directly modified as the hydrophilization step was not necessary for PES and Nylon membranes. It has to be remembered that the objective was to coat the lumen side of the fibers (PP, PES and Nylon). An aqueous monomer-containing solution (concentrations in the range of 0.1 to 2 wt.%) was passed through the lumen side at a pressure of 5 psig for 30 min. Then the excess aqueous solution was removed from the lumen side by purging gently with air at a low flow rate for 20 to 60 seconds. The end caps of the modules were replaced with new ones since the presence of aqueous monomer solution at the dead spaces of the fittings could be problematic when the organic monomer-containing solution was passed. When the aqueous diamine solution was pressurized in the lumen side of the fibers, water present in the pores of the PP/PES/Nylon support would be replaced with diamine solution. Next, xylene solution having monomer in the concentration range of 0.1 to 2 wt.% was introduced from the lumen side at a very low flow rate for the time period equal to the reaction time (1.5 to 10 min) of IP holding the membrane module vertical. After the excess organic solution from the lumen side was removed in the same way as the aqueous solution for one minute, the coating was heat treated. The rate of removal of the excess monomer solutions (aqueous and organic) from the lumen side of the fibers had to be optimized for a defect-free coating; this is discussed in the results section in great detail.

The coating was then heat treated. Different heat treatment techniques of the coating studied included passing hot water at 65°C for 30 minutes, passing hot air at 65

°C for 30 minutes and placing the module in an oven at 110°C for 20 minutes. After the heat treatment, the modules were dried overnight by passing air at ambient temperature through the fibers. Modules were then washed with ethanol to wash out the unreacted monomers before they were characterized.

2.3.2.2 Reverse Procedure. The "reverse procedure" differed form the "regular procedure" only in the sequence of the exposure of the monomer solutions to the membrane. In the reverse procedure, the membrane was first wetted with the organic monomer solution followed by a flow of the aqueous monomer solution through the fiber bore.

2.3.3 Coating Flat PP Membranes by IP

Flat film membranes were always first exposed to the aqueous monomer solution followed by the exposing the membrane to the organic monomer solution. An aqueous monomer solution (0.5 to 2.0 wt.% of monomer) was passed for about 15 min through the flat PP membrane that was previously oxidized by chromic acid solution. Subsequently, the treated membrane was drained, placed and secured on a cylindrical PTFE roller support (Figure 2.5). This assembly was placed in a bath of organic monomer solution (Figure 2.6) of concentration varying between 0.1 and 1 wt.% to coat the flat film membrane. The interfacial polymerization reaction time was varied between 30 seconds and 5 min. The membrane so modified was placed in an oven at 110°C, heat treated for about 20 min, detached from the PTFE roller support and kept under ambient air conditions.

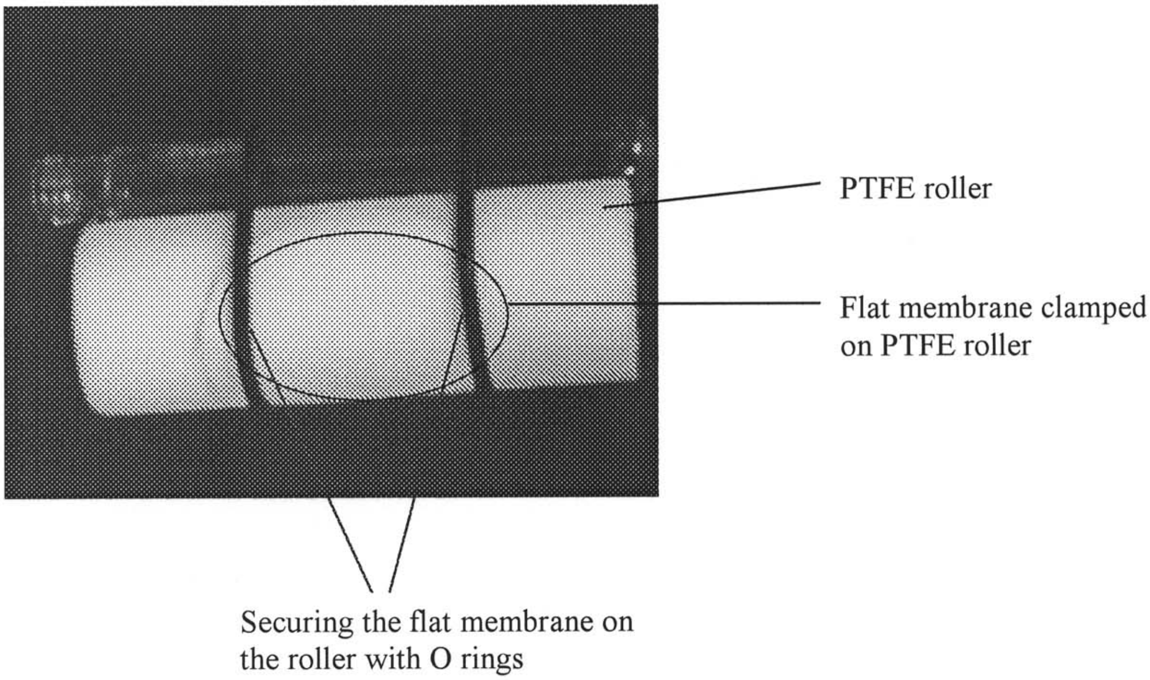

Figure 2.5 Clamping the flat membrane on PTFE roller.

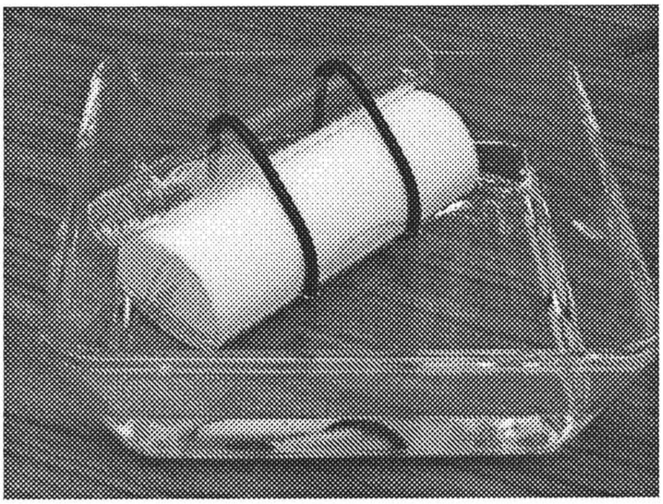

Figure 2.6 Polymerization on the flat film membrane in the organic monomer containing solution bath.

2.3.4 Permanent Hydrophilization of PP Flat Sheet Membranes

2.3.4.1 Hydrophilization by PEI Self-crosslinking. After hydrophilization of the flat PP membrane by the procedure described in Section 2.3.1, an aqueous PEI solution (0.5 to 4 wt.%) was pulled through the membranes for 30 minutes by vacuum using the setup shown in Figure 2.1. The PEI deposited on the surface and in the pores of the membranes was crosslinked by placing the membrane in an oven at 110°C for 20 minutes. The membrane was then dried overnight in ambient air.

2.3.4.2 Hydrophilization by a "Modified IP" Procedure. The "modified IP" procedure consisted of deposition of the amine monomer on hydrophilized PP membranes and contacting the deposited amine with the organic monomer solution to coat the pore interior and the surface of the PP membranes by the polyamide reaction product. The "modified IP" coating procedure was as follows. Flat film membranes were hydrophilized by the procedure described in Section 2.3.1. The membrane was then washed with water by forcing water to go through the membrane by pulling vacuum. Pores of the membrane were then filled with the amine monomer dissolved in either water or a mixture of ethanol and water (0.5 to 6 wt.% of amine). The membranes were next dried by pulling vacuum for longer periods of time (30 min to 5 hours). Then the membrane was soaked in the organic monomer containing solution (0.5 to 2 wt. %) for ten minutes to coat the pore interior and the surface of the membrane with the polyamide reaction product. After polymerization, the modified membrane was heat treated in an oven at 110 °C for 20 minutes.

2.3.5 Coating Nylon by PEI Crosslinking for MSBE

The schematic shown in Figure 2.4 was used to coat the Nylon hollow fibers by self crosslinking of PEI. Aqueous PEI solution was passed through the lumen side of the hollow fiber module at a very low pressure of 1 psig (108.2 kPa) for 5 minutes. The excess aqueous solution of PEI from the lumen side was removed by passing air at a low flow rate. The PEI deposited on the ID of the fibers was crosslinked by placing the module in an oven at 110°C for 20 minutes. The module was then dried in ambient air for 4 hours followed by washing with water to wash out the uncrosslinked PEI, if any.

2.3.6 Modification of PES Hollow Fibers for Heat Transfer Applications

Characteristics of the membrane modules of PES hollow fibers used for this application are provided in Table 2.2. The lumen side of the hollow fiber membrane module was coated by the "regular procedure" of IP, described in Subsection 2.3.2.1. Different concentrations of hydrophobic coating solutions were prepared by adding silicone elastomer and curing agent in the weight ratio of 10:1 in xylene. This coating solution was stirred for ten minutes and was passed through the IP-coated hollow fiber membrane module at a pressure of 5 psig (135.8 kPa) for two minutes while holding the module in a vertical position. The excess coating solution from the lumen side of the fibers was removed by purging gently with air. The coating solution deposited on the lumen side of the fibers was cured in ambient air for 48 hours. After curing, the coated membrane module was tested for water leakage by pressurizing water in the lumen side at 10 psig (170.3 kPa) for eight hours using the setup shown in Figure 2.4. Heat transfer performance of the coated membrane modules were performed subsequent to the water leakage tests.

Table 2.2 Characteristics of PES Hollow Fiber Membrane Modules for Heat Transfer Applications

Module designation	Fiber ID (μm)	Shell ID (cm)	No. of fibers	Length of module (cm)	Surface area* (cm^2)
Module 1	700	0.46	8	15	26.38
Module 2	700	0.46	6	23.5	31.0
Module 3	700	0.46	6	23.2	30.6

* surface area calculated based on ID

2.4 Membrane Characterization

2.4.1 Characterization by SEM and FT-IR

The modified membranes were characterized by a scanning electron microscope (SEM Leo 1530). The samples were carbon coated prior to the SEM characterization carried out at an accelerating voltage of 2-3 kV. In the case of hollow fibers, fibers were taken out of the module and the cross section of the fiber was sliced at an angle to take the SEM pictures of the coating on the inner surface. A schematic of this procedure is provided in Figure 2.7. Carbon coating the lumen side of the hollow fiber that was sliced at an angle is very important to get a good SEM picture of the lumen side. The sliced fibers were placed and oriented in the coating machine in such a way that the lumen side at the sliced part will be coated with carbon. Polyamide coating on the PP support membranes was confirmed by Fourier transform infrared (FT-IR) spectroscopy.

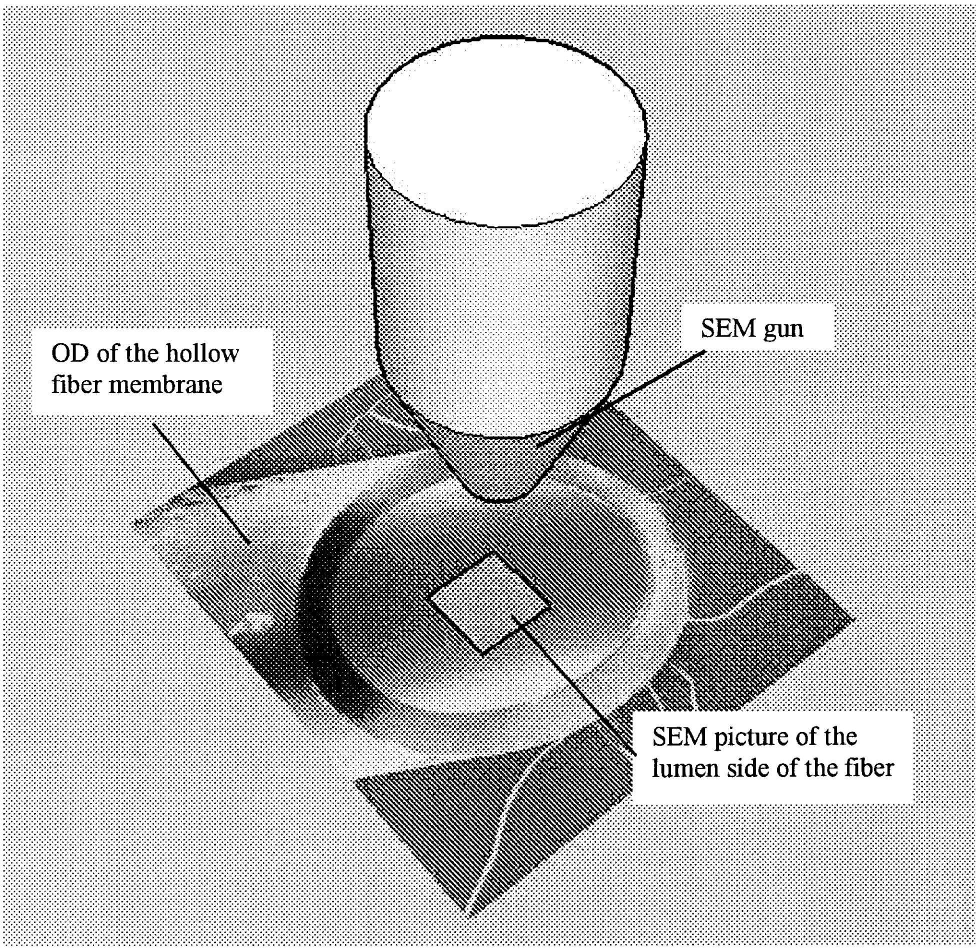

Figure 2.7 Schematic of characterization of the coated hollow fiber membranes by SEM.

2.4.2 Ultrafiltration and Nanofiltration

Hollow fiber membranes were characterized by measuring the reduction in solvent flux and solute rejection. A pump was used to pass the feed solution through the lumen side of the fibers. The valve located at the end of the module was used to pressurize the feed solutions and to control the feed pressure. The experimental set up is shown in Figure 2.4. Permeate was collected through the shell side of the hollow fiber module and analyzed for solute concentration.

For ultrafiltration studies, coated and non-coated hollow fiber membranes were tested for zein rejection and solvent flux reduction with feed solutions of zein in 70% ethanol (rest, water). The zein concentrations of the feed solutions used were 1g/l and 5 g/l; the transmembrane pressures were 7.5 psi (52 kPa) and 20 psi (138 kPa). Concentrations of zein in the permeate were measured by the following method. Zein in the collected permeate was precipitated by adding 6 cc of 1% NaCl solution to 2 cc of permeate; the absorbance of the precipitated solution was measured at 590 nm by the U-2000 UV-VIS spectrophotometer.[82] The calibration curve is shown in Figure 2.8.

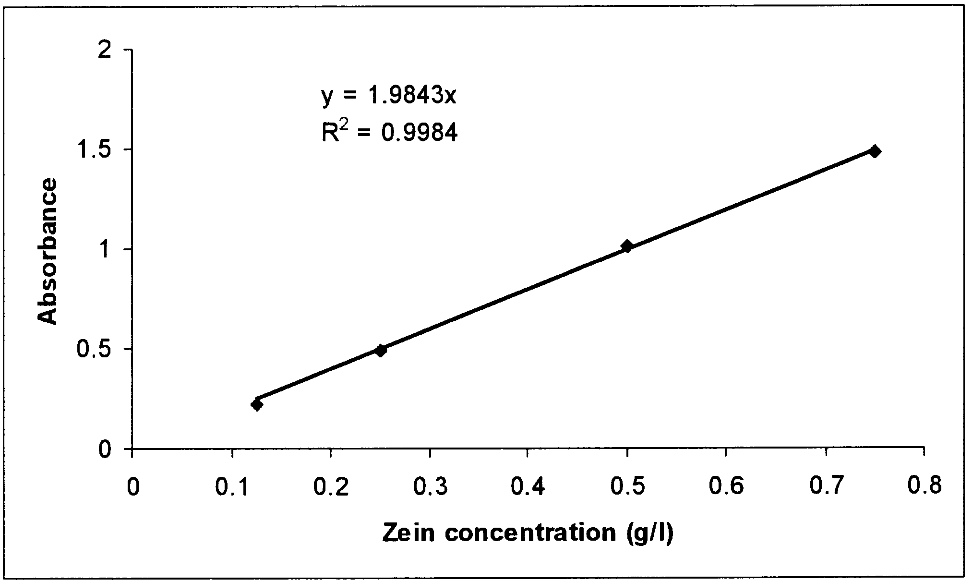

Figure 2.8 Calibration of the protein, zein, in 70% ethanol (rest, water).

Nanofiltration of solutes, safranin O (MW 351) and brilliant blue R (MW 826) dyes, was studied using the coated membranes at a transmembrane pressure of 60 psi (413 kPa). Methanol was used as a solvent for the above-mentioned solutes. Solute concentration in the feed solution was 0.01 wt%. Concentrations of safranin O and brilliant blue R in the permeate were analyzed by the U-2000 UV-VIS spectrophotometer at 530 and 590 nm, respectively.[1] Calibration curve for safranin O in methanol is given in Figure 2.9 and that of brilliant blue in methanol is given in Figure 2.10.

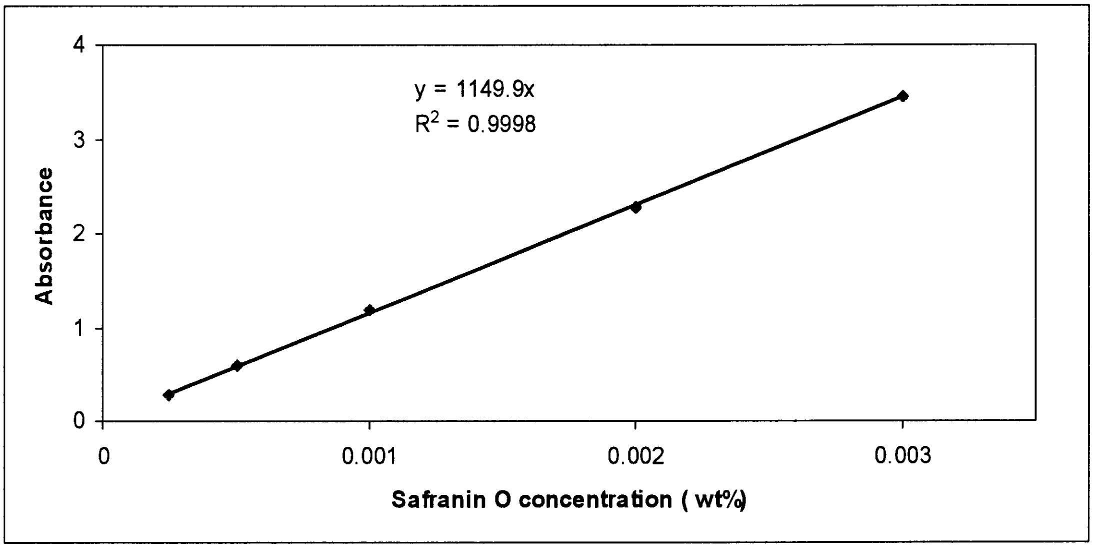

Figure 2.9 Calibration curve for safranin O in methanol.

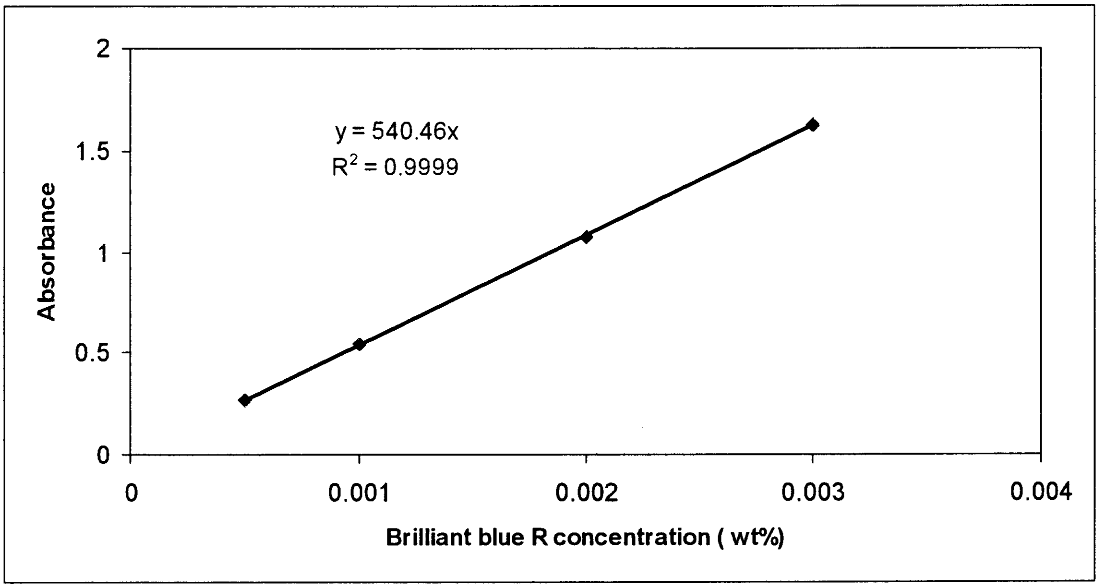

Figure 2.10 Calibration curve for brilliant blue R in methanol.

2.4.3 PP Flat Sheet Membranes Modified for Permanent Hydrophilization

The flat film membranes of PP modified for permanent hydrophilization were characterized by the water breakthrough pressures and the water permeation rates using a flat membrane cell. Water permeation rate and breakthrough pressures were measured without any prewetting with prewetting agents such as ethanol or acetone. For breakthrough pressure measurements, the applied pressure was increased in steps of 5 psi (34.5kPa). Persistency of the hydrophilicity of the modified membranes with the organic solvent exposure was tested by soaking the membranes in xylene for a period of 12 hours and measuring the water flux before and after the soaking.

Permeability of water through the coated flat film membrane was measured using the flat membrane cell (Figure 2.2). The membrane was supported on a porous support and water was pressurized on one side of the membrane using a high pressure nitrogen cylinder. Permeate was collected from the other side of the membrane and the permeate flow rate was measured.

2.5 Performance of the Coated Membranes

2.5.1 Solvent Stability of the Coated Hollow Fiber Membranes for Ultrafiltration and Nanofiltration Applications

Since fabrication of solvent stable membranes is one of the objectives of this thesis, the coated membranes were tested for solvent stability by the following procedure. Membrane modules were soaked in the solvent for a period of 10 weeks at room temperature and tested once every week for solute rejection and solvent flux. Solvents studied for stability of the coated membranes were 70% ethanol (rest, water) and toluene.

