Layer-by-layer Self-assembly Membranes for Solvent Dehydration by Pervaporation

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

In this study, polyelectrolyte membranes were prepared by layer-by-layer self-assembly on top of an interfacially polymerized polyamide substrate, and these thin-film-composite membranes were studied for pervaporative dehydration of ethylene glycol, ethanol and isopropanol.

The performance of composite membranes based on polyethylenimine/poly(acrylic acid) (PEI/PAA) multilayers on a polyamide substrate showed good selectivity and stability for ethylene glycol dehydration. In order to understand the formation process of the polyelectrolyte multilayers, the growth of polyelectrolyte multilayers fabricated on the inner surface of cuvette was investiagted. The membrane surface became increasingly hydrophilic with an increase in the number of polyelectrolyte double layers, which favored water permeation for pervaporative dehydration of organic solvents. Water contact angle on the membrane surface decreased from 68^o to 20^o when 7 polyelectrolyte bilayers were deposited on the polyamide substrate.

Although the (PEI/PAA) based polyelectrolyte membranes showed good performance for dehydration of ethylene glycol, these membranes did not perform well for the dehydration of ethanol and isopropanol at relatively high feed alcohol concentrations. This was found to be caused by insufficient stability of PEI/PAA bilayers and the polyamide substrate in the ethanol and isopropanol. To improve the performance of the composite membranes for dehydration of ethanol and isopropanol, the outermost surface layer was deposited with PEI, followed by crosslinking. A further improvement in the membrane selectivity was accomplished by substituting the PEI with partially protonated chitosan in the last few polyelectrolyte bilayers during membrane fabrication. It was demonstrated that using interfacially polymerized polyamide membrane as a substrate, polyelectrolyte membranes with less than 8 bilayers could be fabricated for the dehydration of alcohol and diol. This represents a siginificant advancement as a large number of polyelectrolyte bilayers (as many as 60) are often needed.

Glutaraldehyde crosslinked polyelectrolyte self-assembled membranes comprising of chitosan and PAA were also prepared for isopropanol/water separation. The resulting membrane showed stable performance with good permeation flux and separation factor. The effects of crosslinking conditions (e.g., concentration and temperature of crosslinking agent, and crosslinking time) on the membrane performance were studied.

Alternatively, using PEI as polycation, when anionic PAA was substituted with alginate in the last few polyelectrolyte bilayers during membrane fabrication, stable membranes with a good performance were obtained without the need of chemical crosslinking. The polyethylenimine/alginate self-assembly membranes showed good selectivity and stability for dehydration of ethanol. For instance, a permeation flux of 0.24 $kg/(m^2 \cdot h)$ and a separation factor of 206 were obtained at room temperature at 10 wt% feed water concentration with a membrane comprising of 10 double layers of polyelectrolytes.

Keywords: Pervaporation, dehydration, polyelectrolyte, self-assembly, crosslinking, glutaraldehyde, chitosan, ethylene glycol, isopropanol, ethanol, alginate, UV-Vis spectrophotometer, membrane.

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To my parents and husband

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Chapter 1

Introduction

1.1 Background

Pervaporation is an important membrane process for liquid separation in chemical industries due to its simplicity and low operating cost [Jonqui`eres et al., 2002; Aptel et al., 1976; Feng and Huang, 1997; Kang et al., 1990; Jiraratananon et al., 2002; Zhu et al., 2007]. It is a relatively new process based on selective permeability of non-porous membranes. Usually polymers or zeolites are the first choice for the separation layer of the membrane [Kondo et al., 1997; Holmes et al., 1996; Van den Berg, 2003]. The process can be described in Figure 1.1 where the liquid mixture is in contact with one side of the membrane and the permeate is collected at the other side as a low pressure vapor. In pervaporation separation of, for example, a binary system, one of the components will be preferentially removed because of its higher sorption or quicker diffusivity in the membrane [Shao and Huang, 2007]. In order to maintain a continuous mass transport, a vacuum pump is applied at the downstream side to provide a driving force by maintaining a permeate pressure lower than the saturated vapor pressure of the feed solution. Therefore, the vaporous permeate can be condensed and collected or released as desired. In addition, the use of a sweeping gas [Neel, 1993; Vallieres and Favre, 2004] in the downstream side of the membrane also can be used to provide the driving force for pervaporation.

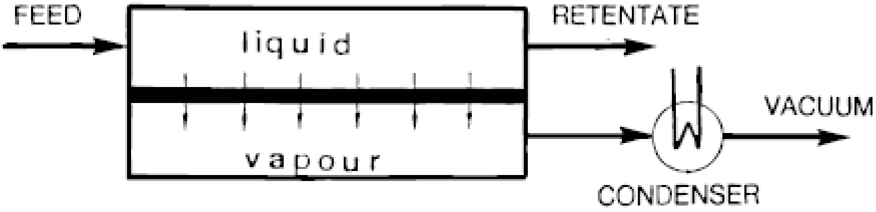


Figure 1. 1 Schematic diagram of the pervaporation [Feng and Huang, 1997]

The phenomenon of pervaporation was first observed by Kober [1917]. The usefulness of pervaporation for separation was recognized by Farber [Heisler et al., 1956]. However, it was in the 1950s that this process was first systematically studied by Binning and co-workers to focus on the separation of organic mixtures [Binning and Stuckey, 1960; Binning et al., 1961; Binning, 1961, 1962]. The studies at that time were limited to only laboratory scales, and did not lead to high performance modules required for commercial application. However, the process was revisited by Perry and coworkers in the 1970s [Strazik and Perry, 1993]. Since then, advances in membrane technology have made it possible to prepare pervaporation systems economically [Baker, 2004].

It is well known that distillation is the most widely used technique to separate liquid mixtures. However, distillation separation of mixtures with an azeotropic composition or with components of close volatility is difficult and in some cases another substance has to be added to the system. Thus pervaporation has many advantages over distillation, including:

(1) simple operation;

(2) energy savings;

(3) azeotropic mixtures can be separated without using additional chemicals ;

(4) it can be easily combined with other separation processes.

Especially, hybrid processes that combine pervaporation and other liquid separating technologies have attracted interest both for lab research and in industrial applications [Lipnizki, 2002; Vane, 2005; Shah et al., 2004; Benedict et al., 2006]. With these developments, it is believed that pervaporation will play an increasingly important role in the chemical processing industry.

Pervaporation has a broad range of applications, which can be grouped into three areas [Smitha et al., 2004]: (i) dehydration of organic solvents (e.g., alcohols, ethers, esters, acids and glycols), (ii) removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma), (iii) separation of organic-organic mixtures (e.g., methyl *tert*-butyl ether/methanol, dimethyl carbonate/methanol).