Coated ultrafiltration membrane modules were soaked in 70 % ethanol (rest, water) at room temperature for a period of 10 weeks and tested once every week for zein rejection and solvent flux at 138 kPa with a feed solution of 1g/l zein in 70 % ethanol. After solute rejection and solvent flux measurements, the membranes were washed for four hours with 70% ethanol solution to wash out the proteins completely from the membranes. Stability of the coated nanofiltration membranes with toluene was studied in a similar fashion at a higher transmembrane pressure (413 kPa). Neither brilliant blue R nor safranin O is soluble in toluene. Therefore, methanol was used as a solvent instead of toluene to study the membrane characteristics (solvent flux and solute rejection). Coated membranes were soaked in toluene; membrane characteristics were studied once in a week using a feed solution of 0.01 wt% of brilliant blue R in pure methanol at 413 kPa. Before measuring the membrane characteristics, toluene in the membrane pores was replaced with methanol by pressurizing methanol in the lumen side at a transmembrane pressure of 413 kPa for three hours. Membranes were washed with pure methanol after the solute rejection and solvent flux measurements. Next, methanol in the membrane pores was replaced with toluene before the membrane was soaked in toluene.

2.5.2 Membrane Solvent Back Extraction

2.5.2.1 Breakthrough Pressure and Chemical Stability Studies. The breakthrough pressure is the value of the pressure difference between the organic phase and the aqueous phase at the point where phase dispersion is observed.[41] The schematic shown in Figure 2.11 was used to study the breakthrough pressures of the aqueous-organic interface and chemical stability of the coated Nylon 6 hollow fibers. Aqueous-organic phase immobilization at the membrane pore mouth in non-coated and coated Nylon hollow fibers was studied using the water-MIBK system via the following procedure. Membrane pores were filled with water and water was passed through the shell side at a constant pressure. Organic solvent was passed cocurrently through the lumen side at varying pressures higher than the aqueous phase pressure. Experiments were started with a low lumen side pressure; it was increased in steps of 0.5 psi (3.45 kPa) till phase dispersion was observed. Shell side and lumen side pressures were controlled by valves mounted beyond the hollow fiber module. In addition to the breakthrough pressure studies, interfacial tensions between the aqueous-organic-solute systems (water-MIBK, water-MIBK-acetic acid and water-MIBK-phenol) were measured by an interfacial tensiometer (model K8, Kruss, Hamburg, Germany).

The chemical stability of the coating was studied by passing aqueous caustic solution (0.5 M) through the shell side and an organic solvent (MIBK) in the lumen side at a higher pressure than the aqueous phase for extended periods of time. Nondispersive operation was used as a measure of the stability of the coating since possible damage to the coating will lead to phase dispersion at a pressure difference of 2 psi (13.78 kPa) between the phases.

2.5.2.2 Solvent Back Extraction Studies. A schematic of the experimental setup for solvent back extraction of solutes (phenol and acetic acid) from MIBK into an aqueous solution is shown in Figure 2.11. For reactive extraction, 0.1M phenol in MIBK was extracted into 0.25M aqueous caustic solution. Acetic acid extraction from 3 vol% of acetic acid in MIBK into water was used as a model system for nonreactive extraction.

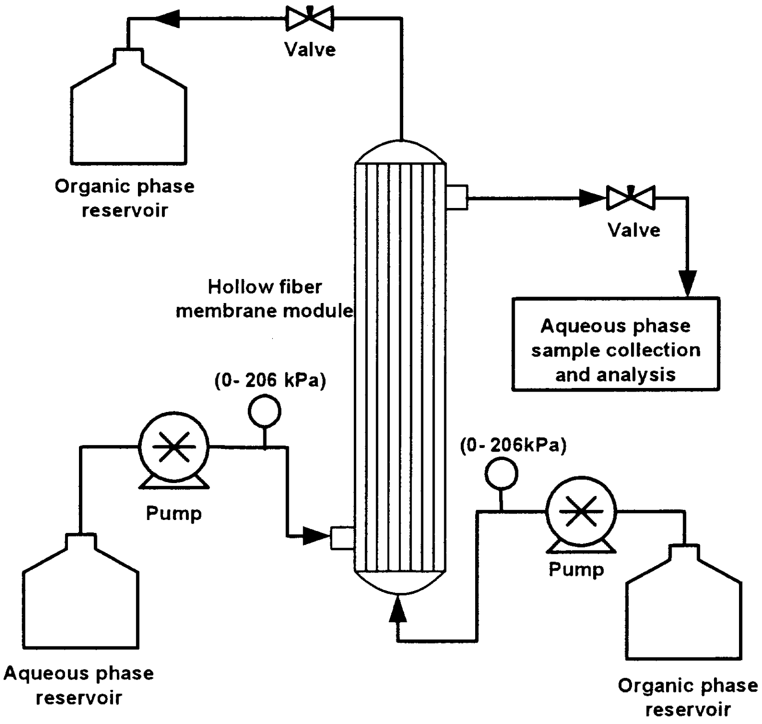

Figure 2.11 Experimental setup for membrane solvent back extraction.

The organic phase was passed through the lumen side and the aqueous phase was passed through the shell side in all experiments. For hydrophilic hollow fiber modules, experiments were started by pressurizing the aqueous solution in the shell side of the module at 3 psig (122 kPa) for a couple of minutes so that the membrane pores were completely filled with the aqueous solution. Then, the aqueous phase pressure was lowered to 1 psig (108.2 kPa) and the aqueous solution was passed continuously. The MIBK solution was passed cocurrently through the lumen side at a pressure higher than the aqueous phase pressure and less than the breakthrough pressure. In the case of hydrophobic hollow fiber modules, the organic solution first was passed through the lumen side to fill the pores of the membrane with the organic phase. Next, the aqueous phase was passed through the shell side at a pressure greater than the organic phase pressure.

Freshly prepared aqueous and organic solutions were used for each set of experiments. After running the system for 30 min (for each set of data taking) to reach steady state, aqueous samples were collected and analysed for solute concentrations. Phenol in water was analyzed by the following technique. A 0.5 ml aliquot of alkaline phenol solution was diluted by first adding 5 ml of solution A (4.767 g sodium borate 10-hydrate, 0.352 g sodium hydroxide, and 0.06 g 4-amino-antipyrine in 1L distilled water) followed by adding 10 ml of solution B (4.767 g sodium borate and 10-hydrate, 0.352 g sodium hydroxide, and 0.15 g potassium ferricyanide in 1L distilled water). Absorbance of this solution was measured by the UV-VIS spectrophotometer at the wavelength of 520 nm.[19] The calibration curve of absorbance vs. phenol concentration in the aqueous sample is given in Figure 2.12. Acetic acid in water was analyzed by titrating against sodium hydroxide solution. Flow rates were measured and pressures were carefully monitored throughout the experiments.

2.6 Heat Transfer

Heat transfer performance of the PES hollow fiber coated with polyamide and silicone were tested for heat transfer performance in collaboration with other investigators in the laboratory. Hot brine of 4% NaCl concentration at 90°C to 95 °C was passed through the lumen side or shell side of the module and cold water (16°C to 25°C) was passed countercurrently through the other side of the module. Since the coating was on the lumen side, the lumen side pressures were always maintained higher than the shell side pressures to prevent the possible detachment of the coating from the support. Shell side and tube side inlet and outlet temperatures were continuously monitored; brine and water flow rates were measured. Any leakage through the coating will increase the conductivity of water. Conductivity of water was continuously measured to monitor the leakage, if any.

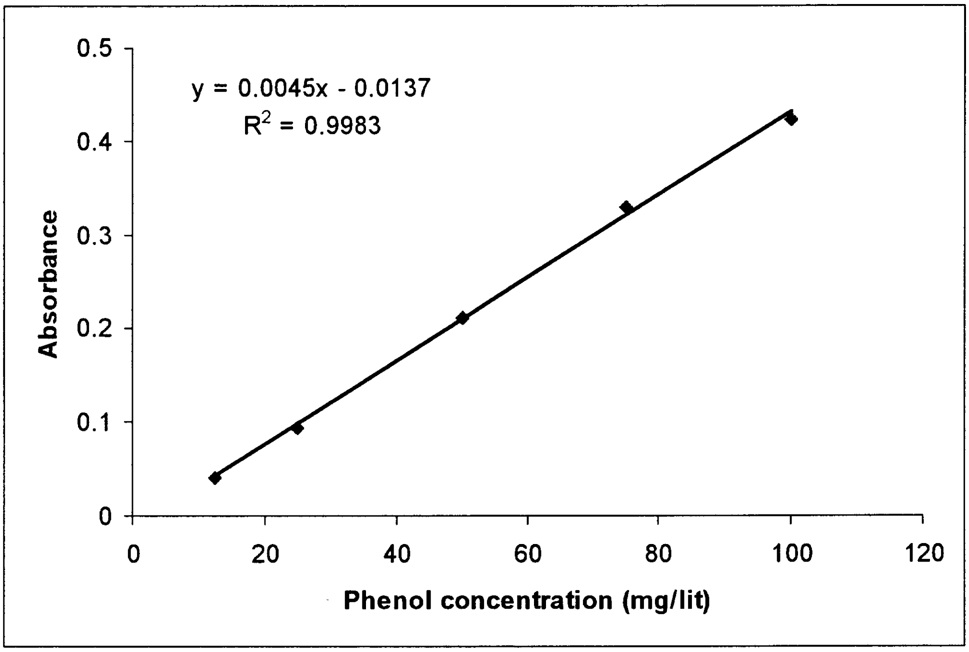

Figure 2.12 Calibration curve for analyzing phenol in MIBK.

2.7 Calculation Procedures

2.7.1 Calculation of Solute Rejection and Solvent Flux in Ultrafiltration and Nanofiltration Membranes

The percentage rejection of solute is given by

$$R = 100\left(1 - \frac{C_{permeate}}{C_{feed}}\right) \tag{2.1}$$

Transmembrane pressure, ΔP, is defined as the pressure difference across the membrane and the solvent flux at a particular transmembrane pressure is given by

$$\text{Solvent flux} = \frac{\text{volumetric flow rate of the permeate}}{\text{membrane area}} \tag{2.2}$$

2.7.2 Considerations on Mass Transfer Coefficient Calculations in MSBE

Overall mass transfer coefficients in MSBE were calculated from experimental data using the following equations:

$$Q_{org}\left(C_{org-in} - C_{org-out}\right) = K_o\left(\Delta C\right)_{LM} * \left(\mathrm{A_m}\right) \tag{2.3a}$$

$$\left(\Delta C\right)_{LM} = \frac{\left(C_{org-in} - mC_{aq-in}\right) - \left(C_{org-out} - mC_{aq-out}\right)}{\ln\left(\left(C_{org-in} - mC_{aq-in}\right)/\left(C_{org-out} - mC_{aq-out}\right)\right)} \tag{2.3b}$$

The overall mass transfer coefficient of the solute, K_o, based on the organic phase in a hydrophilic hollow fiber membrane with aqueous phase-filled pores and organic phase flowing in the lumen side is given by

$$1\Big/K_o d_i = \left(1\Big/k_o d_i\right) + \left(m\Big/k_{mw} d_{lm}\right) + \left(m\Big/k_w d_o\right) \tag{2.4}$$

Here the membrane resistance k_{mw} is given by

$$k_{mw} = \frac{D_{Aw}\varepsilon_m}{t\tau_m} \tag{2.5}$$

For an instantaneous chemical reaction in the aqueous phase (reactive extraction system), Equation 2.4 becomes

$$1/K_o \cong \left(1/k_o\right) \tag{2.6}$$

The overall mass transfer coefficient of the solute, K_o, based on the organic phase in a hydrophobic hollow fiber membrane with organic filled pores and organic phase flowing in the lumen side is given by

$$1/K_o d_o = \left(1/k_o d_i\right) + \left(1/k_{mo} d_{lm}\right) + \left(m/k_w d_o\right) \tag{2.7}$$

In the presence of an instantaneous chemical reaction in the aqueous phase (reactive extraction system), Equation 2.7 will be reduced to

$$1/K_o d_o \cong \left(1/k_o d_i + 1/k_{mo} d_{lm}\right) \tag{2.8}$$

Here the membrane resistance k_{mo} is given by

$$k_{mo} = \frac{D_{Ao}\varepsilon_m}{t\tau_m} \tag{2.9}$$

The diffusion coefficients of phenol and acetic acid were calculated using the Wilke-Chang equation.[83] The tortuosity of the hydrophobic membranes was considered to be 2.6.[84] The tortuosity of the hydrophilic Nylon hollow fibers was estimated from the following correlation:[85]

$$\tau = \frac{(2-\varepsilon)^2}{\varepsilon} \tag{2.10}$$

Graetz solution[84] was used to estimate theoretically the tube-side mass transfer coefficients in hydrophobic and hydrophilic hollow fibers. Graetz solution is given by[86]

$$N_{Sh-t} = 0.5\left(\frac{d_i}{L}\right) N_{\mathrm{Re}-t} N_{Sc-t}\theta \tag{2.11}$$

where

$$\theta = \frac{1-\sum_{n=1}^{\infty}\left\{-4\left(B_n/\beta_n^2\right)\left(d\phi/dr_+\right)_{r_+=1}\exp\left[\left(1-\beta_n^2 L/r_i/N_{\mathrm{Re}-t}N_{Sc-t}\right)\right]\right\}}{1+\sum_{n=1}^{\infty}\left\{-4\left(B_n/\beta_n^2\right)\left(d\phi/dr_+\right)_{r_+=1}\exp\left[\left(1-\beta_n^2 L/r_i/N_{\mathrm{Re}-t}N_{Sc-t}\right)\right]\right\}} \tag{2.12}$$

β_n and B_n in Equation 2.12 are given by

$$\beta_n = 4(n-1)+8/3; \quad \mathrm{n} = 1,2,3... \tag{2.13}$$

$$\frac{-B_n}{2}\left(\frac{d\phi_n}{dr_+}\right)_{r_+=1} = 1.01276\beta_n^{-1/3} \tag{2.14}$$

Shell-side mass transfer coefficients in hydrophobic and hydrophilic fibers were calculated from the following correlation:[84]

$$N_{Sh-s} = \alpha(1-\phi)\left(\frac{D_h}{L}\right)N_{\mathrm{Re}-s}^{0.66}N_{Sc-s}^{0.33} \tag{2.15}$$

where the value of α is 5.8 for hydrophobic fibers and 6.1 for hydrophilic fibers.

2.7.3 Calculation of Overall Heat Transfer Coefficients in Modified PES Hollow Fiber Modules

Overall heat transfer coefficient in the coated hollow fiber module was calculated by the following equation and compared with the literature data for solid PP hollow fibers:

$$U = \frac{Q}{A_m \Delta T_{lm}} \tag{2.16}$$

Here ΔT_{lm} and Q are obtained from the following equations

$$\Delta T_{lm} = \frac{\left(T_{t,in}-T_{s,out}\right)-\left(T_{t,out}-T_{s,in}\right)}{\ln\left(\frac{T_{t,in}-T_{s,out}}{T_{t,out}-T_{s,in}}\right)} \tag{2.17}$$

$$Q = \dot{m}C_p\Delta T \tag{2.18}$$

CHAPTER 3

ULTRAFILTRATION AND NANOFILTRATION

Results for hydrophilization of the PP hollow fiber membranes by chromic acid treatment will be presented first. This will be followed by the presentation of the results and corresponding discussion of the membrane modification for fabrication of ultrafiltration and nanofiltration membranes. Results of solvent stability studies carried out will also be presented along with the results of ultrafiltration and nanofiltration.

3.1 Hydrophilization

Hydrophilization of PP support membranes was carried out prior to the coating by interfacial polymerization. Initially, hollow fiber membrane modules were treated with a chromic acid solution of high concentration ($K_2Cr_2O_7$, H_2O, H_2SO_4: 1, 2, 29.4) for a shorter period of time (5 minutes). Later, the chromic acid concentration to treat the membranes was halved ($K_2Cr_2O_7$, H_2O, H_2SO_4: 1, 19, 29.4) and the membranes were treated for longer periods of time (60 minutes). At the same time, a hot chromic solution at 65 °C was used instead of treating the membranes with chromic acid solution at room temperature, because oxidation of chromic acid is effective at high temperatures. Chromic acid solution when passed through the fibers, could not wet the membranes and hence the pore mouth and the pore interior of the PP membrane were not hydrophilized. When water was pressurized in the fibers to wash the fibers after chromic acid treatment, water did not permeate through the membranes because only lumen side of the fibers was hydrophilized with chromic acid; pore mouth and the pore interior were not hydrophilized.

In order to hydrophilize the pore mouth and the pore interior of the membranes, the fibers were first prewetted with acetone and the chromic acid solution was then pressurized in the fibers. Acetone is miscible with the chromic acid solution and hence acetone in the membrane pores will be easily replaced with chromic acid with the applied pressure. Employing acetone as a wetting agent is advantageous over ethanol as acetone is hard to oxidize because it is a ketone. By wetting the pores with acetone prior to chromic acid treatment, chromic solution penetrated into pores of the membrane and hydrophilized the pore mouth and pore interior. After passing acetone through the hollow fibers and filling the membrane pores with acetone, one should not use air to remove the excess acetone from the lumen side as air when passed through the fibers would evaporate acetone from the membrane pores. Instead, chromic solution was immediately passed through the fibers and the chromic acid solution that comes out of the module for the first couple of minutes of the treatment was discarded. Water was permeated through the membranes when water was pressurized in the fibers. Prewetting with acetone helped uniform hydrophilization of PP hollow fiber membranes. After treating the fibers for thirty minutes, chromic acid solution in the reservoir was replaced with fresh chromic solution and the membranes were treated for thirty more minutes.

3.2 Ultrafiltration

As mentioned in Section 1.7, only a successful combination of hydrophilization of the fibers (when PP is used as support), IP procedure (“regular or “reverse”), nature of the monomers and the reaction times, removing the excess monomers from the lumen side, and heat treatment technique will lead to a non-defective and uniform coating in hollow fibers. As hydrophilization is the first step involved in the coating process of hydrophobic fibers, a successful procedure for hydrophilization of PP hydrophobic fibers was first developed (Section 3.1). The order of the optimization of the other steps is as follows: IP procedure (“regular or “reverse”), heat treatment technique, removing the excess monomers from the lumen side, nature of the monomers and the reaction times. Zein concentration in the feed solution used for characterization of all fabricated ultrafiltration membranes was 1 g/l unless otherwise mentioned.

3.2.1 Coating on X-10 Hollow Fibers (Module A)

Solvent flux and zein rejection measurements for bare and coated membranes on X-10 hollow fibers modified to fabricate ultrafiltration membranes are presented in Table 3.1 along with each membrane’s IP modification history. During the modification of X-10 hollow fibers, IP procedure (“regular or “reverse”) and heat treatment techniques were optimized.

The reactive monomer system of 1,6-hexanediamine-sebacoyl chloride was used to coat all X-10 hollow fiber membrane modules. Excess aqueous/organic monomer containing solutions were removed from the lumen side by purging it gently with air at a flow rate of 3 cm^3/s for 1 minute. The lowest possible flow rate of $20*10^{-3}$ cm^3/s was used to pass the organic/aqueous monomer containing solution through the fibers to minimize the drag force (on the nascent coating) involved during the coating process. Different heat treatment techniques studied were: passing hot water at 65 °C for 30 minutes; passing hot air at 65 °C for 30 minutes.

Table 3.1 Solvent Flux and Zein Rejection in Hollow Fiber Membranes

Membrane	Solvent flux* ($cm^3/(cm^2 \cdot s)$)	Zein rejection (%)	SEM picture	Reactants' [†††] concentrations	Polymerization time
X-10 (bare)	$4*10^{-4}$	0	Similar to Figure 2	-	-
X-20 (bare)	$8*10^{-4}$	0		-	-
X-10[†]	$3.9*10^{-4}$	11	Figure 7a	1 wt.% SC 1 wt.% HD	1.5 min
X-10[††]	$18*10^{-6}$	97	Figure 8	2 wt.% SC 2 wt.% HD	2.5 min
X-20	$53*10^{-6}$	73	Figure 9	0.5 wt.% PEI 0.5 wt.% IPD	10 min
X-20	$4.2*10^{-5}$ **	91	Figure 11	0.5 wt.% PEI 0.5 wt.% IPD	10 min

*at 52 kPa

**at 138 kPa

[†] Coated by wetting the hydrophilized surface with the organic solution followed by the aqueous solution

[††] Three layered coating, contact time was the same for each layer as specified

[†††] SC - sebacoyl dichloride, HD - 1,6-hexanediamine, IPD – iso-phthaloyl dichloride, PEI - poly(ethyleneimine)

The PP X-10 hollow fibers in the module were first modified by the "reverse procedure" as described in Subsection 2.3.2.2. It is well known that only the diamine monomer can partition into the organic solvent, but dichloride monomer cannot partition into water and hence the thin film is formed in the organic phase.[59] For this reason, the support was wetted with the organic monomer containing solution after hydrophilization because the IP layer formed in the organic phase could bind to the support better.

However, the membrane module coated by the above procedure offered only 11% rejection for zein with no reduction in the solvent flux. A SEM picture of the coating (Figure 3.1a) suggests it was very similar to the support membrane (Figure 1.3), indicating that there was no coating. From this observation, it was concluded that by wetting the support with the organic solution after hydrophilization, the hydrophilized groups created earlier on the surface of the support might have been inverted toward the interior of the support and hence the coating lacked the binding to the support.[71] Although there will be formation of the coating during the IP process, the coating might have been washed away when the characterization studies were carried out. For this reason, the inner surface of the fibers were afterwards always first wetted with the aqueous monomer solution before passing the organic monomer solution for the rest of the membrane modification of hydrophobic fibers ("regular procedure" as described in the Subsection 2.3.2.1).

Next, different modes of heat treatment were studied using 2 wt.% monomer concentrations with the reaction time of 2.5 minutes. SEM pictures and characterization by zein rejection indicated that heat treatment by passing hot water through the fibers immediately after the IP process produced a number of defects (Figure 3.1b). These defects could have resulted from the drag created on the nascent IP film by the flow of hot water. To cover these defects, the coated fibers were coated again by the same procedure as the first coating without the hydrophilization step. The hydrophilization step was not needed because the polyamide coating was already hydrophilic. A 97% rejection of zein was achieved after the third layer of coating and the SEM picture of this layer of the membrane is shown in Figure 3.2. Although this picture shows some defects in the third coated layer, it appears that these defects are covered with the nondefective sections of the second and first layers resulting in a good rejection of the protein zein. Even though a good rejection of zein was achieved after three layers of coating, the solvent flux was reduced 22 times compared with the support membrane.

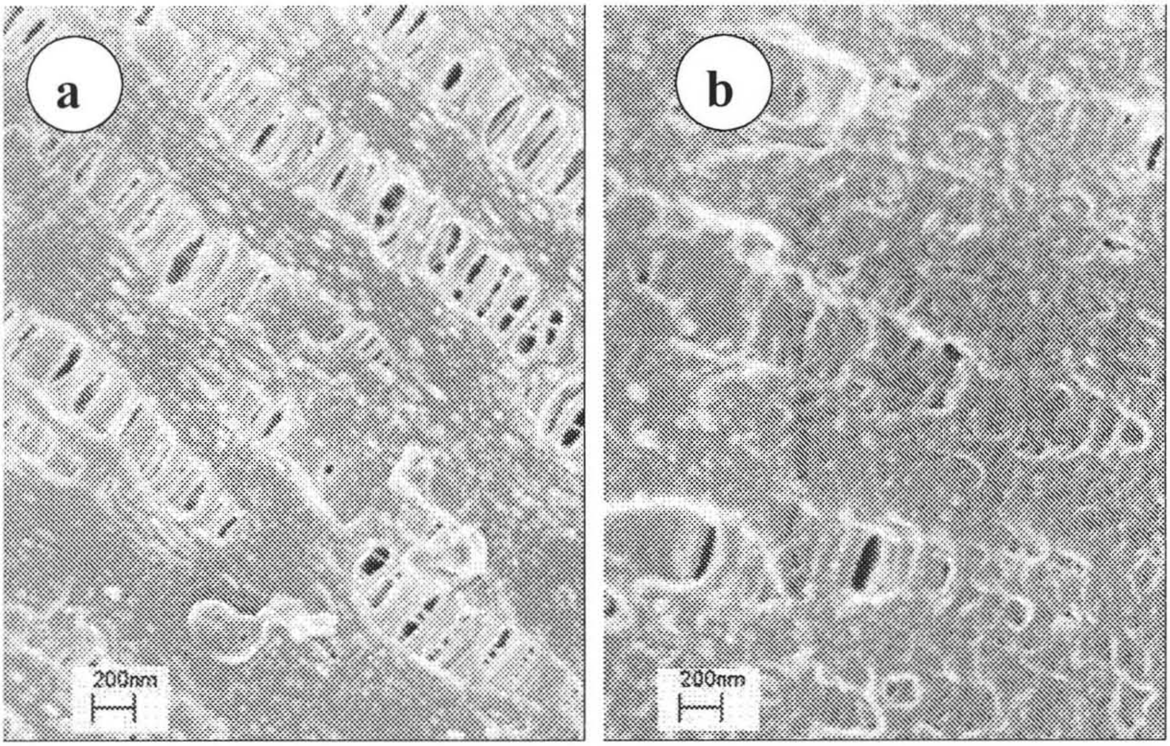

Figure 3.1 a) Surface of the coated X-10 hollow fiber, coated by wetting the hydrophilized surface with organic solution followed by aqueous solution; b) defects in the coated surface of X-10 hollow fiber, heat treated by passing hot water after IP.

Heat treatment by passing hot air through the fibers was also studied and did not yield fruitful results. The surface of the coating that was heat treated by passing hot air at 65 °C for 30 minutes is shown in Figure 3.3. The next heat treatment technique studied was to place the coated module in an over at 110 °C for 20 minutes. Additional studies of optimization of the steps including the heat treatment in an oven were carried out in X-20 hollow fibers which are larger in diameter than X-10 hollow fibers.

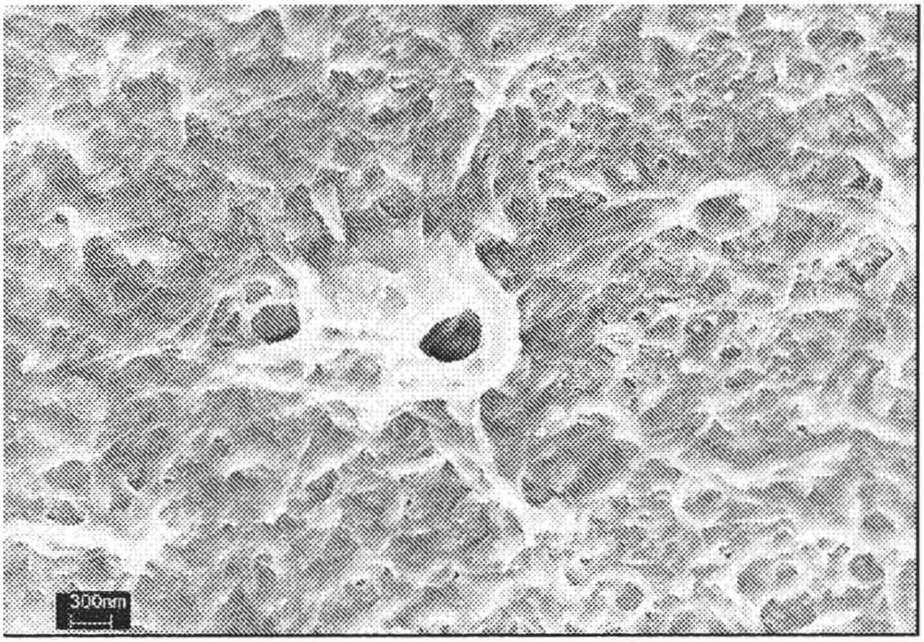

Figure 3.2 Surface of the third coated layer on X-10 hollow fiber support.

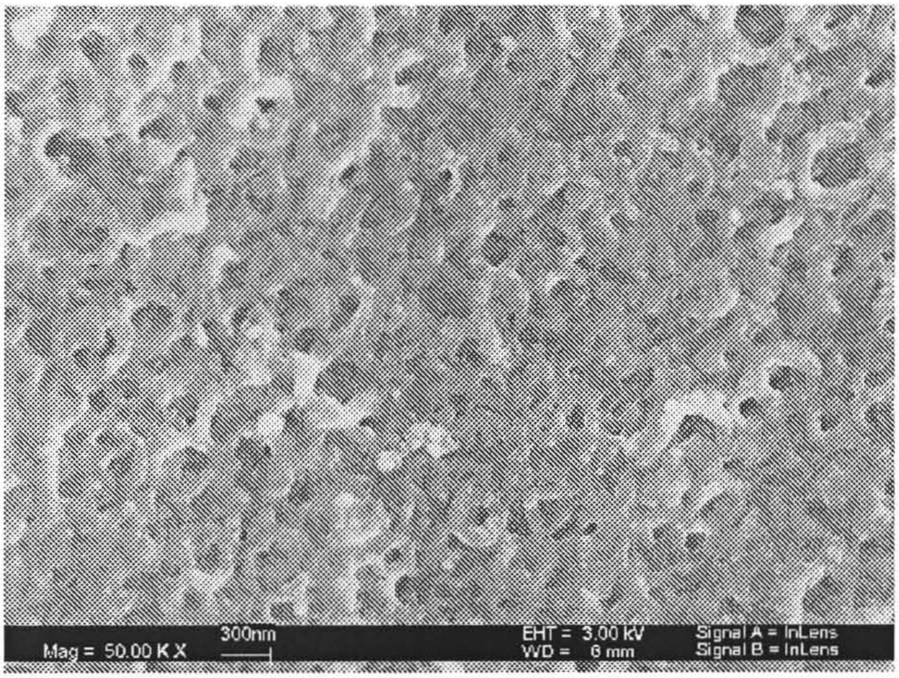

Figure 3.3 Surface of X-10 PP hollow fiber membrane heat treated by passing hot air.

3.2.2 Coating on X-20 Hollow Fibers (Module B)

Since PP X-20 hollow fibers are available in larger inner diameter than X-10 fibers, further studies were carried out using X-20 fibers with the expectation of improving the coating characteristics. Removing the excess aqueous/organic monomer solutions from the lumen side, the nature of the monomers and the reaction times, and heat treatment of the coating were optimized in the modification of X-20 hollow fibers. Table 3.1 provides the solvent flux and zein rejection measurements in the modified X-20 hollow fiber membranes.

The reactive monomer system of poly(ethyleneimine)-isophthaloyl dichloride was primarily used to coat X-20 hollow fiber membranes. After complete optimization of the coating process, the nature of the coating with the reactive monomer system of 1,3-phenylenediamine-trimesoic acid trichloride was also studied. During the polymerization process, the organic monomer containing solution was kept standing still inside the lumen of the fibers instead of passing it the through the fibers. This was carried out as follows. The organic solution was initially passed through the fibers holding the module vertical; when the organic solution appeared at the other end of the module, the flow of the organic solution through the fibers was stopped. After a period of up to 10 minutes, considered as the reaction time, the organic solvent was removed from fibers and the excess was removed by blowing gently with air. Then the coating was heat treated by placing the module in an oven at 110 °C for 20 minutes.

The zein rejection achieved in the membrane coated with 0.5 wt% PEI and 0.5 wt% IPD by employing the above mentioned coating procedure was 73% (Table 3.1). The reduction in solvent flux from that of the support was 15 times. These results indicate that uniform and nondefective coating can be achieved in the X-20 hollow fibers by the employed heat treatment technique of placing the module in an oven at 110 °C for 20 minutes. The flow involved during the IP process was minimized by stopping the flow of the organic monomer solution. By doing so, a situation similar to the conditions used in coating on flat films was developed. The larger ID of the X-20 fibers could also have helped in producing a nondefective coating by reducing the shear on the nascent polyamide film at the time of removal of the organic solution after polymerization. Although the coating appeared very uniform and nondefective compared to the coatings on X-10 coated with different monomers, some defects were still observed in the coating (Figure 3.4). These defects explain the lower zein rejection (73%).

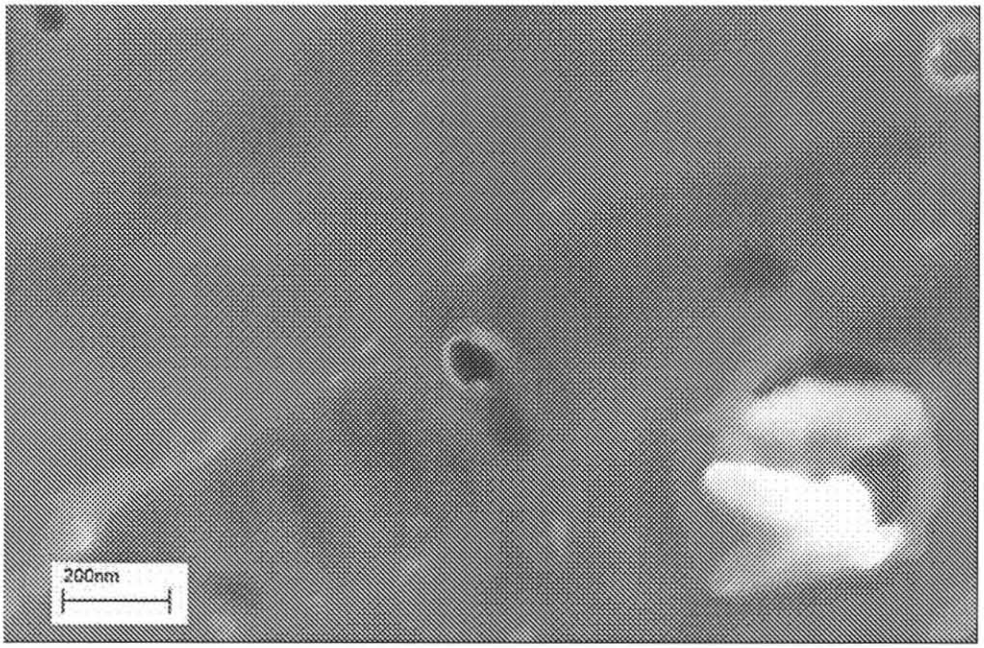

Figure 3.4 Defect in the coated surface of X-20 hollow fiber.

Next, uniform and controlled removal of excess aqueous/organic monomer solutions form the lumen side of the fibers was optimized. During the removal process of the excess aqueous monomer solution from the lumen side, the PP hollow fibers were transparent because the pores in the fiber wall were filled with the aqueous monomer solution. When air was passed through the fibers, removal of the aqueous solution from the lumen side of the fibers was visible through the transparent module casing and the transparent fibers. Thus, the lowest air flow rate, air pressure and the time of removal that removes the aqueous solution from the lumen side were measured. An air flow rate of 1.5 cm^3/s at 2 psig (115.1 kPa) and 20 seconds of removal time were the lowest values for complete removal of excess aqueous solution from X-20 hollow fibers. The same conditions would also apply to the removal of the excess organic solution from the fibers after completion of the polymerization process.

Good zein rejections (91%) were now achieved following the above mentioned excess removal procedure and using the same experimental conditions (0.5 wt% PEI, 0.5 wt% IPD, polymerization time: 10 min) on X-20 fibers. Defects in the coating were reduced by employing the optimized excess removal conditions; however a small number of defects in the coating resulted in a 91% rejection of zein instead of 99% rejection. Kistler and Cussler[81] also reported that they encountered defects when hydrophillic hollow fibers were coated by interfacial polymerization. However, 97% zein rejection was achieved at the same transmembrane pressure (138 kPa) with a feed solution of 5 g/l zein in 70% ethanol (rest, water). Higher rejection of zein with higher concentration of protein in the feed solution is probably due to the adsorption of protein on the surface of the coating and subsequent fouling of the membrane.

The solvent flux of the coated X-20 membranes for ≈ 91% zein rejection was 2 to 10 times lower than the solvent (70% ethanol) fluxes in different ultrafiltration membranes which were reported as not truly solvent resistant.[17] Solvent stability of such a coated membrane was studied and the results are presented in Figure 3.5. Both the zein rejections and the solvent fluxes were stable for an experimentally studied period of 10 weeks indicating that the coated membranes were stable in ethanol solutions. It is worth mentioning the extent of solvent stability of the ultrafiltration membranes studied by Shukla and Cheryan for the same model system.[17] Out of a number of ultrafiltration membranes tested, cellulose and polysulfone based membranes failed in a few weeks of solvent exposure. Although polyacrylonitrile-based membranes appeared to have the longest stability periods among the tested membranes, their performance declined slowly with time.

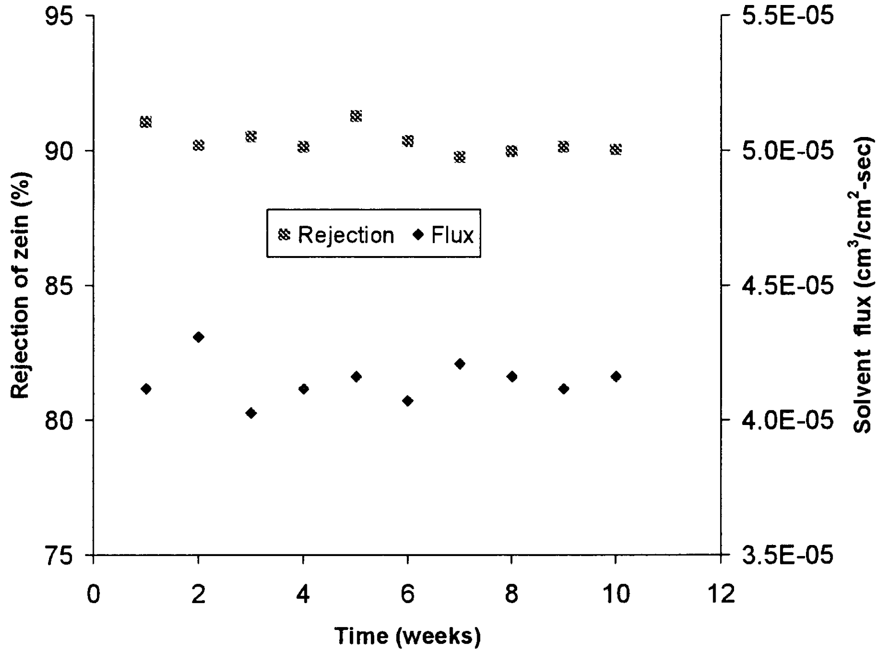

Figure 3.5 Solvent stability of the coated PP X-20 hollow fiber membranes: solvent flux and zein rejection with time (zein concentration = 1 g/l; ΔP = 138 kPa).

The coating (Figure 3.6) on X-20 hollow fiber membranes with PEI and IPD was very uniform. Although the reaction time was 10 minutes, the coating thickness was less than 0.1µm. The impressions of the support pore structure can also be observed in Figure 3.6. The bulkiness of the PEI polymer explains this behavior which is different from that of 1,6-hexanediamine. When X-20 hollow fibers were coated with 0.5 wt% of 1,3-Phenylenediamine and 0.5 wt% of trimesoic acid trichloride in xylene for ten minutes, the surface of the coating was rough with a ridge-and-valley structure (Figure 3.7) whereas the coating with the reactive monomer system of PEI and IPD was very smooth (Figure 3.6). These observations are in accordance with those in the literature that aromatic amines produce coatings with a rough surface.[69] When a tri-functional monomer (trimesoic acid trichloride) is used instead of a bi-functional monomer (IPD), the polymer develops in a three dimensional network producing a ridge-and-valley structure. Fouling is a prominent membrane phenomenon in membrane processes which decreases the membrane flux and reduces the membrane separation efficiency. Fouling increases with an increased roughness of the membrane surface; hence one would like to produce a coating having a smooth surface. From this perspective, the reactive monomer system of PEI-IPD is advantageous over the other reactive monomer system.

3.2.3 Optimized Coating Procedure

The optimized procedure developed for a defect-free coating on the lumen side of the hydrophobic X-20 PP hollow fibers is summarized in this section. Pores of the hollow fibers were first wetted with acetone by passing acetone through the lumen side at 2 psig (115.1 kPa) for 2 minutes. The chromic acid solution ($K_2Cr_2O_7$, H_2O, H_2SO_4: 1, 19, 29.4) at 65 °C was next circulated through the bore of the fibers at 5 psig. After 30 minutes of treatment, the chromic acid solution in the reservoir was replaced with a fresh batch of chromic acid solution. The chromic acid solution was washed with water for 30 minutes at a transmembrane pressure of 10 psi (68.9 kPa). Then the aqueous monomer solution was passed through the fibers for 30 minutes at 5 psig. The excess aqueous solution from the lumen side was removed by passing air at a flow rate of 1.5 cm^3/s and 2 psig (115.1 kPa) for 20 seconds. Next, the organic monomer solution was passed through the fibers at a flow rate of $20*10^{-3}$ cm^3/s followed by removal of the excess organic solution removal by blowing air at 1.5 cm^3/s flow rate and 2 psig (115.1 kPa) for 20 seconds. The coated module was then heat treated in an oven at 110 °C for 20 minutes.

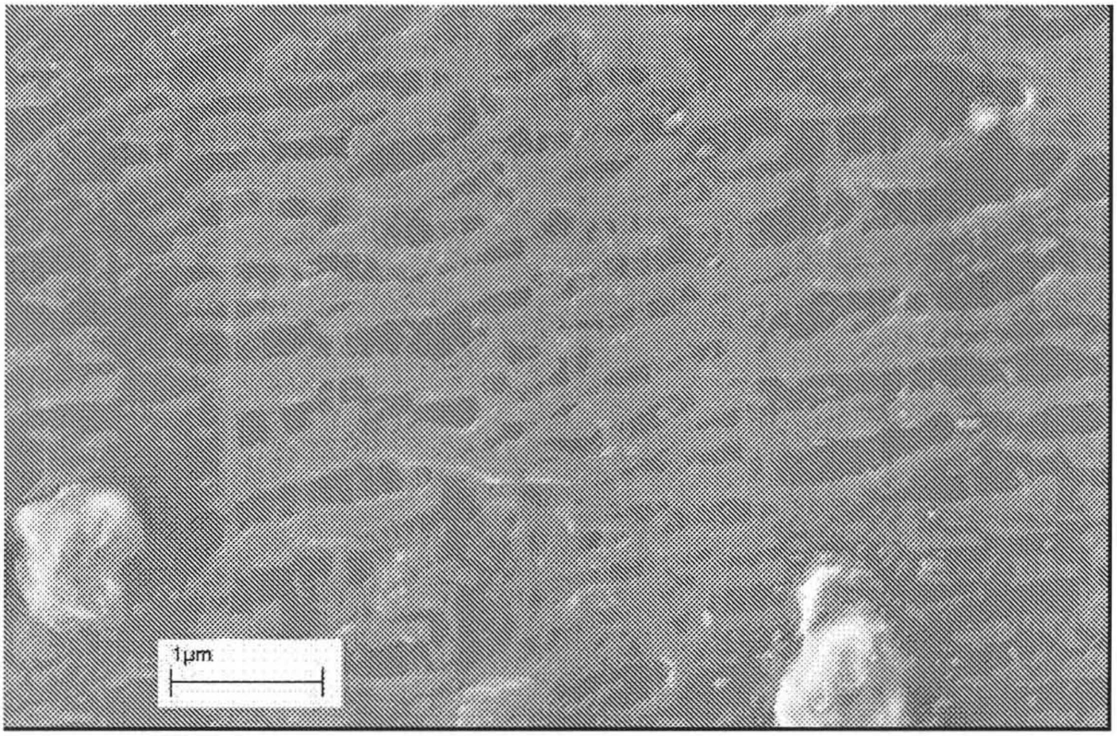

Figure 3.6 Surface of the coated X-20 hollow fiber.

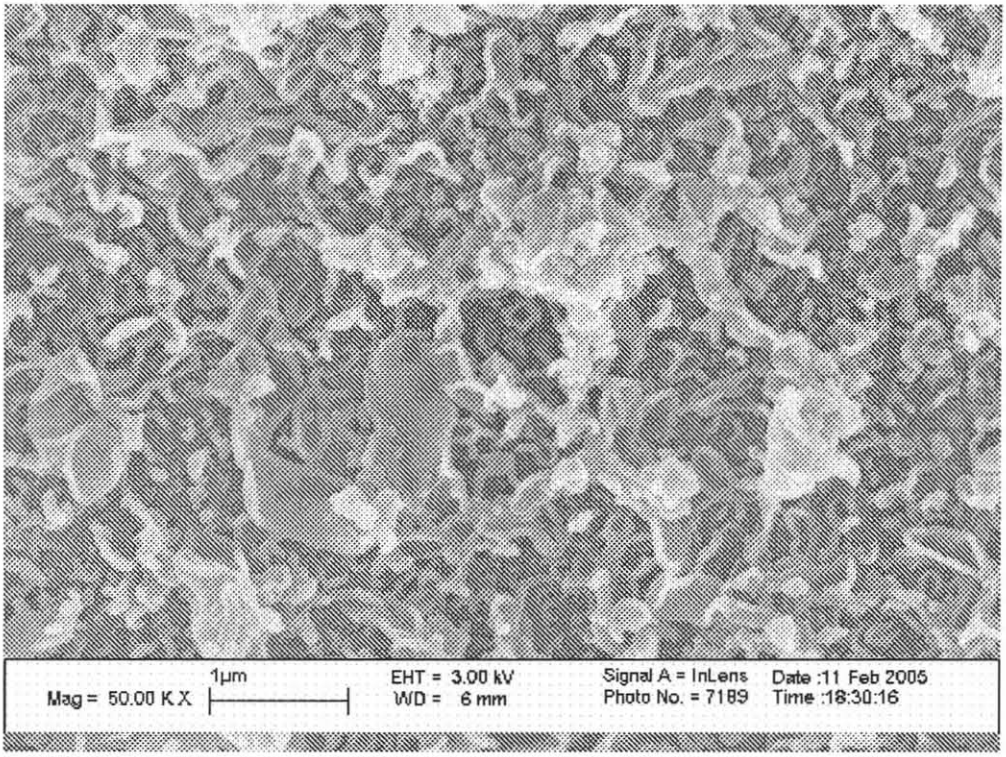

Figure 3.7 A rough coating on X-20 hollow fiber (0.5 wt% 1,3-phenylenediamine , 0.5 wt% trimesoic acid trichloride, polymerization time: 10 minutes).