Among the applications mentioned above, the dehydration of organic solvents is the best developed commercially. More than 60 pervaporation units were in operation around the world for solvent dehydration in early 2000 [Vane, 2005; Shah et al., 2004; Benedict et al., 2006]. The industrial success of solvent dehydration is attributed to both the preferential sorption and diffusion of water molecules in hydrophilic membranes due to their much smaller molecular size than other organic solvents [Koros et al., 1995].

Removal of organics from water is a long-standing topic for environmental protection. Rubbery membranes (e.g., poly(dimethyl siloxane)) are mainly used for such applications. However, the concentration polarization on the membrane surface is important for this application because at low concentrations of organics in the feed, the organics can be depleted on the membrane surface and a concentration-polarized layer could be formed easily in the vicinity of the membrane surface which will result in a lesser extent of separation [Nguyen et al., 1987; Raghunath and Hwang, 1992 a and b; Psaume et al., 1988; Nijhuis et al., 1993].

The separation of organic-organic mixtures represents the most challenging application for pervaporation [Villaluenga and Tabe-Mohammadi, 2000]. Most liquid pairs in this category that are of industrial importance include [Benedict et al., 2006] polar/non-polar mixtures (e.g., methanol/MTBE) [Dogihere et al., 1994; Jae et al., 1998], aromatic/aliphatic mixtures (e.g., benzene/*n*-hexane) [Yamasaki and Mizoguchi, 1997; Wang et al., 1999], aromatic/alicyclic mixtures (e.g., benzene/cyclohexane) [Ray et al., 1997], and isomers (e.g., p-xylene, m-xylene, and o-xylene) [Chen et al., 2000; Schleiffelder et al., 2001; Wegner et al., 1999]. There have been some limited successes in the separation of polar/non-polar liquid mixtures, but not much progress in the separation of the other liquid pairs.

Pervaporation can be used as a standalone unit. It can also be combined with other unit operations such as distillation to form a hybrid process. Hybrid processes have been successfully used on an industrial scale [Lipnizki et al., 1999]. Pervaporation is now considered as a potential solution for separating aromatic hydrocarbons (e.g., toluene and benzene) from petroleum-derived liquid mixtures (e.g., gasoline) from energy/cost saving and environmental protection points of view [Smitha et al., 2004; Villaluenga and Mohammadi, 2000]. With recent high prices and fluctuations in crude oil supply, pervaporation has attracted significant attention as a potential process in bio-refinery and food industries that deal with heat-, stress-, and/or chemical sensitive bio-chemicals [Lipnizki et al., 2002; Vane, 2005; Huang and Vane, 2006; Huang and Baker, 2008.].

Electrostatic assembly of polyelectrolyte multilayers is regarded as a versatile and efficient method to fabricate hydrophilic membranes having a thickness within nanometer scales [Castelnovo and Joanny, 2000]. The first experiment on the fabrication of a polyelectrolyte multilayer was conducted by Decher et al. [1992]. Through layer-by-layer (LbL) self-assembly with ionic polymers, polyelectrolyte multilayers are formed under electrostatic attractions between oppositely charged groups in the polyelectrolytes involved.

This process has several advantages over other techniques because it is a simple, environmentally benign and potentially economical process [Chen et al., 1997]. It has a great potential for applications in many areas, including drug delivery, dental adhesives [Scranton et al., 1995; Kota, 1996], blood-compatible implant coatings, membranes for artificial kidney, contact lenses, and scaffold materials for tissue regeneration [Mendelsohn et al., 2000].

Polyamide is a suitable membrane material for water and wastewater treatment because of its good thermal stability, mechanical strength, and resistance to organic solvents. However, it needs to form composite membranes because a dense structure will lead to low permeation rates. Interfacially polymerized polyamide membranes are now widely used commercially for reverse osmosis. Therefore, the polyamide substrate is a niche application for making hydrophilic pervaporation membranes to dehydrate organic solvents because it has a charged surface for easy fabrication of polyelectrolyte multilayers.

An interfacially polymerized polyamide membrane was chosen as a substrate in this study for the following considerations: 1) it has a negatively charged surface, which favors initial deposition of a polycation during electrostatic self-assembly of the polyelectrolytes, 2) the polyamide membrane itself is a thin-film composite membrane with an ultrathin dense skin layer and a microporous support, and thus relatively smaller number of polyelectrolyte bilayers is needed to achieve an adequate selectivity as compared to cases where ultrafiltration or microfiltration membranes are used as a substrate, 3) interfacial polymerization to produce thin film composite membranes is a well established technique, and the use of such membranes as a substrate for pervaporation membranes represents an expansion of their scope of applications.

1.2 Research Objectives

The objectives of this research work were to study polyelectrolyte/polyamide composite membranes for solvent dehydration by pervaportion. Different operating and fabrication parameters that affect the membrane performance were studied. The detailed research objectives were as follows:

1) To fabricate a polyelectrolyte multilayer membrane using LbL self-assembly based on polyethyleimine/poly(acrylic acid) (PEI/PAA) for dehydration of ethylene glycol, isopropanol and ethanol.
2) To investigate the formation of polyelectrolyte multilayers on the inner surface of the cuvette and the effects of deposition conditions (i.e., polyelectrolyte solution concentration, deposition time and deposition temperature) on the performance of the membrane.
3) To evaluate the stability of the polyelectrolyte multilayer membrane based on (PEI/PAA) after solvent treatments (isopropanol and ethanol) due to the poor selectivity for isopropanol and ethanol dehydration.
4) To enhance the performance of PEM membrane for isopropanol and ethanol dehydration by surface chemical crosslinking the topping polyelectrolyte layer and gradual replacement of alternative polyelectrolytes.

1.3 Outline of the Thesis

This thesis consists of eight chapters, organized as follows:

Chapter 1 presented an overview of the objectives and the rationale of choosing interfacially polymerized polyamide membrane as the substrate to fabricate polyelectrolyte composite membrane by electrostatic LbL self-assembly.

A literature review on fundamentals of pervaporation, polyeletrolyte composite membranes and stability of polymeric membranes was provided in chapter 2.

Chapter 3 focused on PEI/PAA membranes self-assembled on a polyamide substrate for dehydration of ethylene glycol.

The growth of polyelectrolyte multilayers on the surface of quartz cuvettes was monitored by UV-Vis spectrophotometry. The effects of different fabrication parameters on the formation of polyelectrolyte multilayers and the performance of polyelectrolyte/polyamide composite membranes were investigated in Chapter 4.