3.2.4 Coating on PES (Module C) and Nylon (Module D) Hollow Fibers

The cross sectional area for the lumen side flow in Modules C and D are slightly larger than that of Module B. Since the air flow rate to remove excess aqueous/organic solutions from the lumen side depends on this cross sectional area, slightly higher flow rates of air (3 cm^3/s for Module C and 2.25 cm^3/s for Module D) were employed to maintain the same velocity of air flow in the fibers; the pressure at which the air was passed and the removal time were the same. Since PES and Nylon hollow fibers are hydrophilic, hydrophilization by the chromic acid treatment was not necessary. Other coating conditions were same as that of the optimized coating procedure for X-20 hollow fibers.

The PES hollow fibers were coated with 0.5 wt% of PEI and 0.5 wt% of IPD for ten minutes. At the applied pressure of 138 kPa, around 95% zein rejection and a solvent flux of 2.47*10^{-5} cm^3/(cm^{2}s) were achieved. The flux in the coated PES fibers was 1.7 times lower than the flux in coated X-20 hollow fibers although the modification was done via the same coating conditions. Differences in the surface porosity and pores of the X-20 and PES hollow fibers support explain this behavior.[57] Coated PES membranes were tested for solvent stability and the data are provided in Figure 3.8. Zein rejection gradually decreased to 79% in the period of four weeks and the solvent flux was increased. These results are in accordance with the solvent stability studies reported by Shukla et al.[17] that PES membranes are not stable in alcohols.

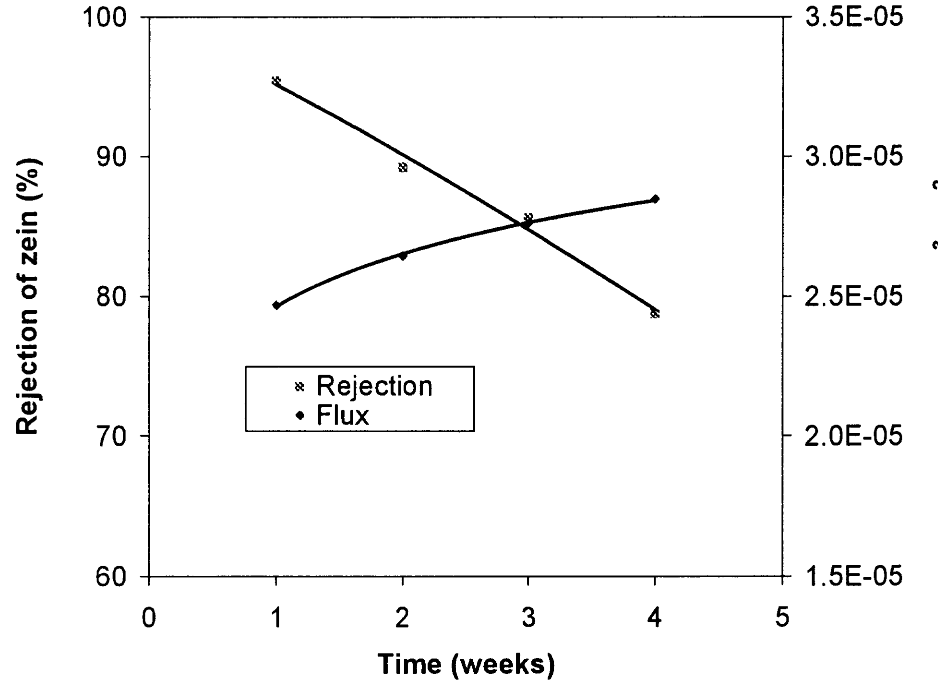

Figure 3.8 Solvent stability of the coated PES hollow fiber membranes in ethanol: solvent (70% ethanol) flux and zein rejection with time (zein concentration = 1 g/l; ΔP = 138 kPa).

The Nylon hollow fiber membrane has larger pores and a wider pore size distribution on the lumen side than the other fibers. Therefore, TFC membranes on porous Nylon supports will not be suitable for pressure driven membrane processes such as ultrafiltration. However, the lumen side of the Nylon hollow fibers was coated by interfacial polymerization because of its high solvent stability compared with PES. Nylon hollow fibers were coated with 2 wt% of PEI and 2 wt% of IPD for ten minutes. Higher concentrations of monomers (2 wt%) were used as larger pores and a wider distribution of pores have to be coated. Zein rejections in coated membranes were less than 20% at 138 kPa. From these poor zein rejection data, it was interpreted that the coating on the larger pores could not withstand the high pressures employed during the testing.

3.3 Nanofiltration

Nanofiltration membranes were fabricated on both the X-20 hollow fiber and flat film membrane supports of PP. Characterization of the coating (solute rejection and solvent flux) and solvent stability studies were carried out in hollow fiber membrane modules (Module B). Pressure dependence of the solvent flux in the modified membranes was studied using flat film membranes. As the concentrations of monomers for IP increase, the pore size of the coating will decrease.[70] Hence, membranes were fabricated using higher monomer concentrations and employing the optimized procedure that was developed for the fabrication of the ultrafiltration membranes. The monomer concentrations studied for fabrication of ultrafiltration membranes were 0.5 wt% whereas for nanofiltration, the monomer concentrations studied were 0.75 wt%, 1.0 wt% and 2.0 wt%. The same reaction time of 10 minutes was used. The optimized coating procedure described in Section 3.2.3 was employed to modify the X-20 hollow fiber membranes.

Modification conditions of the hollow fiber membrane modules along with the coating characteristics studied with methanol solutions of brilliant blue R and safranin O are provided in Table 3.2. This table illustrates the behavior of the solute rejection and the solvent flux with the increase in the monomer concentrations of the coating. Rejection of brilliant blue R in the membrane coated with 0.5 wt% of monomers was 78%. With the increase in concentration of the monomers used for the coating to 0.75 wt%, the rejection of brilliant blue R was increased to 88%. Rejection was not further improved with the increase in monomer concentrations 1 wt%. However, the solvent flux was gradually reduced with the increase in monomer concentrations used for the coating.

Table 3.2 The Behavior of Solute Rejection and the Solvent Flux (Measured at 413 kPa) with an Increase in the Monomer Concentrations Used for the Coating in Hollow Fiber Membrane Modules

Reactants concentrations	Feed solution: 0.01 wt% of brilliant blue R in methanol		Feed solution: 0.01 wt% of safranin O in methanol	
	Brilliant blue R rejection (%)	Methanol flux ($cm^3/(cm^2 \cdot s)$)	Safranin O rejection (%)	Methanol flux ($cm^3/(cm^2 \cdot s)$)
0.5 wt% PEI 0.5 wt% IPD	79	$1.83*10^{-4}$	38	$1.81*10^{-4}$
0.75 wt% PEI 0.75 wt% IPD	88	$1.69*10^{-4}$	43	$1.69*10^{-4}$
1.0 wt% PEI 1.0 wt% IPD	88	$1.38*10^{-4}$	45	$1.40*10^{-4}$
2.0 wt% PEI 2.0 wt% IPD	-	-	45	$0.95*10^{-4}$

Rejection of safranin O was increased from 38% to 43% when the monomer concentrations for the coating were increased from 0.5 wt% to 0.75 wt%. Safranin O rejection in the membranes coated with 0.75 wt%, 1.0 wt% and 2 wt% monomer concentrations were nearly the same. These solute (brilliant blue R and safranin O) rejection results indicate that only a limited variation in pore size of the coating can be achieved by varying the concentrations of the monomers for the studied reactive monomer system of PEI-IPD. The values of methanol flux (Table 3.2) achieved in the membranes were the same with both the feed solutions of brilliant blue R in methanol and safranin O in methanol because feed solutions had very low dye concentrations (0.01 wt%). The steady state flux of methanol obtained by Whu et al.[1] in the commercially available nanofiltration membranes having a 400 molecular weight cut off (MWCO) for a feed solution of 0.01 wt% of safranin O in methanol at 1034 kPa was $1.97*10^{-4}$ $cm^3/(cm^2 \cdot s)$. The solvent flux values normalized with the pressure in the membranes fabricated here were at least two times higher than the normalized solvent flux in the commercial membrane having a 400 MWCO.

To better understand the nature of the coating, rejection of zein was also studied in the hollow fiber membranes coated with 0.75 wt% monomer concentrations. A zein rejection of 97% was achieved with a solvent (70% ethanol) flux of $1.17*10^{-4}$ $cm^3/(cm^2 \cdot s)$ at a transmembrane pressure of 413 kPa. Flux of methanol in the same membrane was $1.69*10^{-4}$ $cm^3/(cm^2 \cdot s)$. Lower flux values of ethanol over methanol was also observed by Musale et al.[4] and Kim et al.[60] in crosslinked poly(acrylonitrile) composite nanofiltration membranes. This may be due to the combined effects of an increase in molecular weight and viscosity of ethanol over methanol.[4, 60] The zein rejection and solvent flux in the membranes coated with 0.5 wt% monomer concentrations measured at 413 kPa were respectively 97% and $1.36*10^{-4}$ $cm^3/(cm^2 \cdot s)$. At 138 kPa, the zein rejection and solvent flux in the same membranes were 91% and

$53*10^{-6}$ $cm^3/(cm^2 \cdot s)$ (Table 3.1). Therefore, zein rejection was increased from 91% to 97% when the transmembrane pressure was increased from 138 kPa to 413 kPa. It is believed that transport mechanism in nanofiltration membranes follows the solution-diffusion model. This model predicts that the solute rejection increases with an increase in pressure. In the solution-diffusion model, the solute flux is independent of the applied pressure at high solute rejections and solvent flux is proportional to the applied pressure.[1, 2] As a result, rejection increases at higher pressures. Rejection of safranin O measured at 413 kPa in the membrane module coated with 0.75 wt% monomer concentrations was 43%. If higher pressures (>413 kPa) can be employed in hollow fiber modules, higher rejections of safranin O can be achieved in the same membrane module. Whu et al.[1] reported that rejection of safranin O in a nanofiltration membrane with 400 MWCO was increased from 45% to 87% with an increase in the transmembrane pressure from 1517 kPa to 3034 kPa.

Pure solvent (methanol) flux dependence on the transmembrane pressure (138 kPa to 689 kPa) was studied using coated flat film membranes rather than hollow fiber membrane modules because of the capability of the flat membrane cell to withstand higher pressures. Pure solvent flux was studied instead of the solvent flux for a protein (zein) or dye (brilliant blue R or safranin O) solution so that the effect (if any) of the solute can be neglected. Figure 3.9 illustrates the effect of applied pressure on the permeate flux of a pure solvent (methanol) in the PP flat film membrane coated with 0.75 wt% of PEI and 0.75 wt% of IPD for ten minutes (88% rejection of brilliant blue R was achieved in the hollow fiber membranes modified with the same coating conditions of monomer concentrations and polymerization time). Results in Figure 3.9 show that the solvent flux increased linearly with transmembrane pressure in the studied pressure range. This observed behavior follows the commonly observed linear relation between the flux and the transmembrane pressure in the absence of a solute.[2] This linear relation also indicates that there was no pore deformation at higher transmembrane pressures.

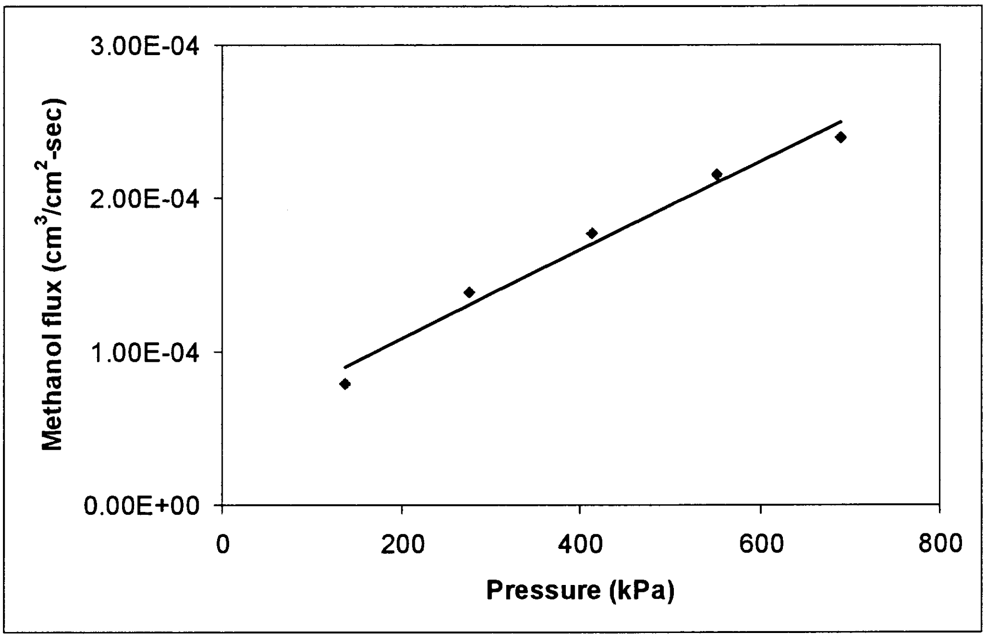

Figure 3.9 Effect of applied pressure on the permeate flux of a pure solvent (methanol) in the coated flat film membranes of PP coated with 0.75 wt% of PEI and 0.75 wt% of IPD for ten minutes.

The methanol flux and brilliant blue R rejection values were stable for the studied period of ten week's exposure to toluene (Figure 3.10). The coated membranes retained their characteristics with a long exposure to toluene. These coated membranes were already proved to be stable in alcoholic solutions (Section 3.2.2). These studies indicate that the polyamide coating on PP support is stable when exposed to a wide range of solvents (alcohols and aromatic hydrocarbons). Kim et al.[60] have reported that in short term stability studies, polyamide coating on polyacrylonitrile ultrafiltration support membrane was solvent resistant to a wide variety of solvents such as alcohols, ketones and hexane. Therefore, the membranes fabricated using a polyamide coating on polypropylene support will provide solvent stability over a wide range of solvents in extended runs.

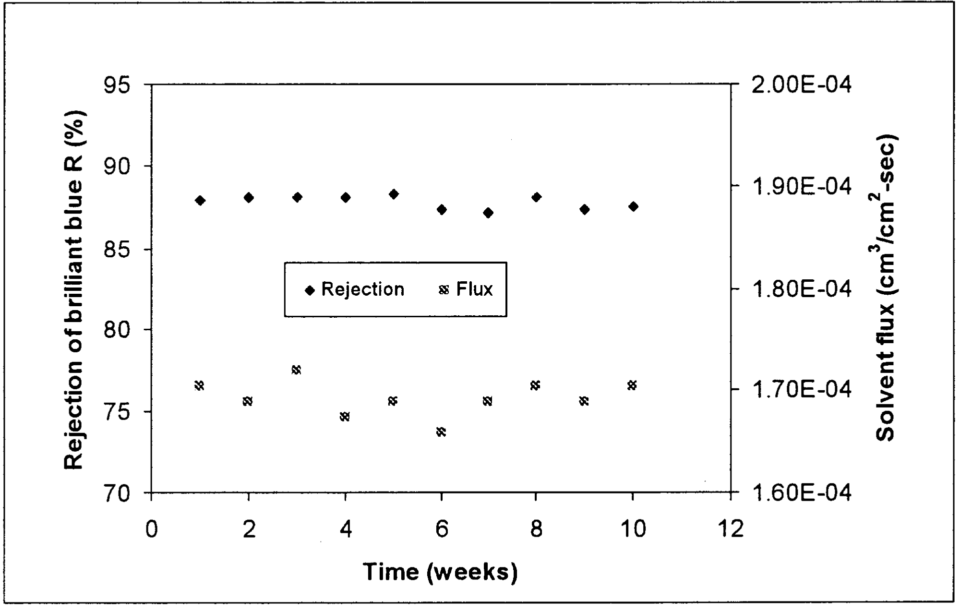

Figure 3.10 Solvent stability of the coated PP X-20 hollow fiber membranes in toluene: solvent (methanol) flux and brilliant blue rejection with time (brilliant blue R concentration = 0.01 wt %; ΔP = 413 kPa).

FT-IR spectrum of the non-coated PP flat film membrane and the polyamide-coated PP flat film membrane were compared in Figure 3.11. The peaks at 1638 cm^{-1} and 1543 cm^{-1} corresponds to the amide.[87] Therefore, it is apparent that the PP membranes were coated with the polyamide material.

3.4 Conclusions

Thin film composite membranes on polypropylene hollow fibers and flat films were successfully prepared by interfacial polymerization on the porous polypropylene support. The support was hydrophilized on a preliminary basis by pre-wetting the membranes with acetone, followed by oxidation with a hot chromic acid solution. This technique allowed achievement of uniform hydrophilization of both the pore mouth and the interior of the hydrophobic support. Treating the PP support membranes using a lower concentration of chromic acid at a higher temperature for a longer period of time provided controlled and uniform hydrophilization. Treating the hydrophilized support with the organic monomer containing solution followed by the aqueous monomer containing solution resulted in poor binding of the coated layer to the support; to obtain an effective coating on the hydrophilized support the aqueous monomer containing solution should be introduced first followed by the organic monomer containing solution.

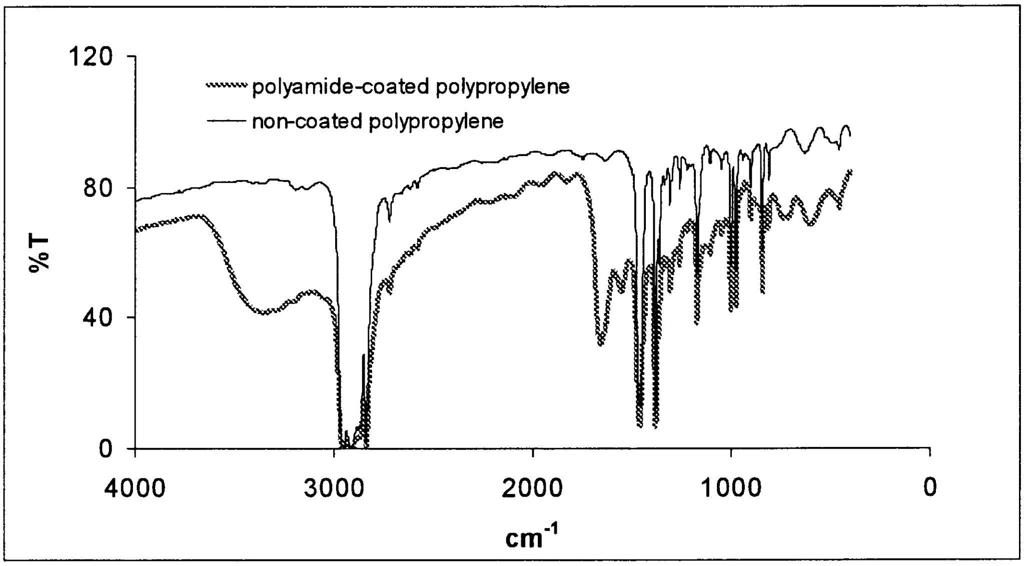

Figure 3.11 FT-IR spectrum of the non-coated and polyamide-coated flat film membrane of PP.

In the case of IP on hollow fibers, removing the excess monomer solutions by blowing air at low flow rates helped in obtaining a uniform coating. Interfacial polymerization carried out in hollow fibers having a larger ID resulted in a better coating by reducing the shear created by the flow of monomer solution on the nascent coating. Better coating was obtained by heat treatment in an oven compared with heat treatment by passing hot water, hot air and curing by ambient air. Interfacially polymerized hollow fiber membranes were characterized by ultrafiltration measurements of the corn protein, zein, in an alcoholic solution. High zein rejection of 97% was achieved at a transmembrane pressure of 413 kPa with a single coating on X-20 hollow fibers. X-20 hollow fibers of PP coated with the monomer system of poly(ethyleneimine) and iso-phthaloyl dichloride appeared to be stable in ethanol solutions. A very thin coating was achieved although the reaction time was ten minutes because of the high molecular weight of the amine monomer (PEI). The reactive monomer system of PEI-IPD produced a very smooth coating and this would reduce the membrane fouling.

The attempts to fabricate solvent resistant TFC membranes on PES and Nylon supports were unsuccessful. The coated PES membrane could not retain its characteristics when treated with alcoholic solutions in an extended run because the PES support could not provide sufficient solvent stability. The coated layer on the Nylon support which has larger pores and a wide pore size distribution could not withstand high transmembrane pressures.

Hollow fiber membranes were successfully coated with higher concentrations of monomers and the coated membranes were characterized by nanofiltration of brilliant blue R in methanol and safranin O in methanol. Only a limited variation in pore size of the coating could be achieved by varying the concentrations of the monomers for the studied reactive monomer system of PEI-IPD. Rejection values of 88% and 43% were achieved for brilliant blue R and safranin O, respectively at a transmembrane pressure of

413 kPa in a hollow fiber membrane module coated for ten minutes with 0.75 wt % monomer concentrations of PEI and IPD. The rejections could be further increased by increasing the operating pressures. However, hollow fiber membrane modules have to be specially fabricated with metal fittings to handle higher pressures. Normalized methanol flux in the fabricated membranes was at least two times higher than the flux in commercial nanofiltration membranes for a particular rejection level. Increase in the solvent flux in the coated flat film membranes was proportional to the applied transmembrane pressure in the studied pressure range. The coating was able to withstand the applied pressure of 689 kPa and pore deformation was not observed at such a high pressure. The coating was also stable to continued exposure to toluene for the studied period of ten weeks. This proves that the polyamide coating on PP has solvent resistance to alcohols and aromatic hydrocarbons.

CHAPTER 4

PERMANENT HYDROPHILIZATION OF PP FLAT SHEET MEMBRANES

Polypropylene flat film membranes were first hydrophilized by prewetting with acetone and treating with hot chromic acid solution before they were modified for permanent hydrophilization by PEI crosslinking or the "modified IP" procedure. The detailed procedure of chromic acid treatment is described in Section 3.1. The optimum concentration of chromic acid was same as the concentration that was optimized for hollow fiber modules. The results for permanent hydrophilization by PEI crosslinking will be presented first followed by the results of modification by the "modified IP" procedure.

4.1 Hydrophilization by PEI Self-Crosslinking

Porous flat film membranes of PP were modified by the modification procedure described in Section 2.3.4.1. The breakthrough pressures and the water permeation rates of the membranes modified by PEI crosslinking for different PEI concentrations are provided in Table 4.1. No water permeation was observed through the membranes modified with 0.5 wt% and 2 wt% aqueous solutions of PEI even at a transmembrane pressure of 65 psi (448 kPa). When PEI was deposited and crosslinked on the PP flat film membranes with a 4 wt% of aqueous solution of PEI, water permeated through the modified membrane when the transmembrane pressure was between 55 psi (379 kPa) and 60 psi (414 kPa). The water permeation rate after the modification was $6.7*10^{-6}$ $cm^3/(cm^2s)$. But, the water permeation rate was reduced drastically to $8.2*10^{-7}$ $cm^3/(cm^2s)$

after a twelve hour exposure of the modified membrane to xylene. This indicated that the hydrophilicity of the PEI crosslinking was not persistent enough to withstand an exposure to organic solvents. The possibility of chain mobility and the inversion of the hydrophilic groups of the crosslinked PEI with the exposure to xylene may explain this behavior.[71] Reorganization of the polymer chains with the organic solvent exposure in some hydrophilic membranes was also observed by Bruggen et al..[14] Since hydrophilicty of the modified membranes did not persist with the organic solvent exposure, permanent hydrophilization by PEI cross linking was not further persued.

Table 4.1 Breakthrough Pressures and Water Flux in Polypropylene Flat Membranes Modified using PEI Crosslinking

Reactants concentrations	Breakthrough pressure (kPa)	Water permeation rate ($cm^3/(cm^2\ s)$)
0.5 wt.% PEI	>448	-
2 wt.% PEI	>448	-
4 wt.% PEI	Between 379 and 414	$6.7*10^{-6}$ at 414 kPa

4.2 Hydrophilization by a "Modified IP" Procedure

Two different methods were employed for permanent hydrophilization of porous flat films of PP by the "modified IP" procedure. One of them was depositing PEI on the pore interior of the PP membrane from a solution of the amine dissolved in a mixture of water and ethanol. The other method was depositing PEI from the solution of amine dissolved only in water. Employing a mixture of ethanol and water instead of water as a medium to dissolve and deposit PEI, ensures the complete vaporization of the medium because of the lower overall vapor pressure of the ethanol and water mixture. When the membrane pores were filled with 2 wt % of PEI in 50 vol% of aqueous ethanol solution and vacuum was pulled through the membrane, evaporation of the medium and deposition of the PEI was achieved in less than 30 minutes. Then, the membrane was soaked in 2 wt% iso-phthaloyl dichloride in xylene for ten minutes and heat treatment was followed. The breakthrough pressure of water through such a coated membrane was between 45 psi (310 kPa) and 50psi (345 kPa), and the water flux at a transmembrane pressure of 50 psi (345 kPa) was 16.7 $*10^{-6}$ $cm^3/(cm^2\ s)$. These modified membranes retained their water flux with organic solvent (xylene) exposure.

Water was employed as a medium instead of mixture of ethanol and water to deposit PEI on the PP pore interior for the next set of experiments. Hydrophilization helps the uniform deposition of PEI on the pore interior. Employing ethanol as medium could invert the hydrophilized groups towards the polymer interior. Therefore, one would like to completely eliminate the possibility of inversion of the hydrophilized groups to provide good binding between the support and the coating. Hence water was used as a medium instead of a mixture of ethanol and water. Membrane pores filled with the aqueous PEI solution was dried for five hours to ensure complete evaporation of water. The membranes were then soaked in xylene containing iso-phthaloyl dichloride for ten minutes and heat treatment was followed. The values of the breakthrough pressures for water and water permeation rates for flat films modified employing water as a medium are provided in Table 4.2. As PEI concentration for the modification was increased from 0.5 wt.% to 3 wt.%, the breakthrough pressures for water was decreased. The surface of such a coated membrane is provided in Figure 4.1. When the PEI concentration was further increased to 6 wt%, the breakthrough pressure was increased. This phenomenon is explained as follows. When a high PEI concentration (6 wt.%) was used for coating, the surface of the flat film was most likely covered with PEI that was dried out of water instead of depositing only on the pore interior. As a result, a thin film composite membrane was formed and the breakthrough pressure was increased. It was confirmed from a SEM picture (Figure 4.2) of the flat membrane modified by 6 wt% of aqueous PEI and 2 wt% iso-phthaloyl dichloride in xylene.

Table 4.2 Breakthrough Pressure and Water Flux in Polypropylene Flat Membranes Modified by the "Modified IP" Procedure and Employing Water as a Medium for PEI Deposition

Reactants concentrations	Breakthrough pressure (kPa)	Water permeation ($cm^3/(cm^2\ s)$)
0.5 wt.% PEI, 0.5 wt.% IPD	>448	-
2 wt.% PEI, 2 wt.% IPD	Between 310 and 345	$18.3\ {*}10^{-6}$ at 345 kPa
3 wt.% PEI, 2 wt.% IPD	Between 241 and 276	$33{*}10^{-6}$ at 276 kPa
6wt.% PEI, 2 wt.% IPD	Between 379 and 414	$9.9{*}10^{-6}$ at 414 kPa

Best results (low breakthrough pressure and high water flux) were obtained when the membrane was modified with a 3 wt% aqueous solution of PEI and 2 wt% of iso-phthaloyl dichloride in xylene. Water flux and breakthrough pressure in the membranes modified with the same monomer concentrations, but employing different mediums for PEI deposition (mixture of water and ethanol as a medium and water as a medium) were nearly the same. This indicates that the medium for PEI disposition has no significant effect on coating. Hydrophilicity of the polyamide coating depends on the nature of the monomers (functional groups and the chain length) used for the coating. For example, hydrophilicity of the polyamide decreases with an increase in the hydrocarbon chain length of the monomer.[15, 88] Consequently, by selectively choosing the monomers for the coating, lower breakthrough pressures of water and hence better hydrophilicity can be achieved.

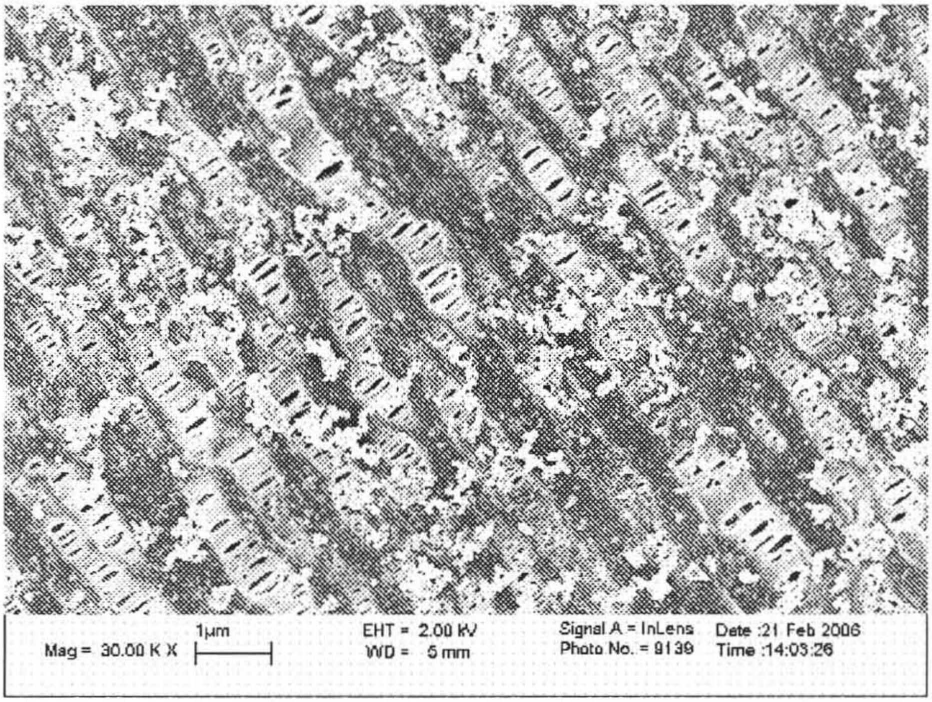

Figure 4.1 Surface of PP flat membrane coated by "modified IP" procedure with 3 wt% of aqueous PEI and 2 wt% IPD in xylene.

4.3 Conclusions

The technique of PEI crosslinking was not successful for permanent hydrophilization of PP flat film membranes as the modified membranes lost their hydrophilicity with the exposure to organic solvent. Both methods (mixture of ethanol and water as a medium and water as a medium to dissolve and deposit PEI) of membrane modification by the "modified IP" procedure appear promising for permanent hydrophilization of PP.

Membranes modified with 3 wt% of aqueous PEI solution and 2 wt% of iso-phthaloyl dichloride in xylene provided lowest breakthrough pressures and highest water flux out of all of the membrane modification experiments carried out.

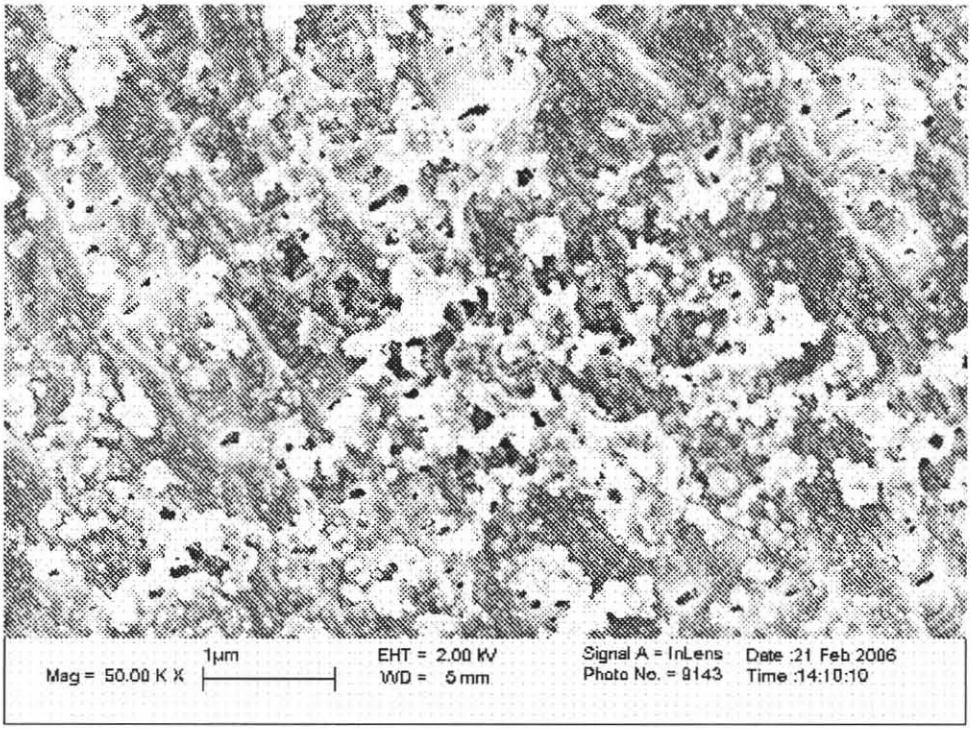

Figure 4.2 Surface of PP flat membrane coated by "modified IP" procedure with 6 wt% of aqueous PEI and 2 wt% IPD in xylene.

CHAPTER 5

MEMBRANE SOLVENT BACK EXTRACTION

The results for modification of PP membranes by the "modified IP" procedure and Nylon fibers by the "regular IP" procedure will be presented first. The results from coating the Nylon fiber by PEI-crosslinking vis-à-vis the breakthrough pressures and the observed mass transfer coefficients will be presented next. Results of reactive back extraction of phenol from MIBK into caustic solution will be presented followed by the results for non-reactive back extraction of acetic acid from MIBK into water.

5.1 Membrane Modification

5.1.1 Modification of PP by "Modified IP" Procedure

Results and discussion for permanent hydrophilization of PP by the "modified IP" procedure are provided in Section 4.2. The lowest breakthrough pressure achieved for water was between 241 and 276 kPa and water cannot immediately wet these modified PP membranes. Hence, these modified membranes are not suitable to carry out membrane solvent back extraction with the membrane pores containing the aqueous phase.

5.1.2 Modification of Nylon Hollow Fibers by IP

It is known that lowering the monomer concentrations for IP will produce a coating with smaller pores.[70] Nylon hollow fibers were coated with 0.125 wt % PEI and IPD monomer solutions by the coating procedure described in Subsection 2.3.2.1; the reaction time was ten minutes. The SEM picture of the surface of such a coating is provided in Figure 5.1. It is evident from this SEM picture that using low values of monomer concentrations produced defects in the coating rather than producing a coating with small pores. This technique of IP can not therefore be employed to produce membranes having pore sizes between those needed for ultrafiltration and microfiltration. If higher concentrations of monomers ($\geq$ 0.25 wt%) are used, the pore size of the coated membranes will be in the range of a lower end of the ultrafiltration membranes. Modification of Nylon by IP was not further studied for MSBE as the membranes modified by this technique were unlikely to be suitable for MSBE.

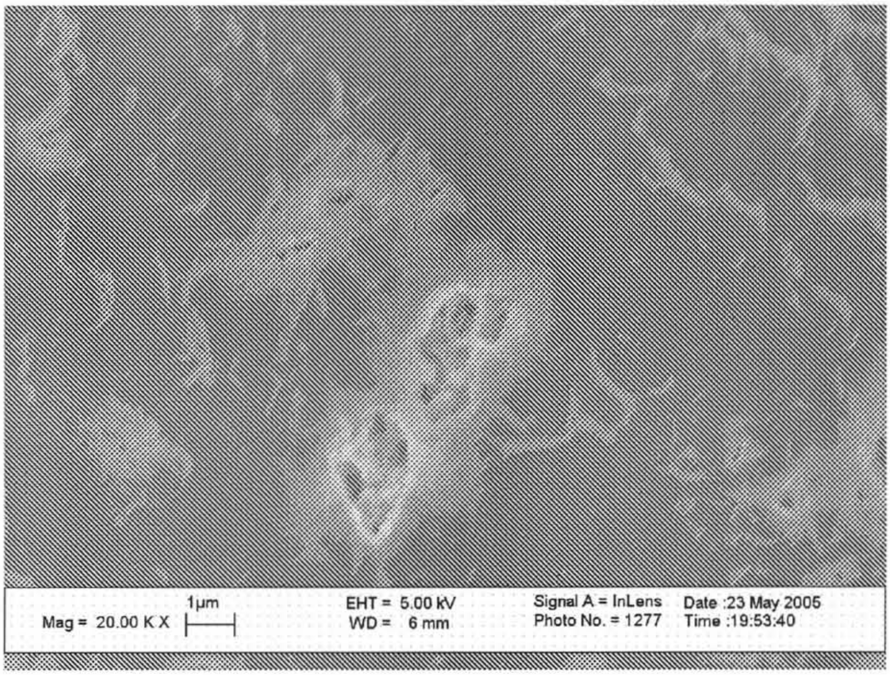

Figure 5.1 Surface of Nylon fiber coated with low monomer concentrations (0.125 wt % PEI and 0.125 % IPD).

5.1.3 Modification of Nylon Hollow Fibers by PEI Self-Crosslinking

Coating on hydrophilic Nylon fibers was carried out using different concentrations of aqueous PEI solutions (2, 4 and 6 wt%). Coating on the surface of hydrophilic membranes by crosslinking PEI appears to be a convenient and simple procedure and beneficial over other coating techniques like interfacial polymerization (IP) for the following reasons. Only one reactive solution is involved; this decreases the number of steps in the coating procedure. Defect-free and uniform coating can be achieved in the hollow fibers because flow of the reactive solution is not involved during the formation of the coating since crosslinking of PEI takes place during heat treatment. Kistler el al.[81] reported that they encountered the defects when interfacial polymerization technique was used for coating on the surface of porous hollow fibers.

To develop a better understanding of the nature of the coating, SEM pictures of the inner and outer surfaces of the non-coated Nylon fiber are shown in Figures 1.5 and 1.6, respectively. This noncoated Nylon fiber has pores of about 0.2 μm to 1.5 μm on the surface of the ID. The surface of the coated membrane with 4% PEI aqueous solution is shown in Figure 5.2. The coating appears uniform and the pore dimensions are in the range of 0.05 to 0.2 μm. Nondispersive operation carried out for extended periods of time indicated the formation of a nondefective coating. It was intended to coat only on the inside surface of the fibers because PEI insolubilization in the cross section rather than on the inside surface of fibers reduces the porosity and adds additional resistance to mass transfer. Therefore, the presence of PEI in the cross section of the fibers during the coating was eliminated by passing aqueous solution at low pressures and hence ended up coating only on the inner surface of the fibers. The SEM picture of the cross section of the coated fibers (Figure 5.3) shows an absence of crosslinked PEI in the cross section. The continuous thin line on the inner surface of fiber in Figure 5.3 is the PEI coating; the approximate coating thickness is about 0.4 μm.

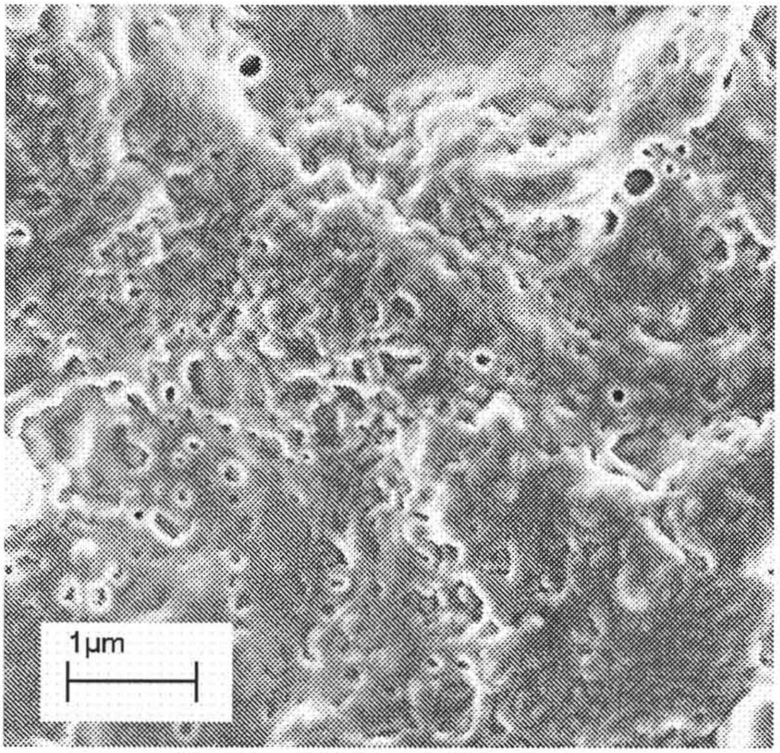

Figure 5.2 Coating on inner surface of Nylon 6 hollow fiber (coated with 4 wt% PEI aqueous solution).

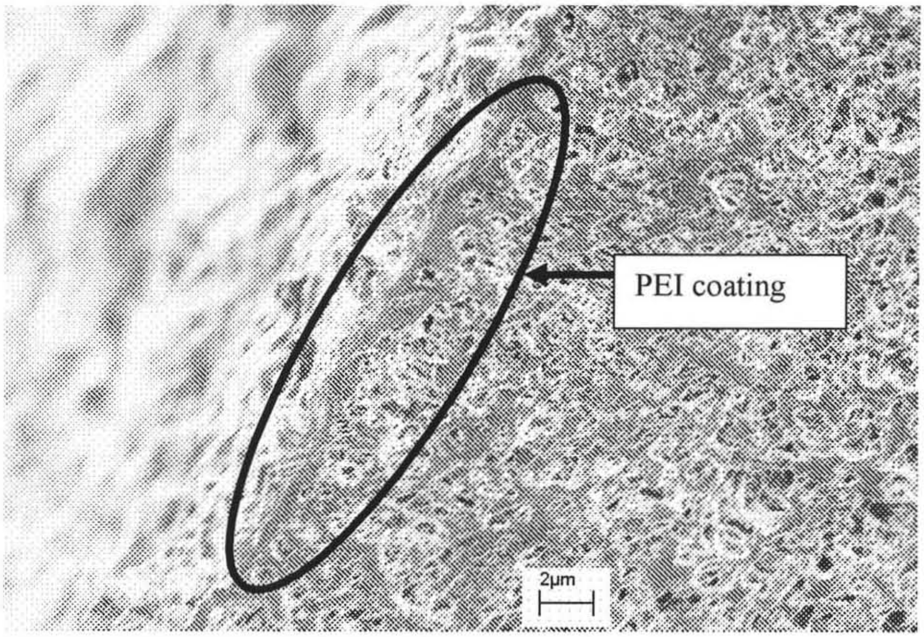

Figure 5.3 Cross section of the coated Nylon 6 fiber (coated with 4 wt% PEI aqueous solution).

The effect of PEI concentration on the coating characteristics was studied via the performance of reactive back extraction of phenol and measurement of the breakthrough pressure. The results for coating with different concentrations (2, 4 and 6 wt%) of aqueous PEI solutions are presented in Table 5.1 The breakthrough pressure in the non-coated fibers was 3.45 kPa and increased up to 120 kPa with an increase in the PEI concentration used for the coating. The experimentally measured value of the interfacial tension for the water-MIBK system is 9.5 dyne/cm and is in accordance with the value reported in the literature.[89] With added solutes like phenol or acetic acid, the interfacial tensions measured remained almost constant. If θ in Equation 1.1 may be assumed to be constant for non-coated and coated hydrophilic fibers, the ratio of the breakthrough pressures between the non-coated and the coated fibers will be inversely proportional to the ratio of their respective pore radii. Estimation of pore radius from this relation for 2%, 4% and 6% PEI coated fibers will be 55, 24 and 15 nm, respectively (pore radius of the non-coated fiber is approximated as 0.5 μm). The values from SEM pictures are also in the same range.

Table 5.1 Effect of PEI Concentration on the Breakthrough Pressure and Reactive Back Extraction Performance in Coated Hydrophilic Hollow Fibers

PEI concentration for coating (wt%)	Breakthrough pressure for MIBK-water system, ΔP_b (kPa)	Reactive back extraction of phenol* K_o (cm/s)
0% (Non-coated)	3.45	$0.68*10^{-3}$
2%	31.0	$1.61*10^{-3}$
4%	72.4	$1.12*10^{-3}$
6%	120	$0.94*10^{-3}$

* at $Q_{org} = 0.33$ cm^3/s, $Q_{aq} = 0.45$ cm^3/s.