While the PEI/PA membranes showed good performance for dehydration of ethylene glycol, the membrane selectivity for dehydration of ethanol and isopropanol was unsatisfactory. Therefore, Chapter 5 focused on the stabilities of the polyamide substrate and the polyelectrolyte multilayers, separately, in order to pinpoint the root cause of the poor membrane selectivity to ethanol and isopropanol. Attempts were then made to modify polyelectrolyte/polyamide membranes to improve membrane selectivity and stability.

Crosslinking was found to be effective in improving membrane stability and selectivity. Crosslinked polyelectrolyte/polyamide membranes based on chitosan/PAA were fabricated for isopropanol dehydration and the results were presented in Chapter 6.

Chapter 7 looked into the feasibility of using alginic acid as an alternative polyelectrolyte to modify the membrane to further improve the membrane selectivity for ethanol dehydration.

Chapter 8 summarized the general conclusions drawn from the research, and the original contributions of the thesis work and recommendations for future work were also presented. In order to have a clear understanding of this thesis, Figure 1.2 is hereby presented to describe the relationship of each chapter.

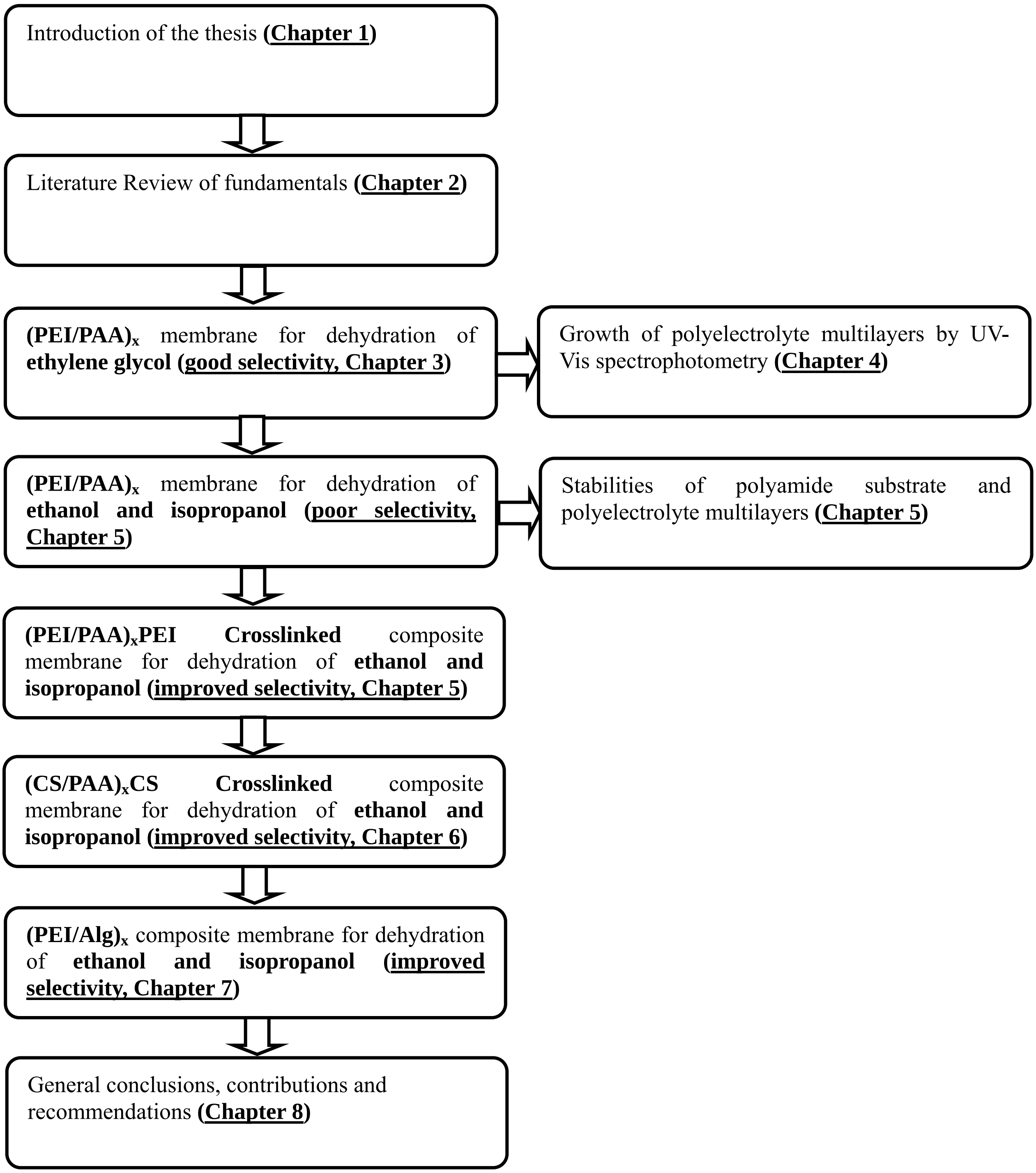


Figure 1. 2 Relationships between chapters in the thesis

Chapter 2

Literature Review

Pervaporation is an efficient membrane process for liquid separation and has attracted significant interest from both academia and industry [Neel, 1991; Feng and Huang, 1997]. It is considered to be one of the most promising separation processes for a wide variety of liquid mixtures. For example, because of the moderate operating temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of azeotropic and constant-boiling mixtures [Kondo, 1997; Holmes, 1996; Van den Berg et al., 2003]. In addition to the dehydration of organic solvents and the removal of organics from aqueous streams, pervaporation has also emerged as a potential process for separation of heat-, stress-, and /or chemical-sensitive biochemicals [Lipnizki et al., 2002; Vane, 2005; Huang et al., 1999; Huang et al., 2002].

This chapter attempts to provide a review of the fundamentals of pervaporation and membranes used in pervaporation. The prior work on LbL self-assembly of polyelectrolytes is also reviewed here as it will be used for solvent dehydration in this study.

2.1 Fundamentals of pervaporation

2.1.1 Characteristics of pervaporation

Pervaporation involves the permeation of a penetrant across a membrane. The separation of a mixture is based on the difference of the permeation rates of different components through the membrane. This process involves phase change from liquid (feed) to vapour (permeate) as the permeate pressure is kept below the saturated vapour pressure of the liquid feed.

Pervaporation can be carried out batchwise or continuously. For continuous pervaporation, the liquid feed contacts one side of the membrane and a certain component in the feed will pass through the membrane preferentially. This component is enriched on the other side of the membrane as permeate vapour. Usually, the permeate is collected as a liquid after condensation.

The membrane performance can be characterized in terms of permeation flux and permeate composition. The permeation flux, which depends on both the intrinsic permeability and the effective thickness of the membrane, is a measure of the mass of a component that permeates through a specific area of the membrane over a given period of time. It can be defined as:

$$J = \frac{Q}{A \cdot t} \qquad (2.1)$$

where J = permeation flux, kg/(m^2·hr);

Q = amount of the permeate, kg;

A = area of membrane, m^2;

t = operating time, hr.

The selectivity of a membrane for separating a binary mixture consisting of components i and j can be expressed by the separation factor α,

$$\alpha_{ij} = \frac{Y_i/Y_j}{X_i/X_j} \qquad (2.2)$$

where α_{ij} = separation factor;

Y_i, Y_j = concentration of component i and j in permeate, respectively;

X_i, X_j = concentration of component i and j in feed, respectively.

2.1.2 Mass transport in pervaporation

There are several models to describe mass transport in pervaporation [Binning et al., 1961; Kedem, 1989; Okada and Matsuura, 1991; Shieh and Huang, 1998]. Among them, the solution-diffusion and pore flow models are commonly accepted. According to the solution-diffusion model, the mass transport can be divided into three steps, as shown in Figure 2.1, consisting of

(1) Sorption of the liquids into the membrane on the feed side;

(2) Diffusion of the sorbed components in the membrane;

(3) Desorption of the permeant on the downstream side of the membrane as a vapor.

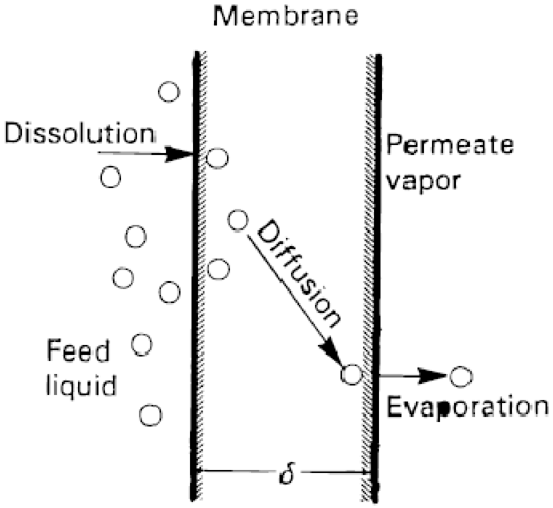


Figure 2. 1 Schematic description of solution-diffusion model [Feng and Huang, 1997]

The solution-diffusion model, which has become the most popular model accepted by the majority of membrane researchers, was originally developed by Graham [Lonsdale, 1982] to describe the permeation of gases through dense rubber membranes.

The flux, J_i of a component, *i*, is related to the gradient of the chemical potential and can be described by a simple equation as follows:

$$J_i = -L_i \frac{d\mu_i}{dx} \qquad (2.3)$$

where J_i = flux of component i;

$d\mu_i/dx$ = chemical potential gradient of component i;

L_i = coefficient relating chemical potential driving force with flux;

Restricting to the driving forces generated by concentration and pressure gradients, the chemical potential can be written as:

$$\mu_i = \mu_i^0 + RT\ln(\gamma_i c_i) + v_i(p - p_i^0) \qquad (2.4)$$

where μ_i^0 = chemical potential of pure i at the pressure p_i^0;

c_i = molar concentration of component i;

γ_i = activity coefficient of component i;

v_i = molar volume of component i;

p_i^0 = saturated vapor pressure of component i.

The solution-diffusion model assumes that the pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed as a concentration gradient, as illustrated in Figure 2.2 [Wijmans and Baker, 1995]. Combining equations 2.3 and 2.4, and defining term $RTL_i/\gamma_i c_i$ as the diffusion coefficient D_i;

$$J_i = -RTL_i/\gamma_i c_i \cdot (dc_i/dx) = -D_i \cdot (dc_i/dx) \qquad (2.5)$$

and integrating over the thickness of the membrane then gives

$$J_i = -D_i \cdot (\Delta c_i/\delta) \qquad (2.6)$$

where δ is the thickness of the membrane.

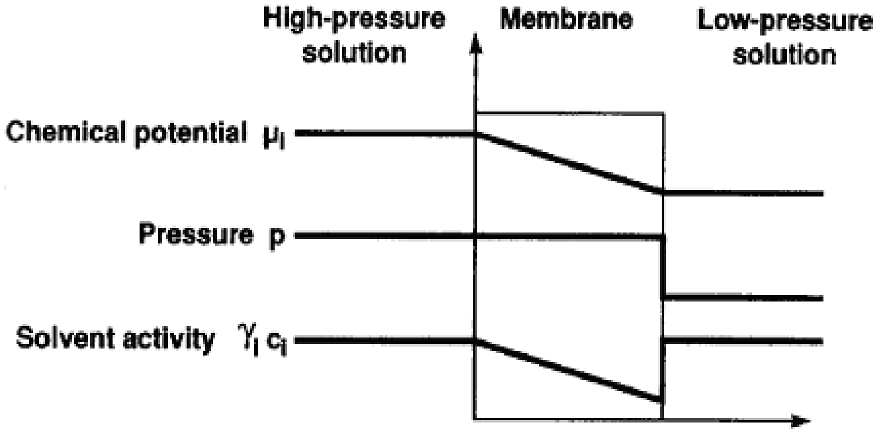


Figure 2.2 Profile of chemical potential and pressure for membrane based on the solution-diffusion model [Wijmans and Baker, 1995]

Figure 2.3 describes the mass transport according to the pore flow model, which considers that permeants are separated by pressure-driven convective flow through tiny pores. The liquid separation is achieved when certain permeants are excluded from some of the pores in the membrane through which other permeants move. The mass transport consists of three steps:

(1) Liquid transport from the pore inlet to the liquid-vapor phase boundary;

(2) Evaporation at the phase boundary;

(3) Vapor transport from the phase boundary to the pore outlet.

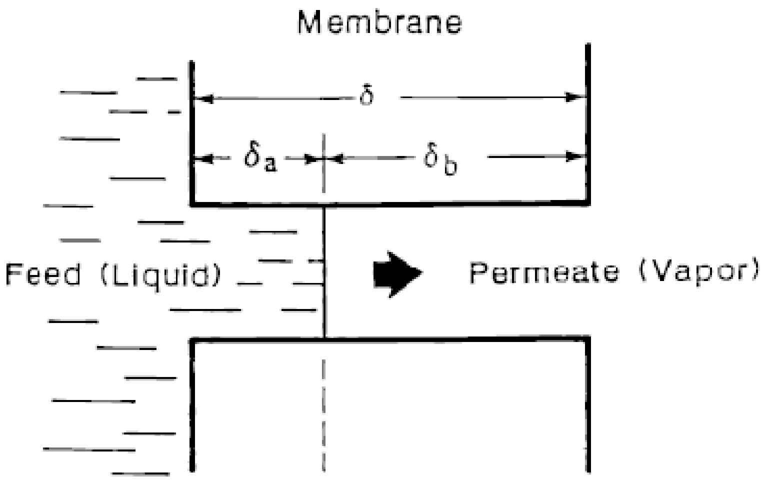


Figure 2. 3 Schematic description of pore-flow model [Feng and Huang, 1997]

This model also assumes that the concentrations of solvents and solute within a membrane are uniform and that the chemical potential gradient across the membrane is expressed only as a pressure gradient, as illustrated in Figure 2.4 [Wijmans and Baker, 1995]. Therefore, combining equation 2.3 and 2.4, the equation for flux can be written as:

$$J_i = -L_i v_i (dp_i/dx) \qquad (2.7)$$

Integrating the equation then gives

$$J_i = -k \cdot \Delta p_i/\delta \qquad (2.8)$$

where *k* is a coefficient, equal to $L_i v_i$, and δ is the thickness of the membrane.