At an organic phase flow rate of 0.33 cm^3/s, the overall mass transfer coefficient for the reactive back extraction system in the non-coated hydrophilic fibers was $0.68*10^{-3}$ cm/s; it was increased to $1.61*10^{-3}$ cm/s when the membrane was coated with an aqueous PEI solution of 2 wt%. The values of the overall organic phase-based mass transfer coefficients in the membrane coated with 4 and 6 wt% aqueous PEI solutions were $1.12*10^{-3}$ cm/s and $0.94*10^{-3}$ cm/s, respectively. These values are higher than that in the non-coated fibers and smaller than the mass transfer coefficients in the fibers coated with aqueous solution of 2 wt% PEI. Pore size of the coating decreases as the PEI concentration used for the coating increases. This increases the breakthrough pressures of the aqueous-organic interface; but it also decreases the interfacial area available for the mass transfer of the solute. With the 2 wt% PEI coating, potential replacement of the aqueous phase in the membrane pores with the organic phase due to an excess organic phase pressure is avoided thus preventing an increase in the membrane resistance for solute transport. With the 4 and 6 wt% of PEI coating, the additional membrane resistance due to the coating dominates the mass transfer and hence lower overall mass transfer coefficients are observed. Coating with 4 wt% PEI was employed quite often because of the wide range of phase pressure difference that can be used.

5.2 Reactive Back Extraction

In reactive back extraction, phenol is back extracted into an aqueous solution having a relatively high caustic concentration (0.25 M). Hence the aqueous phase resistance may be neglected. Equations 2.6 and 2.8 were used to calculate the overall mass transfer coefficients in hydrophilic and hydrophobic hollow fibers, respectively. The experimental values of the overall mass transfer coefficients for back extraction of phenol in hydrophobic, non-coated and coated hydrophilic hollow fibers are plotted against the organic phase flow rate in Figure 5.4a. With an increase in the organic phase flow rate, the overall mass transfer coefficients increased in hydrophobic fibers and in coated hydrophilic fibers. But, the overall mass transfer coefficients were constant in non-coated hydrophilic fibers with an increase in the organic phase flow rate.

Basu et al.[19] reported that overall mass transfer coefficients varied with the organic phase flow rates in the same experimental system studied when flat film membranes were used. The difference in the observed behavior between the hydrophilic flat film membranes and non-coated hydrophilic hollow fiber membranes could be explained from the pressure drop occurring at low flow rates in the lumen side of the hollow fibers.

Organic phase flowing through the lumen side of the hollow fibers encounters some pressure drop even at low flow rates. Even at such low pressure drops, organic phase pressure is increased enough for it to penetrate partially into the micropores and replace the aqueous phase. This increases the membrane phase resistance as the organic phase penetrates the membrane pores and offers more resistance to solute transport than the remaining aqueous phase in the pores of the membrane. Although the tube side mass transfer coefficient will increase with an increase in the organic phase flow rate, the overall mass transfer coefficients may remain constant in these non-coated hydrophilic hollow fibers because of the change in membrane resistance along the membrane length. This increase in organic phase penetration will occur at the highest organic phase pressure regions.

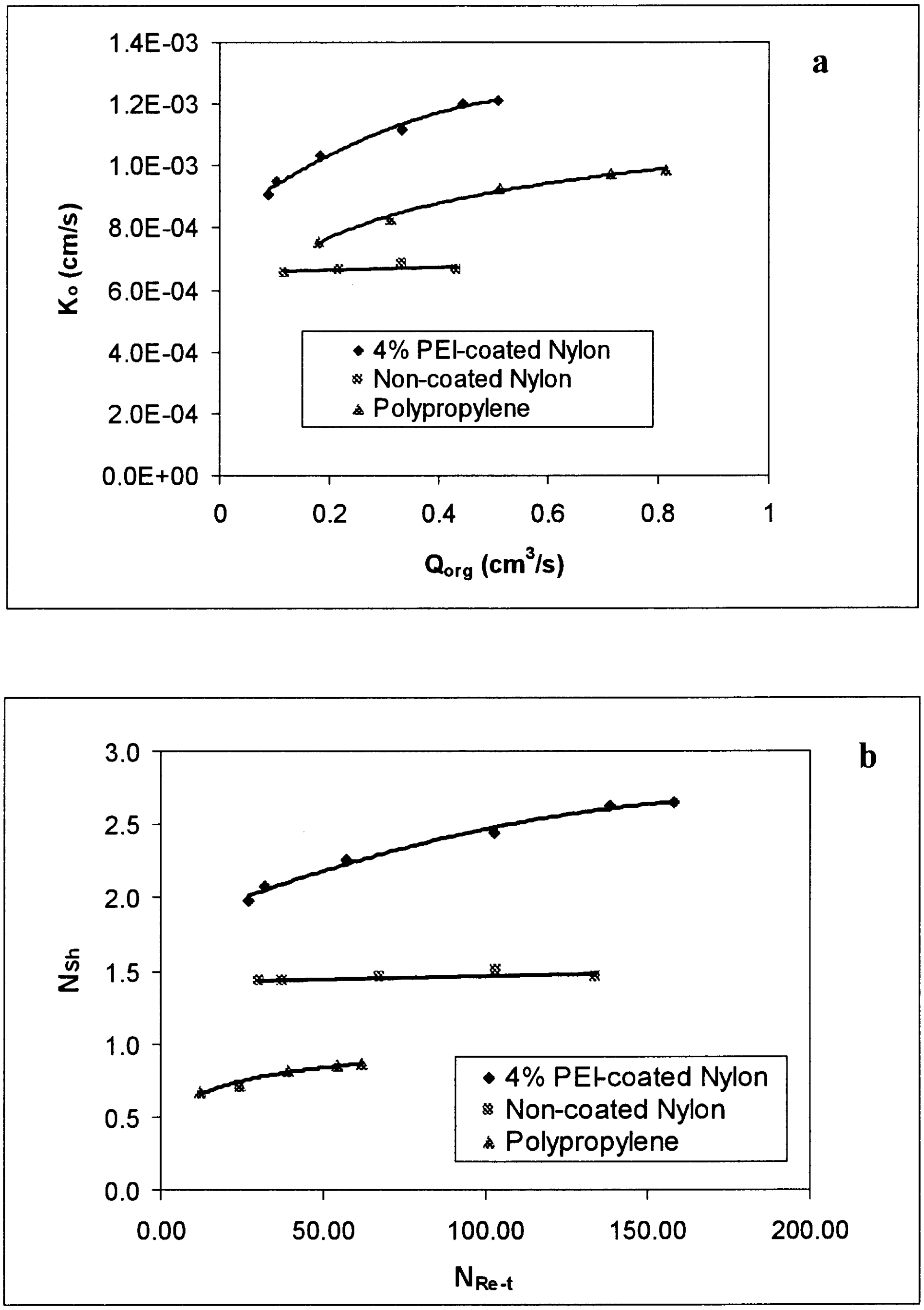

Figure 5.4 Effect of organic phase flow rate variation on extraction of phenol from MIBK into an aqueous caustic solution in hydrophobic, non-coated and coated hydrophilic hollow fiber membranes. a) Overall mass transfer coefficient vs. organic phase flow rate; b) Sherwood number vs. tube-side organic phase Reynolds number.

In the case of coated hydrophilic hollow fibers, the membrane pores have a reduced pore size which increases the breakthrough pressures of the aqueous-organic interface and therefore provides a stable interface for the mass transfer of the solute. As a result, replacement of the aqueous phase in the membranes pores with the organic phase will be prevented and the overall mass transfer coefficients will increase with increased organic phase flow rates in coated hydrophilic fibers. In fact, an increase in the overall mass transfer coefficient with an increase in the organic phase flow rate is observed in coated hydrophilic fibers prepared with 4 wt% PEI (Figure 5.4a). Further even though the hydrophilic fibers have a larger diameter and therefore lower velocities at a given flow rate, they exibit higher mass transfer coefficients than the hydrophobic Celgard PP fibers. In Figure 5.4b, the same data are plotted as the Sherwood number against the Reynolds number. One clearly observes the considerable enhancement in Sherwood number for the coated fibers at a given Reynolds number.

The above mentioned phenomena can be studied in greater detail by plotting the tube-side organic-phase Sherwood numbers against the Graetz number. The tube-side Sherwood numbers in hydrophilic and hydrophobic hollow fibers were calculated from the experimental data using Equations 2.6 and 2.8, respectively. Theoretical values of the tube-side Sherwood numbers estimated from the Graetz solution (Equation 2.11) are compared with the experimental values in hydrophobic, non-coated and coated hydrophilic hollow fibers in Figure 5.5. Tube-side Sherwood numbers in hydrophobic hollow fibers followed the theoretical values obtained from the Graetz solution closely whereas the tube-side Sherwood numbers are much lower in non-coated hydrophilic hollow fibers and are constant with an increased Graetz number.

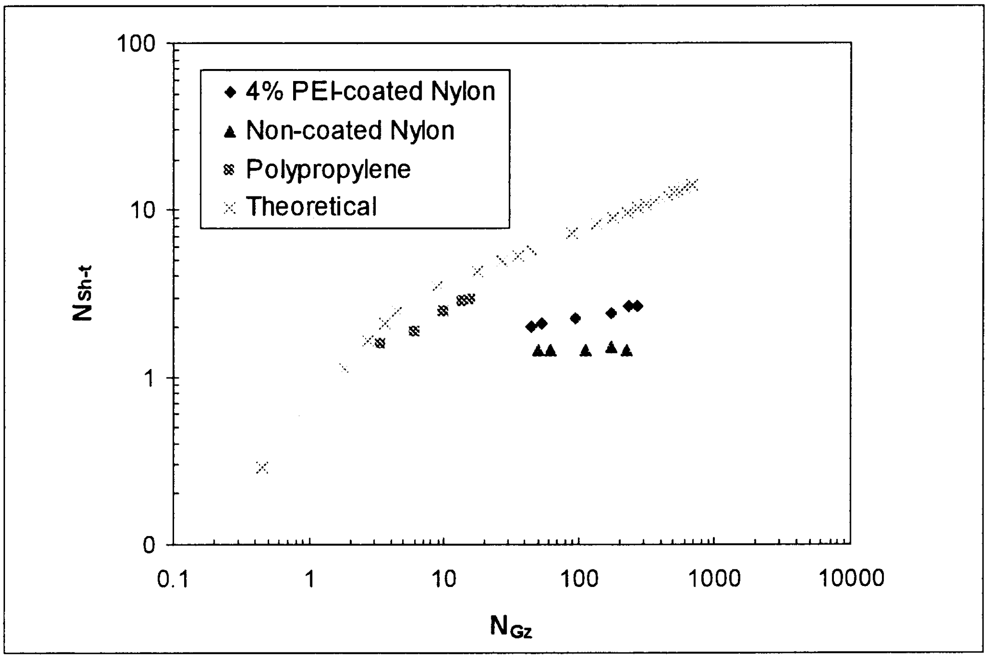

Figure 5.5 Theoretical and experimental tube-side Sherwood numbers in hydrophobic, non-coated and coated hydrophilic hollow fiber membranes for back extraction of phenol from MIBK into caustic solution.

For coated hydrophilic hollow fibers, the tube-side Sherwood numbers increased with an increase in the Graetz number and are higher than that in non-coated hydrophilic fibers. However the values are smaller than the theoretical values. The membrane resistance was assumed to be negligible in the calculation of N_{Sh} in coated hydrophilic fibers because the membrane pores were filled with the aqueous phase and instantaneous reactive back extraction was taking place at the aqueous-organic interface. However, the coated layer offers additional resistance to mass transfer and this additional resistance was factored into the tube–side mass transfer coefficients in the calculations since the membrane resistance was assumed to be zero. It would be appropriate to account for the increase in membrane resistance with the coating by incorporating the membrane resistance term for the calculation of tube-side Sherwood numbers from the experimental values of overall mass transfer coefficients. The exact coating characteristics such as porosity and the thickness are unknown to account for the increase in membrane resistance with the coating.

5.3 Nonreactive Back Extraction

For nonreactive back extraction of acetic acid from MIBK into water in either hydrophilic or hydrophobic fibers, the resistances of both aqueous phase and organic phase are present. Since the partition coefficient of the system has a value of 0.52 (a case of $m \approx 1$)[41], all three mass transfer resistances (tube-side, membrane phase and shell-side) will have a significant affect on the overall mass transfer coefficient. The overall mass transfer coefficients in the hydrophobic, non-coated and coated hydrophilic hollow fibers were calculated and compared by the following procedure. Individual mass transfer coefficients were estimated from the correlations and the overall mass transfer coefficients calculated (Equation 2.4 for hydrophilic fibers and Equation 2.7 for hydrophobic fibers) from these individual mass transfer coefficients and compared with the corresponding experimental values to evaluate the non-reactive membrane back extraction system.

The data in Table 5.2 imply that most likely the shell-side transfer coefficient estimate was an overestimate leading to values higher than the actual. Regardless, it is evident also from Table 5.2 that the membrane resistance dominates the tube-side and shell-side resistances as the overall mass transfer coefficients remained nearly constant in hydrophobic fibers with change in the flow rates of the aqueous phase and the organic phase. D'Elia et al.[42] also reported that extraction of acetic acid from water into MIBK was controlled by the membrane resistance and a reduction of the membrane resistance will improve the overall mass transfer coefficient. As acetic acid prefers to some extent to be in the aqueous phase rather than in the organic phase, the membrane phase has to be filled up with the aqueous phase to have the least possible membrane resistance by employing hydrophilic fibers for extraction of acetic acid (either from MIBK into water or from water into MIBK). Aqueous phase resistance is less important than the organic phase resistance as acetic acid prefers to be in aqueous phase over MIBK. Therefore, organic phase resistance can be minimized by having high flow rates of MIBK.

Table 5.2 Effect of Organic and Aqueous Phase Flow Rates on Experimental and Calculated Overall Mass Transfer Coefficients in Hydrophobic Fibers for a Nonreactive Back Extraction System

Q_{org} (cm^3/s)	Q_{aq} (cm^3/s)	K_o (cm/s) Experimental	K_o (cm/s) Calculated*
0.23	0.57	$1.38*10^{-4}$	$2.35*10^{-4}$
0.41	0.57	$1.44*10^{-4}$	$2.41*10^{-4}$
0.59	0.57	$1.46*10^{-4}$	$2.44*10^{-4}$
0.76	**0.57**	$1.47*10^{-4}$	$2.45*10^{-4}$
0.76	**0.62**	$1.57*10^{-4}$	$2.56*10^{-4}$
0.76	**0.78**	$1.66*10^{-4}$	$2.85*10^{-4}$
0.76	**0.95**	$1.89*10^{-4}$	$2.98*10^{-4}$

* Calculated from Equations 2.7, 2.11 and 2.15

Acetic acid back extraction was studied in coated hydrophilic fibers as the coating will improve the stability of the water-MIBK interface and avoid the displacement of the aqueous phase from the membrane pores. High breakthrough pressures in the coated fibers will also allow high organic flow rates through the fibers. The variation of the overall mass transfer coefficients in noncoated and coated hydrophilic fibers with different organic flow rates were compared with the calculated values in Figure 5.6. The overall mass transfer coefficients in the noncoated and coated hydrophilic fibers are almost identical. But, the coated membranes support nondispersive operation over a wide range of transmembrane pressures as the coated membranes will posses much higher breakthrough pressures. The coating prevents the possible organic phase penetration into the membrane pores. The overall mass transfer coefficients remained nearly constant with the coating as the coating also adds additional membrane resistance to the solute transport. This additional membrane resistance of the coating also explains the lower experimental overall mass transfer coefficients than the calculated values, in addition to the overestimation of the shell-side coefficient value.

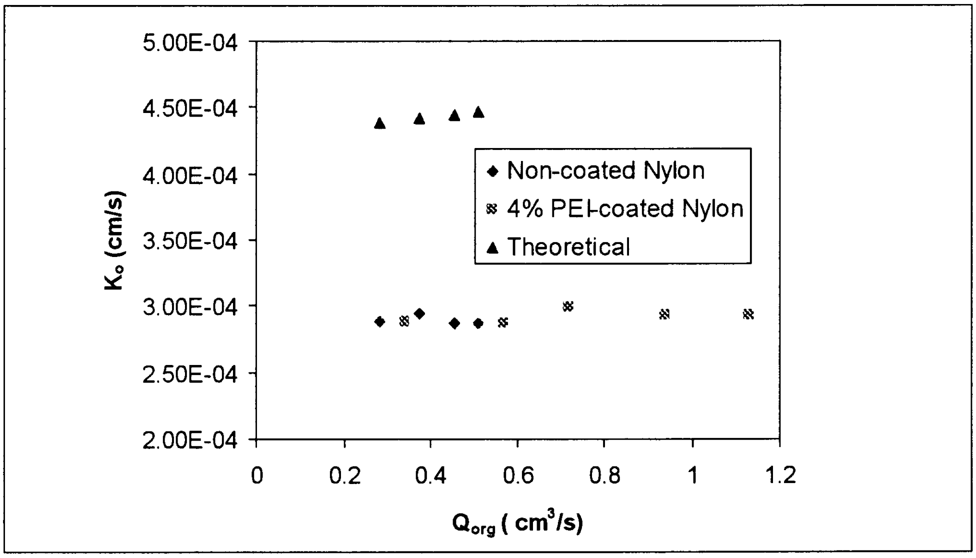

Figure 5.6 Overall mass transfer coefficient vs. organic flow rate in non-coated and 4 wt% PEI-coated hydrophilic hollow fiber membranes for nonreactive back extraction system at an aqueous phase flow rate of 0.86 cm^3/s.

5.4 Stability of the PEI-Coated Membranes

Polyamide displays a wide pH tolerance range (acceptable pH range 3 -11).[21] Therefore, the coated membranes can be used for solvent back extraction with basic and dilute acidic stripping solutions. Nondispersive operation was carried out continuously for an experimentally studied period of five days and the aqueous-organic interface appeared very stable. This indicates that the coating was very stable to 0.25M caustic solutions.

5.5 Conclusions

The benefits of employing hydrophilic hollow fiber membranes with the membrane pores filled with the aqueous phase for efficient membrane solvent back extraction were studied in porous Nylon hollow fibers coated on the ID with PEI which underwent self crosslinking. As PEI concentration for the coating was increased, the pore size of the coating was reduced and the breakthrough pressures were increased. Higher breakthrough pressures prevented the replacement of the aqueous phase in the membrane pores with the organic phase and provided a stable aqueous-organic interface for the solute extraction.

The overall mass transfer coefficients improved significantly with the coating in the reactive back extraction system as the resistance to the mass transfer is primarily from the organic phase and the membrane pores were filled only with aqueous phase. In the case of the nonreactive back extraction system, both organic and aqueous phase resistances contribute to the overall mass transfer resistance. The advantage of filling the membrane pores with the aqueous phase in nonreactive back extraction is due to the fact that the solute prefers to be in the aqueous phase over the organic phase ($m = 0.52$). This advantage was balanced by the decrease in the interfacial area for mass transfer due to the coating. Hence overall mass transfer coefficients are not increased drastically by the coating even though the membrane pores are filled only with aqueous phase. But the coating helped to achieve non-dispersive operation over a wide range of transmembrane pressures. If the Nylon 6 fiber wall thickness were a few times smaller, the performance will significantly improve in non-reactive back extraction where $m \approx 1$.

Coating by PEI crosslinking on the inner surface of Nylon hollow fiber membranes was convenient, free from defects and appeared promising. Among the coatings with different PEI concentrations (2, 4, 6 wt%), coating with 4 wt% of PEI solution is beneficial for the studied aqueous-organic phase system as it provided a reasonable breakthrough pressure (72.5 kPa) and improved the overall mass transfer coefficients significantly. Comparison of mass transfer coefficients in coated membranes with that in hydrophobic membranes demonstrated that by employing hydrophilic membranes having an appropriate pore size, one can improve the efficiency of membrane solvent back extraction vis-à-vis hydrophobic membranes.

CHAPTER 6

HEAT TRANSFER

The objective of making a leak proof coating was first pursued. Then, the heat transfer performance of the coated modules was studied. Results and discussion of the membrane modification will be presented first followed by their heat transfer performance.

6.1 Membrane Modification

The primary objective of the membrane modification in this case was to fabricate a TFC membrane by coating the lumen side of the porous PES hollow fibers with a water-impervious layer. Therefore, attention was paid to making an impervious coating rather than controlling the coating characteristics such as thickness and morphology of the coating. These coating characteristics will have the least effect on the heat transfer performance (the effect of the coating roughness is an unknown at this time). Membrane modification conditions for different membrane modules are provided in Table 6.1. Module 1 was coated with an 1 wt% aqueous solution of 1,6-hexanediamine and an 1 wt% sebacoyl chloride solution in xylene; the reaction time was two minutes. When water was pressurized in the lumen side of the coated module at 10 psig (170.1 kPa), water permeated to the shell side through the coating. The coated material is a polyamide; it is hydrophilic and also swells a little with water. To prevent water leakage through the coating, two more layers of polyamide coating was applied to the lumen side. The procedure for the additional coating layers was same as that of the first layer of coating.

After the three-layered coating was developed, water did not permeate from lumen side to the shell side when water was pressurized in the lumen side at 10 psig (170.1 kPa).

Table 6.1 Conditions for Modification of PES Hollow Fiber Modules for Heat Transfer

Module designation	Coating conditions	
	Layer 1	Layer 2
Module 1	1wt% 1,6-hexanediamine 1 wt% Sebacoyl chloride Polymerization time: 2 minutes No. of coatings: 3	-
Module 2	0.5 wt% Poly(ethyleneimine) 0.5 wt% Isophthaloyl dichloride Polymerization time: 10 minutes No. of coatings: 1	1.0 wt% silicone elastomer in xylene
Module 3	2 wt% 1,3-Phenylenediamine 2 wt% Trimesoic acid trichloride Polymerization time: 20 minutes No. of coatings: 1	2.0 % wt% silicone elastomer in xylene

Next, Module 2 was coated with Poly(ethyleneimine)-Isophthaloyl dichloride reactive monomer system, because improved and uniform coating was observed in the coating studies carried out in PP hollow fibers with this reactive monomer system over 1,6-hexanediamine-Sebacoyl chloride. Instead of adding layers of polyamide to prevent the water permeation, the first layer of polyamide coating was further coated with a coating solution of 1% silicone in xylene. The modified membrane module was impervious to water at 10 psig (170.1 kPa) with the hydrophobic coating of silicone on polyamide. The reactive monomer system of 1,3-Phenylenediamine-Trimesoic acid trichloride was also studied to fabricate TFC membranes for heat transfer in Module 3. After the first layer of polyamide coating in the lumen side of the hollow fibers in Module 3 with monomer concentrations of 2 wt% and a reaction time of 20 minutes, 2 wt% of silicone coating was applied. The fabricated TFC membrane was also impervious to water at 10 psig (170.1 kPa).