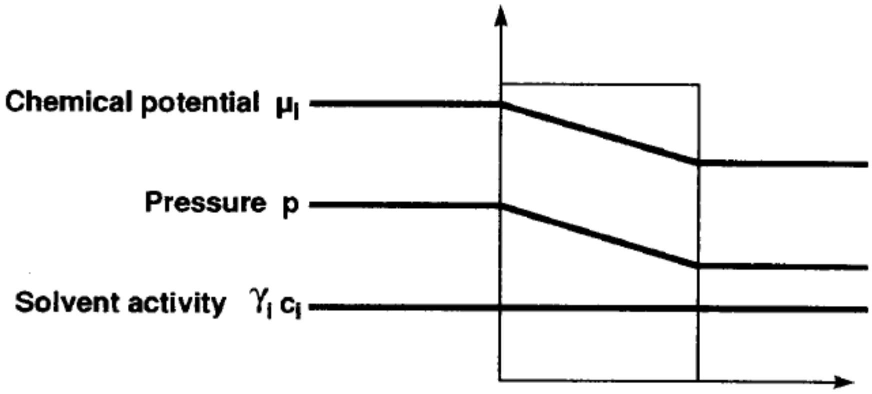


Figure 2.4 Profile of chemical potential and pressure for membrane based on pore-flow model [Wijmans and Baker, 1995]

2.2 Polymeric materials for pervaporation

Almost all polymeric materials can be used as pervaporation membranes. There are three types of polymeric membranes: glassy polymer membranes, rubbery polymer or elastomeric membranes, and ionic polymer membranes. Generally speaking, glassy polymers and ionic polymers are suitable for making water-selective membranes used for solvent dehydration, whereas rubbery polymer membranes are favored for selective removal of organic compounds from water. For the separation of organic-organic mixtures, it is not yet very clear whether glassy or rubbery polymers are more appropriate, and both types of polymers show some pervaporation selectivity.

2.2.1 Classification of pervaporation membranes

In developing pervaporation membranes, three issues should be addressed: the permeation flux, the selectivity and membrane stability. First of all, the permeation flux depends on both the intrinsic permeability and the effective thickness of a membrane. From this point of view, the composite membrane is superior to homogenous membrane used for pervaporation because composite membranes can provide high fluxes due to the much smaller thickness of a homogenous layer supported on a porous substrate. On the other hand, the selectivity is the most important for choosing suitable membrane materials. High selectivity can be achieved by polymer modification such as crosslinking, grafting, blending, copolymerization and incorporation of adsorbent materials. The permeation flux in some cases should yield to selectivity when choosing a membrane if both a high permeate flux and high selectivity can not be obtained at the same time. Furthermore, the membrane stability is affected by the chemical, mechanical and thermal properties of the membrane material. In view of this, composite membranes with a selective layer and a microporous substrate are preferred in developing high performance pervaporation membranes.

The membranes used in pervaporation can be also classified according to the nature of the separation being performed. Hydrophilic membranes are used to remove water from organic solutions. These membranes are typically made of polymers with glass transition temperatures above room temperatures. Poly(vinyl alcohol), poly(acrylic acid), poly(vinyl pyrrolidone), chitosan and polyelectrolytes are examples of hydrophilic membrane materials. Hydrophobic membranes are used to recover organics from aqueous solutions, and they are typically made from elastomer materials. The flexible nature of these polymers makes them ideal for allowing organics to pass through. Polyethylene, polypropylene, poly(vinylidene fluoride), poly(terafluoro ethylene) are typical hydrophobic polymers. Table 2.1 lists some of the commonly used membranes.

Table 2. 1 Widely used pervaporation membrane materials [Baker, 2004]

Dehydration of organics Water/ethanol Water/isopropanol Water/glycol	Microporous polyacrylonitrile coated with 5-20μm layer of cross-linked poly (vinyl alcohol) is the most commonly used commercial material. Chitosan and polyelectrolyte membranes such as Nafion have equivalent properties.
VOC/water separation Toluene/water Trichloroethylene/water Methylene chloride/water	Membranes comprising silicone rubber coated onto polyimide, polyacrylonitrile ot other microporous supports membranes are widely used. Other rubbers such as ethylene-propylene terpolymers have been reported to have good properties. Polyamide-polyether block copolymers have been used for pervaporation of some polar VOCs.
Organic/organic separation	The membranes used depend on the nature of the organics. Poly (vinyl alcohol) and cellulose acetate have been used to separate alcohols from ethers. Polyurethane-polyimide block copolymers have been used fro aromatic/aliphatic separation.

2.2.2 Membrane material selection for pervaporation

As mentioned before, the most important factor that affects the performance of pervaporation is membrane selectivity. Based on the solution-diffusion model, membrane selectivity is determined by the sorption and diffusion selectivities. There are several approaches to membrane material selection, and they are mainly based on empirical observations [Feng and Huang, 1997].

(1) Solubility parameter approach

The solubility parameter is a parameter that expresses the nature and magnitude of the interaction between molecules and can be defined as the square root of cohesive energy densities. When applied to the membrane system, the solubility parameter can give a measurement of the interaction between permeating molecules and the membrane. In other words, the interaction measured by the solubility parameter is uniquely determined by given permeant-membrane systems. It means that when a membrane contacts a solvent, if the solubility parameter difference between the membrane and the solvent is small, the membrane could swell in the solvent. On the other hand, if the solubility parameter difference is large, the membrane could have little interaction with the solvent and no or little swelling will happen. Therefore, the solubility parameter has been one of the most important parameters to determine whether the membrane can swell in the solvent.

(2) Surface thermodynamic approach [Van Oss et al., 1983; Lee et al., 1989]

Two interfacial free-energy parameters ΔF_{123} and ΔF_{132} were designated as the surface free energy between water and membrane in the presence of an organic compound and that between water and organic compound in the presence of the membrane, respectively. If the value of ΔF_{123} is negative, it implies preferential sorption of the organic compound into the membrane. And if ΔF_{132} has a very large value, it means good separation of the organic compound from water in the membrane.

(3) Liquid chromatography (LC) approach [Sourirajan and Matsuura, 1985; Balint et al., 1993]

If a liquid chromatography column is packed with the polymer membrane material and solvent A is used as carrier, the retention time for solvent B in the column can be detected by injecting a small amount of solvent B into LC column. The retention data are a measurement of the interaction between solvent B and the membrane material in the presence of solvent A on a relative scale. Similarly, the interaction between solvent A and the membrane material in the presence of solvent B can also be obtained. For a given separation of A from B, the polymer membrane material can be selected if it exhibits a large difference in the retention times of the two components (A and B). Sourirajan and Matsuura [1985] have used this approach to characterize polymer materials for reverse osmosis and ultrafiltration membranes.

(4) Contact angle approach [Farnand and Noh, 1989]

This approach was intended to measure the contact angle of a compound with the membrane surface in order to give an approximate determination if the membrane could be used to reject or attract this compound. This approach is similar to the surface thermodynamics approach in nature.

(5) Polarity parameter approach [Shimidzu and Yoshikawa, 1991]

Shimidzu and Yoshikawa [1991] found that if the membrane polarity is close to the water polarity, the membrane tends to be water selective and the separation factor tends to decrease as the polarity parameter of the membrane deviates from that of water.

2.3 Polyelectrolyte composite membrane

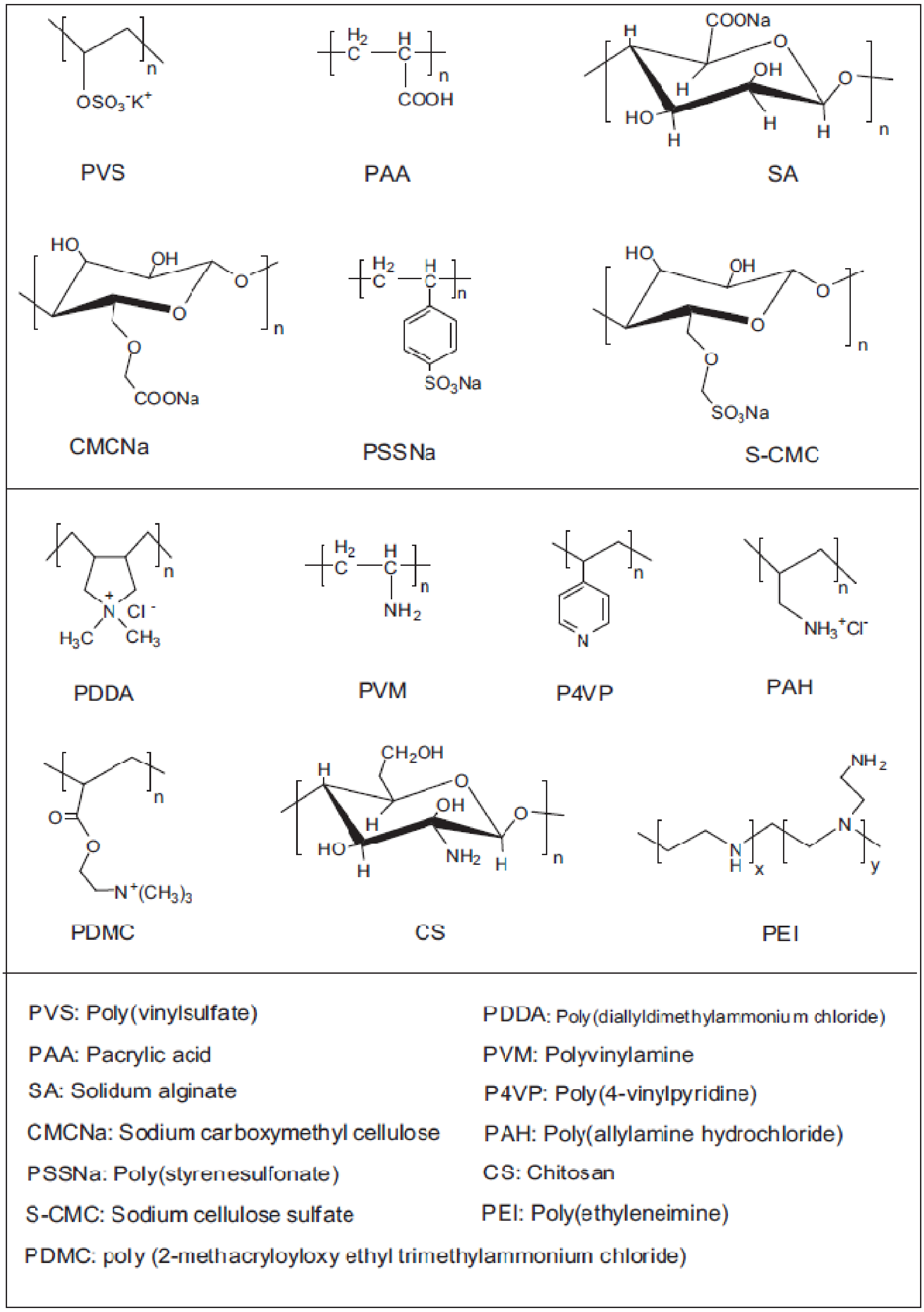
Non-covalent interactions have attracted attention for forming new molecular and supra-molecular architectures with a range of length scales during the past decades. For polymer thin films, electrostatic LbL self-assembly based on non-covalent interactions, which was first introduced by Decher in 1991 [Hammond, 2000; Decher and Hong, 1991], has attracted tremendous interest in recent years because of its versatility and simplicity. It has been applied to numerous areas including flocculation in water treatment [Seki et al., 1984; Kobayashi and Yamadzaki, 1985; Muller et al., 1999], surface modification [Wang et al., 1998; Buchhammer et al., 1994], drug delivery systems [Ito et al., 1992], and tissue engineering [Wang et al., 1997]. Therefore, a good understanding of the structure, technique and mechanism of LbL assembly is important for developing polyelectrolyte based pervaporation membranes, especially for solvent dehydration due to its excellent hydrophilicity.

2.3.1 Polyelectrolyte multilayers

Polyelectrolytes, by definition, are macromolecules which can be dissociated into highly charged polymeric molecules in water or other ionizing solvents. Based on the degree of dissociation in solvents, they can be considered as “strong” or “weak” polyelectrolytes. When a polyelectrolyte is completely dissociated, it can be regarded as a strong polyelectrolyte. On the contrary, if it is only partially dissociated, it is generally considered to be a weak polyelectrolyte. The polyelectrolytes can be also classified into polycation and polyanion depends on what type of charge they have.