6.2 Heat Transfer Performance

Configurations and the testing conditions for studying heat transfer performance in the modified hollow fiber membranes are provided in Table 6.2. Variation of the overall heat transfer coefficients with a flow rate variation of one of the flow streams keeping the flow rate of the other stream constant was studied. All the figures of heat transfer performance presented in this section and the respective calculations are from the report submitted to the Office of Naval Research (ONR).[90] Variation of the overall heat transfer coefficients (calculated from Equation 2.16) in Modules 1, 2 and 3 with the linear velocity of one of the flow streams are provided in Figures 6.1, 6.2 and 6.3, respectively. These figures also provide the magnitude of the overall heat transfer coefficients and the maximum values of the overall heat transfer coefficients achieved. The highest values of overall heat transfer coefficient values achieved in Module 1, Module 2 and Module 3 were 3000, 1900 and 1800 W/m^{2}K, respectively. The overall heat transfer coefficients in solid PP hollow fibers were in the range of 647 to 1314 W/m^{2}K for the water-water system.[54] A comparison of the performance of the modified PES fibers and the solid PP fibers clearly indicates that modified PES hollow fibers modules showed better performance.

Conductance values of the water stream will increase rapidly if there is any leak between the brine and water streams. The conductance values of water stream was constant during the experiments carried out in all of the modified modules (Module 1, 2 and 3) and this implies that the coating was leak proof. Values of overall heat transfer coefficient were higher in Module 1 compared with the values in Module 2 and Module 3. From this comparison, it appears that a three layered coating of polyamide performed better than a layer of silicone on polyamide. However it needs to be verified with additional experiments and systematic studies. Coating a layer of silicone over polyamide coating is convenient over a three layered coating of polyamide as the numbers of steps involved in the coating are fewer. By having a silicone coating instead of a number of polyamide coatings, the possibility of swelling of the polyamide with water and hence water permeation will be completely eliminated.

Table 6.2 Heat Transfer Performance Testing Configurations and Conditions

Module designation	Tube side			Shell side		
	Flow stream	Linear flow rate (cm/min)	Inlet temperature (°C)	Flow stream	Linear flow rate (cm/min)	Inlet temperature (°C)
Module 1	4% brine	Varied	90	DI water	3600	20
Module 2	DI water	Varied	16	4% brine	5500	93
Module 3	Tap water	1600	25	4% brine	varied	95

6.3 Conclusions

Thin film composite membranes fabricated on the internal diameter of porous asymmetric PES hollow fiber membranes provided better heat transfer performance over solid PP hollow fibers since the thickness of the barrier for heat transfer is lower in TFC membranes. The coatings by both modification procedures (three layered polyamide coating and silicone coating on polyamide) generated a water-leak-proof coating. Three layered coating appears to provide better heat transfer performance.

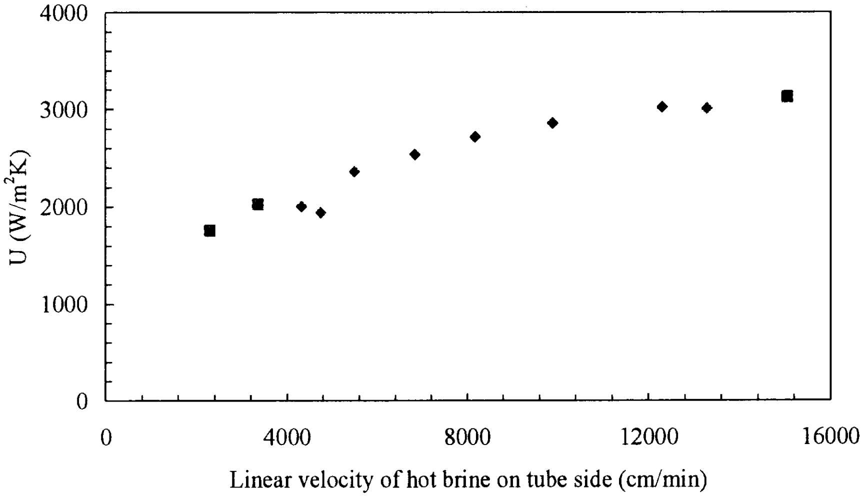

Figure 6.1 Variation of overall heat transfer coefficient of Module 1 with linear velocity of hot brine (4% NaCl) flowing on the tube side at an inlet temperature of 90°C (shell side: D.I. water, inlet temperature 20°C, linear flow rate 3600 cm/min).

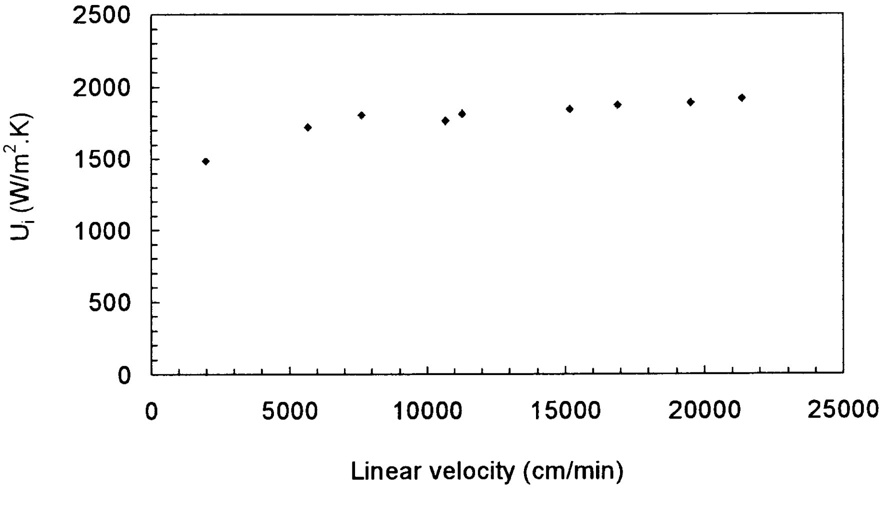

Figure 6.2 Variation of overall heat transfer coefficient of Module 2 with linear velocity of D.I water flowing on the tube side at an inlet temperature of 16°C (shell side: 4%NaCl, parallel flow, inlet temperature 93°C, linear velocity 5500 cm/min).

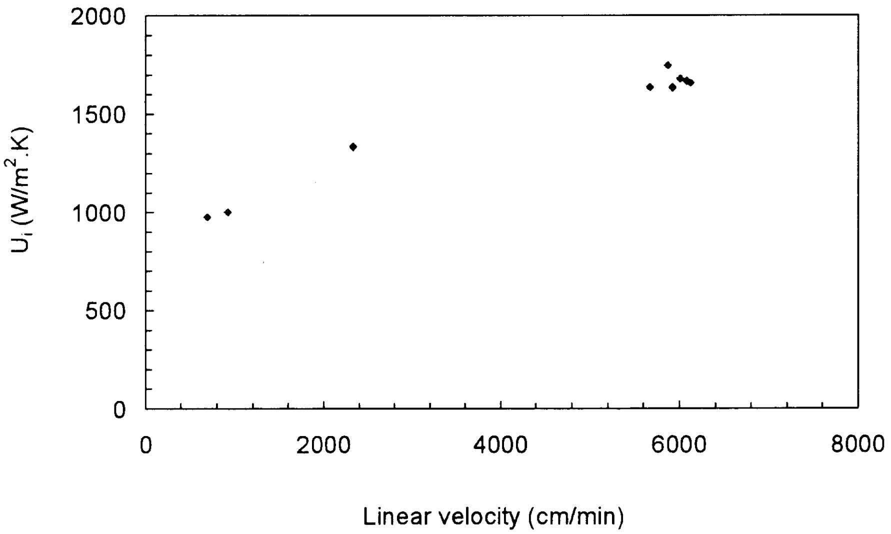

Figure 6.3 Variation of overall heat transfer coefficient of Module 3 with linear velocity of hot brine (4%NaCl) flowing on the shell side at an inlet temperature of 95°C (tube side: tap water, inlet temperature 25°C, linear velocity 16000 cm/min).

CHAPTER 7

GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

Thin film composite membranes on porous polypropylene hollow fibers and flat films were successfully prepared by interfacial polymerization for solvent stable ultrafiltration and nanofiltration applications. Hydrophilization of the PP support by acetone prewetting, followed by oxidation with chromic acid solution facilitated uniform hydrophilization of the PP support and provided good binding between the support and the polyamide coating. A standard procedure for coating the lumen side of the hollow fiber membranes was developed and optimized. Pore interior and surface of PP microfiltration membranes were successfully coated with polyamide for permanent hydrophilization by the "modified IP" technique; the technique of PEI crosslinking was not successful in this case. By selectively choosing the monomers for the "modified IP" technique, lower breakthrough pressures of water and, hence, better hydrophilicity is likely to be achieved.

Nylon hydrophilic hollow fiber membranes were coated successfully on the lumen side by the technique of PEI-self crosslinking. As PEI concentration for the coating was increased, the pore size of the coating was reduced and the breakthrough pressures were increased. The reduced pore sizes provided stable aqueous-organic interface for the solute transport in membrane solvent back extraction and overall mass transfer coefficients were increased significantly with the coating. It was demonstrated that membrane pores filled with the aqueous phase reduce the membrane resistance in

MSBE. Fabricated thin film composite hollow fibers provided better heat transfer performance over solid PP hollow fibers.

The following recommendations are made for future explorations. Thin film composite membranes on PP support can also be fabricated with a sulfonamide rather than amide coating by the technique of IP.[91] This would improve the acid stability of the selective layer and the fabricated membranes could tolerate a wider pH range. The reactive monomer system of 1,3-phenylenediamine and trimesoic acid trichloride provides high crosslinking and also produces a rough coating with a ridge-and-valley structure, whereas, coating by the reactive monomer system of PEI-IPD provides a smooth surface. The microporous membrane support used in the current studies for fabrication of TFC membranes is a microfiltration membrane and has larger pores. The ridge-and-valley structure of the coating on the support having larger pores could withstand higher pressures rather than the smooth coating on the support having larger pores. From this perspective, employing the reactive monomer system of 1,3-phenylenediamine and trimesoic acid trichloride is advantageous as it provides higher rejection of smaller solutes because of higher crosslinking and can withstand higher pressures due to the ridge-and-valley structure of the coating. On the other hand, roughness increases the fouling tendencies of the coating. For permanent hydrophilization of PP microfiltration membranes, the reactive monomers can be selectively chosen to coat the membranes with a polyamide having lower values of contact angles with water.

The coating technique of PEI crosslinking used in this thesis can be applied to a number of applications in the fields of bio-separations, biotechnology, ion exchange and gas separations. Cationic characteristics and the presence of functional amine groups in PEI contribute to the observed behavior. Poly(ethyleneimine) is commonly used for the immobilization of a number of enzymes.[92] It was employed as a intermediate polymer layer by Nguyen et al.[92] on a negatively charged membrane to immobilize bio-macromolecules such as glucose oxydase and heparin for fabrication of glucose biosensors and hemocompatible membranes. As per mechanism, one has to modify the support membranes with negative charge or the membranes have to be selectively chosen for their negative charge. If self crosslinking of PEI is employed, any hydrophilic or mildly hydrophilic membranes can be used as a support; the number of steps involved in the membrane functionalization process will be reduced and the functionalized membranes will be stable since PEI is crosslinked. The polymer PEI was also used as an intermediate layer between the PVDF membrane support and the poly(ethylene glycol) (PEG) coating by Ademovic et al[93] to make PVDF support biocompatible. PEG-PEI graft films were also studied for antifouling coatings in variety of biotechnology applications.[93, 94] Attaching PEI on PVDF support in the above mentioned studies involved a number of steps. The same effect could be achieved by crosslinking of PEI, which is a simple process.

PEI has been used as a ligand for metal chelating, removal of endotoxins and ion exchange.[95, 96] One of the barriers of using PEI for ion exchange membranes is the fixation of PEI on the support membrane. Takata et al.[97] have studied the acid-amide bonding for fixation of PEI on a support membrane which involved a number of steps. Crosslinking of PEI could be an easy way to deposit PEI on the support membrane for fabrication of cation exchange membranes. The role of the amine groups in the PEI molecule were also explored in the literature for CO_2 separation from gas mixtures and separation of alcohols from aqueous solutions.[98] Therefore, one could use the PEI coating on a dense polymeric membrane for selective removal of CO_2 and as a pervaporation membrane for separation of alcohols. For such applications, fabrication of thin film composite membranes by interfacial polymerization employing PEI as a monomer in the aqueous phase, coupled with the crosslinking of PEI can also be explored. For all of the above mentioned applications, methods to achieve controlled crosslinking of PEI are needed.

APPENDIX

DATA TABLES AND SAMPLE CALCULATIONS IN MEMBRANE SOLVENT BACK EXTRACTION

The data tables for membrane solvent back extraction are provided first. Then, sample calculations of individual and overall mass transfer coefficients, Reynolds numbers, Schmidt numbers, Sherwood numbers and Graetz numbers in hydrophilic hollow fiber membrane modules for nonreactive and reactive back extraction will be presented. Calculations for hydrophobic hollow fiber membrane modules were carried out in a similar fashion.

Table A1. Reactive Back Extraction of Phenol in Noncoated Hydrophilic Hollow Fiber Membrane Module (Module E)

Sl. No.	Q_{org} (cm^3/s)	$C_{org\text{-}in}$ (mol/ cm^3)	Q_{aq} (cm^3/s)	$C_{aq\text{-}out\text{-}sodium\ phenoxide}$ (mol/ cm^3)
1	0.432	$0.1*10^{-3}$	0.227	$3.83*10^{-6}$
2	0.332	$0.1*10^{-3}$	0.547	$1.63*10^{-6}$
3	0.217	$0.1*10^{-3}$	0.547	$1.57*10^{-6}$
4	0.119	$0.1*10^{-3}$	0.547	$1.51*10^{-6}$

Table A2. Reactive Back Extraction of Phenol in 4 wt% PEI-Coated Hydrophilic Hollow Fiber Membrane Module (Module E)

Sl. No.	Q_{org} (cm^3/s)	$C_{org\text{-}in}$ (mol/ cm^3)	Q_{aq} (cm^3/s)	$C_{aq\text{-}out\text{-}sodium\ phenoxide}$ (mol/ cm^3)
1	0.087	$0.1*10^{-3}$	0.153	$7.31*10^{-6}$
2	0.102	$0.1*10^{-3}$	0.153	$7.72*10^{-6}$
3	0.182	$0.1*10^{-3}$	0.153	$8.71*10^{-6}$
4	0.331	$0.1*10^{-3}$	0.153	$9.45*10^{-6}$
5	0.445	$0.1*10^{-3}$	0.153	$1.02*10^{-5}$
6	0.509	$0.1*10^{-3}$	0.153	$1.02*10^{-5}$

Table A3. Reactive Back Extraction of Phenol in Hydrophobic Hollow Fiber Membrane Module (Module F)

Sl. No.	Q_{org} (cm^3/s)	$C_{org\text{-}in}$ (mol/cm^3)	Q_{aq} (cm^3/s)	$C_{aq\text{-}out\text{-}sodium\ phenoxide}$ (mol/cm^3)
1	0.178	$0.1*10^{-3}$	0.714	$1.293*10^{-5}$
2	0.312	$0.1*10^{-3}$	0.714	$1.598*10^{-5}$
3	0.512	$0.1*10^{-3}$	0.714	$1.917*10^{-5}$
4	0.714	$0.1*10^{-3}$	0.714	$2.093*10^{-5}$
5	0.813	$0.1*10^{-3}$	0.714	$2.146*10^{-5}$

Table A4. Nonreactive Back Extraction of Acetic Acid in Noncoated Hydrophilic Hollow Fiber Membrane Module (Module E)

Sl. No.	Q_{org} (cm^3/s)	$C_{org\text{-}in}$ (mol/cm^3)	Q_{aq} (cm^3/s)	$C_{aq\text{-}out}$ (mol/cm^3)
1	0.280	$5.241*10^{-4}$	0.86	$2.298*10^{-6}$
2	0.373	$5.241*10^{-4}$	0.86	$2.351*10^{-6}$
3	0.454	$5.241*10^{-4}$	0.86	$2.298*10^{-6}$
4	0.510	$5.241*10^{-4}$	0.86	$2.298*10^{-6}$

Table A5. Nonreactive Back Extraction of Acetic Acid in 4 wt% PEI-Coated Hydrophilic Hollow Fiber Membrane Module (Module E)

Sl. No.	Q_{org} (cm^3/s)	$C_{org\text{-}in}$ (mol/cm^3)	Q_{aq} (cm^3/s)	$C_{aq\text{-}out}$ (mol/cm^3)
1	0.34	$5.24*10^{-4}$	0.86	$1.38*10^{-4}$
2	0.57	$5.24*10^{-4}$	0.86	$1.38*10^{-4}$
3	0.72	$5.24*10^{-4}$	0.86	$1.44*10^{-4}$
4	0.94	$5.24*10^{-4}$	0.86	$1.41*10^{-4}$
5	1.13	$5.24*10^{-4}$	0.86	$1.41*10^{-4}$

Table A6. Nonreactive Back Extraction of Acetic Acid in Hydrophobic Hollow Fiber Membrane Module (Module F)

Sl. No.	Q_{org} (cm^3/s)	C_{org-in} (mol/cm^3)	Q_{aq} (cm^3/s)	C_{aq-out} (mol/cm^3)
1	0.23	$5.24*10^{-4}$	0.57	$1.72*10^{-5}$
2	0.41	$5.24*10^{-4}$	0.57	$1.82*10^{-5}$
3	0.59	$5.24*10^{-4}$	0.57	$1.87*10^{-5}$
4	0.76	$5.24*10^{-4}$	0.57	$1.88*10^{-5}$
5	0.76	$5.24*10^{-4}$	0.62	$1.82*10^{-5}$
6	0.76	$5.24*10^{-4}$	0.78	$1.55*10^{-5}$
7	0.76	$5.24*10^{-4}$	0.85	$1.60*10^{-5}$

Reactive back extraction of phenol from MIBK into aqueous caustic solution in a hydrophilic hollow fiber membrane module coated with 4 wt% aqueous PEI solution (Reference: First row of Table A2):

Organic phase:

$Q_{org} = 0.087\ cm^3/s$
$C_{org\text{-}in} = 0.1*10^{-3}\ mol/cm^3$

Aqueous phase:

$Q_{aq} = 0.153\ cm^3/s$
$C_{aq\text{-}in} = 0\ mol/cm^3$
$C_{aq\text{-}in} = 0\ mol/cm^3$
$C_{aq\text{-}in\text{-}sodium\ phenoxide} = 0\ mol/cm^3$
$C_{aq\text{-}out\text{-}sodium\ phenoxide} = 7.31*10^{-6}\ mol/cm^3$

Calculation of experimental values of overall mass transfer coefficients:

From the material balance,

$$C_{org-out} = C_{org-in} - \frac{Q_{aq}}{Q_{org}}\left(C_{aq-out-\text{sodium phenoxate}} - C_{aq-in-\text{sodium phenoxate}}\right)$$

$$= 0.1*10^{-3} - \frac{0.153}{0.087}\left(7.3*10^{-6} - 0\right) = 87.17*10^{-6}\ \text{mol/cm}^3$$

The logarithmic mean concentration difference from Equation 2.3b is obtained as

$$(\Delta C)_{LM} = \frac{\left(C_{org-in} - mC_{aq-in}\right) - \left(C_{org-out} - mC_{aq-out}\right)}{\ln\left(\left(C_{org-in} - mC_{aq-in}\right) / \left(C_{org-out} - mC_{aq-out}\right)\right)}$$

$$= \frac{\left(0.1*10^{-3} - 0\right) - \left(87.17*10^{-6} - 0\right)}{\ln\left(\left(0.1*10^{-3} - 0\right) / \left(87.17*10^{-6} - 0\right)\right)} = 93.44*10^{-6}\,\text{mol/cm}^3$$

Overall mass transfer coefficient from Equation 2.3a is obtained as

$$K_o = \frac{Q_{org}\left(C_{org-in} - C_{org-out}\right)}{(\Delta C)_{LM} * (\mathrm{A_m})} = \frac{0.087\left(0.1*10^{-3} - 87.17*10^{-6}\right)}{93.44*10^{-6} * (13.2)} = 9.07*10^{-4}\,\text{cm/s}$$

<u>Calculation of $N_{Sh\text{-}t}$, $N_{Re\text{-}t}$, $N_{Sc\text{-}t}$ and $N_{Gz\text{-}t}$:</u>

$$K_o = k_o = 9.07*10^{-4}\,\text{cm/s}$$

$$N_{Sh-t} = k_o d_i / D_{Ao} = 9.07*10^{-4} * 600*10^{-4} / 2.75*10^{-5} = 1.978$$

$$N_{\mathrm{Re}-t} = d_i v / \eta_o = 600*10^{-4} * 3.08 / 6.82*10^{-3} = 27.09$$

$$N_{Sc-t} = \eta_o / D_{Ao} = 6.82*10^{-3} / 2.75*10^{-5} = 248$$

$$N_{Gz} = \pi d_i N_{\mathrm{Re}-t} N_{Sc-t} / 4L = 3.14*600*10^{-4} * 27.09 * 248 / 4*7 = 45.3$$

Nonreactive back extraction of acetic acid from MIBK into water in a noncoated hydrophilic hollow fiber membrane module (Reference: First row of Table A4):

<u>Organic phase:</u>
$C_{org\text{-}in} = 5.241*10^{-4}$ mol/cm^3
$Q_{org} = 0.28$ cm^3/s

<u>Aqueous phase:</u>
$C_{aq\text{-}in} = 0$ mol/cm^3
$C_{aq\text{-}out} = 2.298*10^{-6}$ mol/cm^3
$Q_{aq} = 0.86$ cm^3/s

Calculation of experimental values of overall mass transfer coefficients:

From the material balance,

$$C_{org-out} = C_{org-in} - \frac{Q_{aq}}{Q_{org}}\left(C_{aq-out} - C_{aq-in}\right)$$

$$= 5.241*10^{-4} - \frac{0.28}{0.86}\left(2.298*10^{-6} - 0\right) = 5.17*10^{-4}\,\text{mol/cm}^3$$

The logarithmic mean concentration difference from Equation 2.3b is obtained as

$$(\Delta C)_{LM} = \frac{\left(C_{org-in} - mC_{aq-in}\right) - \left(C_{org-out} - mC_{aq-out}\right)}{\ln\left(\left(C_{org-in} - mC_{aq-in}\right)/\left(C_{org-out} - mC_{aq-out}\right)\right)}$$

$$= \frac{\left(5.241*10^{-4} - 0\right) - \left(5.17*10^{-4} - 0.52*2.298*10^{-6}\right)}{\ln\left(\left(5.241*10^{-4} - 0\right)/\left(5.17*10^{-4} - 0.52*2.298*10^{-6}\right)\right)} = 5.2*10^{-4}\,\text{mol/cm}^3$$

Overall mass transfer coefficient from Equation 2.3a is obtained as

$$K_o = \frac{Q_{org}\left(C_{org-in} - C_{org-out}\right)}{(\Delta C)_{LM} * (\mathrm{A_m})} = \frac{0.28\left(5.241*10^{-4} - 5.17*10^{-4}\right)}{5.2*10^{-4}*13.2} = 2.88*10^{-4}\,\text{cm/s}$$

Calculation of theoretical values of individual and overall mass transfer coefficients:

Membrane mass transfer coefficients:

$$\tau_m = \frac{(2-\varepsilon)^2}{\varepsilon} = \frac{(2-0.75)^2}{0.75} = 2.08$$

$$k_{mw} = \frac{D_{Aw}\varepsilon_m}{t\tau_m} = \frac{1.24*10^{-5}*0.75}{2.08*0.02} = 2.24*10^{-4}\,\text{cm/s}$$

Shell-side mass transfer coefficients:

$$D_h = 4*\frac{\text{cross sectonal area of flow}}{\text{wetted perimeter}} = 7.64*10^{-2}\,\text{cm}$$

$$N_{\mathrm{Re}-s} = D_h v_e/\eta_w = 7.64*10^{-2}*9.82/8.93*10^{-3} = 84.01$$

$$N_{Sc-s} = \eta_w/D_{Aw} = 8.93*10^{-3}/1.24*10^{-5} = 720.16$$

$$N_{Sh-s} = 6.1(1-\phi)\left(\frac{D_h}{L}\right)N_{\mathrm{Re}-s}^{0.66}N_{Sc-s}^{0.33} = 6.1(1-0.473)\left(\frac{7.64*10^{-2}}{7}\right)84.01^{0.66}720.16^{0.33} = 5.73$$

$$k_w = N_{Sh-s}D_{Aw}/D_h = 5.73*1.24*10^{-5}/7.64*10^{-2} = 9.3*10^{-4}\text{cm/s}$$

Tube-side mass transfer coefficients:

$$N_{\mathrm{Re}-t} = d_i v/\eta_o = 600*10^{-4}*9.94/6.82*10^{-3} = 87.45$$

$$N_{Sc-t} = \eta_o/D_{Ao} = 6.82*10^{-3}/3.2*10^{-5} = 213.1$$

$$N_{Gz} = \pi d_i N_{\mathrm{Re}-t}N_{Sc-t}/4L = 3.14*600*10^{-4}*87.45*213.1/4*7 = 125.3$$

The value of θ calculated from Equation 2.12 for the this particular sample calculation is 0.101.

$$N_{Sh-t} = 0.5\left(\frac{d_i}{L}\right)N_{\mathrm{Re}-t}N_{Sc-t}\theta = 0.5\left(\frac{600*10^{-4}}{7}\right)87.45*213.1*0.101 = 8.06$$

$$k_o = N_{Sh-t}*D_{Ao}/d_i = 8.06*3.2*10^{-5}/600*10^{-4} = 4.29*10^{-3}\text{cm/s}$$

Overall mass transfer coefficients:

$$\frac{1}{K_o d_i} = \left(\frac{1}{k_o d_i}\right) + \left(\frac{m}{k_{mw} d_{lm}}\right) + \left(\frac{m}{k_w d_o}\right)$$

$$= \left(\frac{1}{4.29*10^{-3}*600*10^{-4}}\right) + \left(\frac{0.52}{2.24*10^{-4}*0.0783}\right) + \left(\frac{0.52}{9.3*10^{-4}*1000*10^{-4}}\right)$$
$$= 3.80*10^{4}$$

$$\therefore\ K_o = 1/\left(3.80*10^{4} * 600*10^{-4}\right) = 4.38*10^{-4}\text{cm/s}.$$

REFERENCES

1. Whu, J. A.; Baltzis, B. C.; Sirkar, K. K., Nanofiltration studies of larger organic microsolutes in methanol solutions. *J. Membr. Sci.* **2000,** 170, 159-172.