Polyelectrolytes are finding lots of applications in health and personal care industry as thickening reagents [Young and Fu, 1991], rheology modifiers [Vaynberg et al., 2001], viscosity enhancers for shampoos, conditioners, deodorants and body lotions [Vandenberg et al., 1989]. They are also used in water treatment, waste treatment, sludge dewatering [Radoiu et al., 2004; Von et al., 1999] and in the pulp and paper industry.

Polyelectrolyte complexation can be formed when one polyelectrolyte interacts with an opposite charged polyelectrolyte. There are many polyelectrolytes with different charges, structures and properties. Figure 2.5 shows the chemical structures of common polyelectrolytes.



PVS: Poly(vinylsulfate)

PAA: Pacrylic acid

SA: Solidum alginate

CMCNa: Sodium carboxymethyl cellulose

PSSNa: Poly(styrenesulfonate)

S-CMC: Sodium cellulose sulfate

PDDA: Poly(diallyldimethylammonium chloride)

PVM: Polyvinylamine

P4VP: Poly(4-vinylpyridine)

PAH: Poly(allylamine hydrochloride)

CS: Chitosan

PEI: Poly(ethyleneimine)

PDMC: poly (2-methacryloyloxy ethyl trimethylammonium chloride)

Figure 2. 5 Chemical structures of common polyelectrolytes and their abbreviations [Zhao et al., 2011]

Combining two or more polyelectrolytes either as a multilayer or as a complex enables one to obtain various materials (of precisely defined properties), which are the same as the polyelectrolytes in terms of physical structure and morphology [Farhat et al., 1999; Saarinen et al., 2008]. Assembly of polyelectrolyte multilayers using opposite charged polyelectrolytes is a versatile method and has received considerable interest due to their widespread applications [Petzold and Lunkwitz, 1995], such as battery separators, fuel cell membranes, electrically conductive coatings, medical and surgical materials, and chemical sensors and detectors. Shieh and Huang [1997] blended chitosan and poly(acrylic acid) to obtain a polyelectrolyte complex homogeneous membrane for dehydration of ethanol by pervaporation, and a permeation flux of 33 g/(m^2·h) and a separation factor of 2,216 were obtained at room temperature for dehydration of 95 wt% ethanol aqueous solutions [Shieh and Huang, 1997].

2.3.2 The mechanism of LbL self-assembly

Sequential LbL self-assembly is a technique for thin film formation using polyelectrolyte complexation, which was first mentioned by Iler [1966]. Decher and Hong [1991] explored the LbL self-assembly as a new approach in materials science and engineering, and since then, this technique has attracted great attention for various potential applications.

It is generally assumed that the driving force for the formation of polyelectrolyte multilayers is the electrostatic attraction between a charged surface and the polyelectrolyte. The LbL self-assembly can be achieved by four simple steps, as shown in Figure 2.6. For the purpose of illustration, let us consider a negatively charged substrate.

Step 1: Polycations will be adsorbed on the negatively charged surface of the substrate due to the electrostatic attraction;

Step 2: Wash the substrate surface with de-ionized water in order to remove excess polycation molecules which are not strongly adsorbed on the surface;

Step 3: Immerse the substrate into a polyanion solution, where the negative charges will be adsorbed onto the surface;

Step 4: Repeat the above steps and a polyelectrolyte multilayer will be formed.

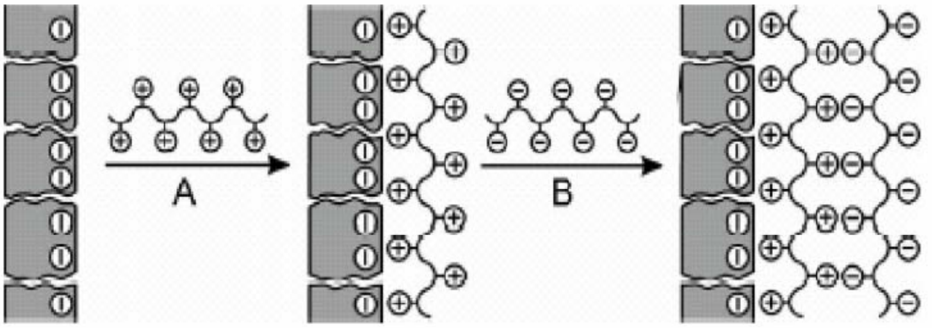


Figure 2.6 Schemetic of LbL assembly [Krasemann et al., 2001]

Therefore, ultra-thin films can be formed using the LbL self-assembly that offers a high flux and selectivity for membrane separation. The number of the layers can be controlled and the multilayers reported in the literature have a thickness that ranges from 10 nm to 10 μm.

Charge overcompensation is important in the formation of polyelectrolyte multilayers. When a negatively charged substrate is in contact with positive charges, the substrate surface will become positive due to the excess positive charges in the cationic polyelectrolyte solution, and this phenomenon is called charge overcompensation. Thanks to the charge overcompensation, subsequent LbL formation can continue. If not, the fabrication process would be stopped [Abbu-Sharkh, 2006; Steitz et al., 2001; Messina, 2004]. Rinsing with water is aiming to remove the weakly bound charged polyelectrolyte molecules so as to prevent their bulk reaction with oppositely charged polyelectrolyte molecules during the adsorption process.

The adsorption of a polyionic layer to a polyelectrolyte multilayer, which is irreversible on the time scale of multilayer assembly, differs from adsorption to rigid, charged surfaces. The adsorption in the LbL self-assembly process consists of two alternate steps: the first is the monolayer adsorption, which is similar to the normal adsorption process, and the other is the multilayer adsorption. For the monolayer adsorption, Joanny et al. [1999] found slight charge overcompensation at a low ionic strength for polyelectrolyte chains. At a high ionic strength, strong charge overcompensation can be provided by loops and tails in the polyelectrolyte. For multilayer formation, Donath et al. [1997] found that (1) each layer deposition is accompanied by charge overcompensation; (2) not only the top layer but also the layers underneath and the surface on the top layer contribute to the particle mobility; (3) the thickness of the top adsorbed hairy layer is in the order of 1nm; (4) about one third of the charged groups of the top layer form ion pairs with the charges in the double layers underneath; (5) Counterion adsorption to the charged groups of the top layer can be observed.

Dubas et al. [1999] addressed the kinetics of multilayer formation, and a two-step process was suggested where the first adsorption occurs in seconds to minutes, followed by a much slower process which takes several hours for chain rearrangements at the surface [Bertrand et al., 2000]. This means that during the fast adsorption step, electrostatic forces dominate because of the transport of chains to the surface by diffusion, and then a slow chain rearrangement occurs, which involves the diffusion of segments into the inner regions of the previously deposited layer [Plech et al., 2000]. Figure 2.7 illustrates the adsorption of polyelectrolyte molecules on a previously deposited layer. First, the polyelectrolyte chains in solution are attracted to the tail and loop segments of the previously deposited layer.