2. Scarpello, J. T.; Nair, D.; Freitas dos Santos, L. M.; White, L. S.; Livingston, A. G., The separation of homogeneous organometallic catalysts using solvent resistant nenofiltration. *J. Membr. Sci.* **2002,** 203, 71-85.

3. White, L. S.; Nitsch, A. R., Solvent recovery from lube oil filtrates with a polyimide membrane. *J. Membr. Sci.* **2000,** 179, 267-274.

4. Musale, D. A.; Kumar, A., Solvent and pH resistance of surface crosslinked chitosan/poly(acrylonitrile) composite nanofiltration membranes. *J. Appl. Polym. Sci.* **2000,** 77, 1782-1793.

5. White, L. S.; Nitsch, A. R., Application of thin film composite membranes to the membrane aromatic recovery system. *J. Membr. Sci.* **2000,** 179, 267-274.

6. Han, S., Wong, H.-T., Livingston, A.G., Application of organic solvent nanofiltration to separation of ionic liquids and products from ionic liquid mediated reactions. *Chemical Engineering Research and Design* **2005,** 83, 309-316.

7. Whu, J. A.; Baltzis, B. C.; Sirkar, K. K., Modeling of nanofiltration - assisted organic synthesis. *J. Membr. Sci.* **1999,** 163, 319-331.

8. Bhanushali, D.; Bhattacharyya, D., Advances in solvent-resistant nanofiltration membranes: Experimental observations and applications. *Annals of the New York Academy of Sciences* **2003,** 984, 159-177.

9. Bhanushali, D.; Kloos, S.; Bhattacharyya, D., Solute transport in solvent-resistant nanofiltration membranes for non-aqueous systems: experimental results and the role of solute–solvent coupling. *J. Membr. Sci.* **2002,** 208, 343-359.

10. Zhang, W.; He, G.; Gao, P.; Chen, Y. K., Development and cheracterization of composite nanofiltration membranes and their application in concentration of antibiotics. *Sep. Purif. Tech.* **2003,** 30, 27-35.

11. Benzinger, W. D.; Parekh, B. S.; Eichelberger, J. L., High temperature ultrafiltration with Kynar poly(vinylidene fluoride) membranes. *Sep. Sci. Technol.* **1980,** 15, (4), 1193-1204.

12. Bo, D.; Kun, Z., Preparation and properties of polyimide ultrafiltration membranes. *J. Membr. Sci.* **1991,** 60, 63-73.

13. Peinemann, K.-V.; Ebet, K.; Hicke, H.-G.; Schanagl, N., Polymeric composite ultrafiltration membranes for non-aqueous applications. *Env. Prog.* **2001,** 20, (1), 17.

14. Bruggen, B. V.; Geens, J.; Vandecasteele, C., Influence of organic solvents on the performance of polymeric nanofiltration membranes. *Sep. Purif. Tech.* **2002,** 37, (4), 783-797.

15. Dickson, J. M.; Childs, R. F.; McCarry, B. E.; Gagnon, D. R., Development of a coating technique for the internal structture of polypropylene microfiltration membranes. *J. Membr. Sci.* **1998,** 148, 25-36.

16. Liu, Z.-M.; Xu, Z.-K.; Wan, L.-S.; Wu, J.; Ulbricht, M., Surface modification of polypropylene microfiltration membranes by the immobilization of poly(N-vinyl-2-pyrrolidone): a facile plasma approach. *J. Membr. Sci.* **2005,** 249, 21-31.

17. Shukla, R.; Cheryan, M., Stability and performance of ultrafiltration membranes in aqueous ethanol. *Sep. Sci. Technol.* **2003,** 38, 1533.

18. Shukla, R.; Cheryan, M., Performance of ultrafiltration membranes in ethanol–water solutions: effect of membrane conditioning. *J. Membr. Sci.* **2002,** 193, 75.

19. Basu, R.; Prasad, R.; Sirkar, K. K., Nondispersive membrane solvent back extraction of phenol. *AIChE J.* **1990,** 36, 450.

20. Mulder, M., *Basic Principles of Membrane Technology*. The Netherlands, Kluwer academic publishers: 1996.

21. Cheryan, M., *Ultrafiltration and Microfiltration Handbook*. Technomic: Lancaster, PA, 1998.

22. Lu, X.; Bian, X.; Shi, L., Preparation and characterization of NF composite membrane. *J. Membr. Sci.* **2002,** 210, 3-11.

23. Nguyen, M. H.; Khan, M. M. A.; Kailasapathy, K.; Hourigan, J. A., Use of membrane concentrated cottage cheese whey in ice-creams. *Austr. J. Dairy Tech.* **1997,** 52, (2), 75-78.

24. Nwuha, V., Novel studies on membrane extraction of bioactive components of green tea in organic solvents: part I. *J. Food Engineering* **2000,** 44, 233-238.

25. Guu, Y. K.; Chiu, C. H.; Young, J. K., Processing of soybean soaking water with a NF-RO membrane system and lactic-acid fermentation of ratained solutes. *J. Agric. Food Chem.* **1997,** 45, (10), 4096-4100.

26. White, L. S., Transport properties of a polyimide solvent resistant nanofiltration membrane. *J. Membr. Sci.* **2002,** 205, 191-202.

27. Verissimo, S.; Peinemann, K.-V.; Bordado, J., Influence of the diamine structure on the nanofiltartion performance, surface morphology and surface charge of the composite polyamide membarnes. *J. Membr. Sci.* **2006,** 279, 266-275.

28. Ahmad, A. L.; Ooi, B. S.; Mohammad, A. W.; Choudhury, J. P., Composite nanofiltration polyamide membrane: A study on the diamine ratio and its performance evaluation. *Ind. Eng. Chem. Res.* **2004,** 43, 8074-8082.

29. Petersen, R. J.; Cadotte, J. E., Thin film composite reverse osmosis membranes. In *Handbook of Industrial Membrane Technology*, Porter, M. C., Ed. Noyes Publications: Park Ridge, New Jersey, 1988.

30. Yun, C. H.; Prasad, R.; Guha, A. K.; Sirkar, K. K., Hollow fiber solvent extraction removal of toxic heavy metals from aqueous waste streams. *Ind. Eng. Chem. Res.* **1993,** 32, 1186.

31. Prasad, R.; Khare, S.; Sengupta, A.; Sirkar, K. K., Novel liquid-in-pore configurations in membrane solvent extraction. *AIChE J.* **1990,** 36, 1592.

32. Prasad, R.; Sirkar, K. K., Hollow fiber solvent extraction of pharmaceutical products: A case study. *J. Membr. Sci.* **1989,** 47, 235.

33. Schlosser, S.; Kertesz, R.; Martak, J., Recovery and separation of organic acids by membrane-based solvent extraction and pertraction: An overview with a case study on recovery of MPCA. *Sep. Purif. Tech.* **2005,** 41, 237.

34. Gonzalez-Munoz, M. J.; Luque, S.; Alvarez, J. R.; Coca, J., Recovery of phenol from aqueous solutions using hollow fibre contactors. *J. Membr. Sci.* **2003,** 213, 181.

35. Klaassen, R.; Jansen, A. E., The membrane contactor: environmental applications and possibilities. *Env. Prog.* **2001,** 20, 37.

36. Ratajczak, W.; Porebski, T.; Plesnar, M.; Brzozowski, R.; Tomzik, S.; Capala, W.; Wieteska, A.; Zebrowski, M.; Malachowski, B.; Karabin, M., Modernization of the phenol and acetone plant at the "Orlen" Polish Oil Company, Przemysl Chemiczny. **2004,** 83, 498.

37. Yeh, H. M.; Chen, Y. K., Membrane extraction through cross-flow rectangular modules. *J. Membr. Sci.* **2000,** 170, 235.

38. Kiani, A.; Bhave, R. R.; Sirkar, K. K., Solvent extraction with immobilized interfaces in a microporous hydrophobic membrane. *J. Membr. Sci.* **1984,** 20, 125.

39. Prasad, R.; Sirkar, K. K., Solvent extraction with microporous hydrophilic and composite membranes. *AIChE J.* **1987,** 33, 1057-1066.

40. Prasad, R.; Sirkar, K. K., Hollow fiber solvent extraction: performances and design. *J. Membr. Sci.* **1990,** 50, 153.

41. Prasad, R.; Sirkar, K. K., Membrane-Based Solvent Extraction. In *Membrane Handbook*, Ho, W. S. W.; Sirkar, K. K., Eds. Chapman and Hall: New York, NY, 1992.

42. D'Elia, N. A.; Dahuron, L.; Cussler, E. L., Liquid-liquid extractions with microporous hollow fibers. *J. Membr. Sci.* **1986,** 29, 309.

43. Bocquet, S.; Gascons Viladomat, F.; Muvdi Nova; J. Sanchez, C.; Athes, V.; Souchon, I., Membrane-based solvent extraction of aroma compounds: Choice of configurations of hollow fiber modules based on experiments and simulation. *J. Membr. Sci.* **2006,** 281, 358.

44. Kertész, R.; Simo, M.; Schlosser, S., Membrane-based solvent extraction and stripping of phenylalanine in HF contactors. *J. Membr. Sci.* **2005,** 257, 37.

45. Coelhoso, I. M.; Silvestre, P.; Viegas, R. M. C.; Crespo, J. P. S. G.; Carrondo, M. J. T., Membrane-based solvent extraction and stripping of lactate in hollow-fiber contactors. *J. Membr. Sci.* **1997,** 134, 19.

46. Lin, S.-H.; Juang, R.-S., Kinetic modeling of simultaneous recovery of metallic cations and anions with a mixture of extractants in hollow-fiber modules. *Ind. Eng. Chem. Res.* **2002,** 41, 853.

47. Ortiz, I.; Galan, B.; Irabien, A., Kinetic analysis of the simultaneous nondispersive extraction and back-extraction of chromium(VI). *Ind. Eng. Chem. Res.* **1996,** 35, 1369.

48. Han, S. J.; Luthra, S. S.; Peeva, L.; Yang, X. J.; Livingston, A. G., Insights into the transport of toluene and phenol through organic solvent nanofiltration membranes. *Sep. Sci. Technol.* **2003,** 38, 1899.

49. Netke, S. A.; Pangarkar, V. G., Extraction of naphthenic acid kerosene using porous and nonporous polymeric membranes. *Sepa. Sci. Technol.* **1996,** 31, 63.

50. Bigg, D. M.; Stichford, G. H.; Talbert, S. G., Applicatiosn of polymeric materials for condensing heat exchangers. *Polym. Eng. Sci.* **1989,** 29, (16), 1111.

51. Bandelier, P.; Deronzier, J. C.; Lauro, F., Plastic heat exchangers. *Mater. Tech.* **1992,** 9-10, 67.

52. El-Desssouky, H. T.; Ettouney, H. M., Plastic compact heat exchangers for single-effect desalination systems. *Desalination* **1999,** 122, 271.

53. Githens, R. E.; Minor, R. W.; Tomsic, V. J., Flexible tube heat exchangers. *Chem. Eng. Prog.* **1965,** 61, (7), 55.

54. Zarkadas, D. M.; Sirkar, K. K., Polymeric hollow fiber heat exchangers: an alternative for lower temperature applications. *Ind. Eng. Chem. Res.* **2004,** 43, 8093-8106.

55. Celgard 2400: Product Properties Brochure, www.celgard.com. **Dec 2006.**

56. Ritchie, A. C.; Bowry, K.; Fisher, A. C.; Gaylor, J. D. S., A novel automated method for the determination of membrane permeability in gas–liquid transfer applications. *J. Membr. Sci.* **1996,** 121, 169.

57. Strathmann, H., Synthetic Membranes and their Preparation. In *Handbook of Industrial Membrane Technology*, Porter, M. C., Ed. Noyes Publications: Park Ridge, New Jersey, 1988.

58. Ultra PES: Product Properties Brochure, Membrana Inc.

59. Morgan, P. W., *Condensation Polymers: By Interfacial and Solution Methods.* Wiley/Interscience: New York, NY, 1965.

60. Kim, I.-C.; Jegal, J.; Lee, K.-H., Effect of aqueous and organic solutions on the performance of polyamide thin-film-composite nanofiltration membranes. *J. Polym. Sci.* **2002,** 40, 2151-2163.

61. Cadotte, J. E.; Rozelle, L. T. *In Situ-Formed Condensation Polymers for Reverse Osmosis Membranes, loc. cit.*; NTIS Report No. PB-229337; November, 1972.

62. Dow Catalog, Filmtec Membranes, pp. 87-89.

63. Cadotte, J. E. Reverse osmosis membrane. U.S. Patent 4,039,440, August 2, 1977.

64. Capfil Nanofiltration Membrane NF50 M10, Product Data Sheet, X-Flow, Company Web-site: http://www.x-flow.com. **Dec 2006.**

65. Verissimo, S.; Peinemann, K.-V.; Bordado, J., Thin-film composite hollow fiber membranes: An optimized manufacturing method. *J. Membr. Sci.* **2005,** 264, 48-55.

66. Verissimo, S.; Peinemann, K.-V.; Bordado, J., New composite hollow fiber membrane for nanofiltration. *Desalination* **2005,** 184, 1-11.

67. Song, Y.; Sun, P.; Henry, L. L.; Sun, B., Mechanisms of structure and performance controlled thin film composite membrane formation via interfacial polymerization process. *J. Membr. Sci.* **2005,** 251, 67-79.

68. Jegal, J.; Min, S. G.; Lee, K.-H., Factors affecting the interfacial polymerization of polyamide active layers for the formation of polyamide composite membranes. *J. Appl. Polym. Sci.* **2002,** 86, (11), 2781-2787.

69. Petersen, R. J., Review: composite reverse osmosis and nanofiltration membranes. *J. Membr. Sci.* **1993,** 83, 81.

70. Mohammad, A. W.; Hilal, N.; Seman, M. N. A., A study on producing composite nanofiltration membranes with optimized properties. *Desalination* **2003,** 158, 73-78.

71. Garg, D. H.; Lenk, W.; Berwald, S.; Lunkwitz, K.; Simon, F.; Eichhorn, K.-J., Hydrophilization of microporous polypropylene Celgard membranes by the chemical modification technique. *J. Appl. Polym. Sci.* **1996,** 60, 2087-2104.

72. Whitefield, R. E.; Miller, L. A.; Wasley, W. L., Fabric stabilization by interfacial polymerization. Part I: polyamides. *Textile Res. J.* **1961,** 31, 704.

73. Mark, J. E., *Polymer Data Handbook.* Oxford University Press: New York, 1999; p 784, 490.

74. Wu, D. Y.; Lee, S.; Stanislaw, G. W.; Wojciech, G. Surface Treatment of Polymers. U.S. Patent 5,922,161, July 13, 1999.

75. Kemperman, A. J. B.; Rolevink, H. H. M.; Bargenman, D.; Van den Boomgaard, T.; Strathmann, H., Stabilization of supported liquid membranes by interfacial polymerization top layers. *J. Membr. Sci.* **1998,** 43-55.

76. Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M., The chromic acid etching of polyolefin surfaces, and adhesive bonding. *J. Colloid Interface Sci.* **1974,** 47, 636.

77. Song, Y.; Liu, F.; Sun, B., Preparation, characterization, and application of thin film composite nanofiltration membranes. *J. Appl. Polym. Sci.* **2005,** 95, 1251-1261.

78. Mao, T. J.; Reegen, S. L., Adhesion of some acrylic polymers and copolymers. In *Adhesion and Cohesion*, Weiss, P., Ed. Elsevier: New York, 1962; p 214-215.

79. Kesting, R. E., *Synthetic Polymeric Membranes.* John Wiley & Sons: Irvine, California, 1985; p 290.

80. Matsushima, N.; Danno, G.-I.; Takezawa, H.; Izumi, Y., Three-dimensional structure of maize a-zein proteins studied by small-angle X-ray scattering. *Biochimica et Biophysica Acta* **1997,** 1339, 14-22.

81. Kistler, K. R.; Cussler, E. L., Membrane modules for building ventilation. *IChemE* **2002,** 80, 53.

82. Craine, E. M.; Jones, C. A.; Boundy, J. A., A rapid turbidimetric method for determination of zein. *Cereal chemistry* **1957,** 34, 456-462.

83. Wilke, C. R.; Chang, P., Correlation of diffusion coefficients in dilute solutions. *AIChE J.* **1955,** 1, 264.

84. Prasad, R.; Sirkar, K. K., Dispersion-free solvent extraction with microporous hollow-fiber modules. *AIChE J.* **1988,** 34, 177-188.

85. Iversen, S. B.; Bhatia, V. K.; Dam-Johansen, K.; Jonsson, G., Characterization of microporous membranes for use in membrane contactors. *J. Membr. Sci.* **1997,** 130, 205.

86. Skelland, A. H. P., *Diffusional Mass Transfer*. Wiley: New York, 1974; p 164.

87. Sadtler, *The Infrared spectra atlas of monomers and polymers*. Sadtler Research Laboratories: Philadelphia, 1980.

88. Roh, I. J., Influence of rupture strength of interfacially polymerized thin-film structure on the performance of polyamide composite membranes. *J. Membr. Sci.* **2002,** 198, 63-74.

89. Shinichiro, G.; Hideo, J.; Koichiro, K.; Kunihisa, Y., Liquid-liquid equilibriums and interfacial tensions of the system acetic acid-water-methyl isobutyl ketone. *Kagaku Kogaku* **1973,** 37, 849.

90. Sirkar, K. K.; Song, L.; Christian, S.; Kosaraju, P. B.; Korikov, A. P.; Zarkadas, D. M. *Solid hollow fiber heat exchangers in thermally-driven desalination processes*; Phase II Final Report to ONR Award No. N000140410810; December 23, 2005.

91. Trushinski, B. J.; Dickson, J. M.; Smyth, T.; Childs, R. F.; McCarry, B. E., Polysulfonamide thin-flm composite reverse osmosis membranes. **1998,** 143.

92. Nguyen, Q. T.; Ping, Z.; Nguyen, T.; Rigal, P., Simple method for immobilization of bio-macromolecules onto membranes of different types. *J. Membr. sci* **2003,** 213, 85-95.

93. Ademovic, Z.; Klee, D.; Kingshott, P.; Kaufmann, R.; Hocker, H., Minimization of protein adsorption on poly(vinylidene fluoride). *Biomolecular Engineering* **2002,** 19, 177-82.

94. Nnebe, I. M.; Tilton, R. D.; Schneider, J. W., Direct force measurement of the stability of poly(ethyleneglycol)–polyethylenimine graft films. *J. Colloid Interface Sci.* **2004,** 276, 306-316.

95. Chen, Z.; Deng, M.; Chen, Y.; He, G.; Wu, M.; Wang, J., Preparation and performance of cellulose acetate/polyethyleneimine blend microfiltration membranes and their applications. *J. Membr. Sci.* **2004,** 235, 73-86.

96. Zhu, B.; Iwata, H.; Ikada, Y., Immobilization of poly(ethyleneimine) onto polymer films pretreated with plasma. *J. Appl. Polym. Sci.* **2000,** 75, 576-582.

97. Takata, K.; Yamamoto, Y.; Sata, T., Modification of transport properties of ion exchange membranes XIV. Effect of molecular weight of polyethyleneimine bonded to the surface of cation exchange membranes by acid–amide bonding on electrochemical properties of the membranes. *J. Membr. Sci* **2000,** 179, 101-107.

98. Toutianoush, A.; Krasemann, L.; Tieke, B., Polyelectrolyte multilayer membranes for pervaporation separation of alcohol/water mixtures. *Colloids and Surfaces* **2002,** 198-200, 881-889.