Then, the newly deposited chains gradually flatten to become part of the second layer, extending to the polyelectrolyte solution to form segments with charge overcompensation. Finally, the effect of charge overcompensation is ready to absorb the next charge layer [Abbu-Sharkh, 2006].

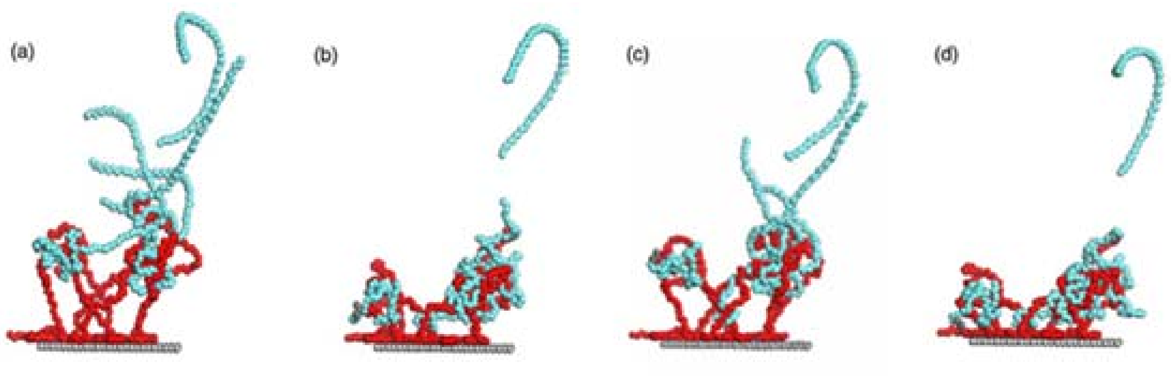


Figure 2.7 Mechanism of adsorption of polyelectrolyte multilayer molecules on a previously deposited layer [Abbu-Sharkh, 2006]

The structure of the multilayer depends not only on the type, charge density and molecular weight of the polyelectrolytes being deposited but also on the processing conditions, for example, ionic strength and the pH of the solution. The type of substrate also influences the structure of the deposited layer; however, its effect is generally limited only to the first three to six layers [Park et al., 2002; Holmes et al., 1996].

2.3.3 Growth of LbL polyelectrolyte multilayer

The growth of polyelectrolyte multilayer is the most crucial step for the LbL self-assembly of composite membranes. The adsorption of the first layer on the charged surface of the substrate is the start of the polyelectrolyte multilayer growth. The layer thickness may change with each deposition step during the multilayer build-up. A linear growth of multilayer thickness with the increase of number of depositions is usually observed for most of multilayer systems [Decher et al., 1992; Sukhorukov et al., 1998; Lvov et al., 1993;

Arys et al., 2001; Lavalle et al., 2002]. However, in some cases, the polyelectrolyte layer growth shows an exponential increase at the first few layers and then follows a linear growth after a number of deposition steps [Caruso et al., 1997]. Seimeiand and Yamada [2000] have studied the growth of the polyelectrolyte multilayers using a quartz crystal microbalance and found that the film thickness was linear for mass-controlled dipping and the accuracy of the layer thickness in the multilayer film was found to be approximately 1nm. Ladam et al. [2000] studied polyelectrolyte multilayers on silica and showed that the structure of the first few deposited layers is influenced by the substrate and that it takes a few layers before a “linear deposition regime” is adopted. Zhao et al. [2010] studied the growth of LbL multilayer films on quartz slide using UV-Vis spectroscopy and the results indicated that the adsorption amount per double layer gradually increased with increasing number of double layers. There are some factors that affect the formation of polyelectrolyte multilayers in the LbL self-assembly process, including molecular weight [Yin et al., 2010; Sui et al., 2003], pH [Kim and Bruening, 2003], and charge density [Steitz et al., 2001]. In addition, the electric field is also found to affect the self-assembly [Zhang et al., 2008; Zhang et al., 2009; Zhang et al., 2008].

There are some studies on the effects of pH and salt on the build-up of polyelectrolyte multilayers during membrane formation. Choi and Rubner [2005] reported that the charge density of a weak polyelectrolyte depends on its local environment. At a low pH, the charge density of a polycation is high and the ionization of a polyanion is restrained. At a high pH, the trend is reversed.

Xie and Granick [2002] reported that polyions inside a multilayer that contains weak polyelectrolytes can adjust their charge density in response to changes of the local environment (e.g., pH and electric field). This can be useful in designing surface sensors for adsorbing ions and polyions.

Wang et al. [2010] demonstrated that post-treatments of weak polyelectrolyte multilayers with salts, acids, and alkali may offer an opportunity for the formation of loose structures and big defects on the multilayers due to conformation changes of the chains. It was also used to improve the stability of the polyelectrolyte multilayer.

Some other factors may also affect the formation of polyelectrolyte multilayers. In the study of Lenk and Meier-Haack [2002], composite membranes for pervaporation of water/alcohol mixtures were prepared by consecutive alternating adsorption of poly(acry1ic acid) and poly(ethylenimine) on a polyamide-6 substrate. The influence of preparation conditions on the pervaporation separation properties of polyelectrolyte multilayer composite membranes was studied. Variation of both polyelectrolyte concentration of the dipping solution and adsorption time had an effect on the membrane performance.

2.4 Aromatic polyamide membrane

To get a high permeation rate without sacrificing selectivity, thin film composite membranes consisting of an interfacially polymerized selective thin layer on the surface of a porous membrane support are usually prepared [Huang et al., 2010]. Interfacially polymerized thin film composite membranes have been used mainly for reverse osmosis [Zhou et al., 2006, Jeong et al., 2007, Chen et al., 2008, Liu et al., 2009] and nanofiltration [Zhang et al., 2003, Mohammad et al., 2005, Li et al., 2006, Buch et al., 2008, Yoon et al., 2009]. Aromatic polyamide membranes derived from *m*-pheylenediamine crosslinked with trimesoyl chloride are now the most dominating thin film composite membranes in commercial reverse osmosis and ultrafiltration applications. These membranes are negatively charged under typical operating conditions (pH >4) because of the presence of carboxyl groups on the membrane surface. Figure 2.8 shows a schematic diagram of the chemical structure of the aromatic polyamide membranes. Although they are prone to fouling by cationic contaminants, they could be a good choice for use as substrates for LbL self-assembled pervaporation membranes because of the following: (1) the thin film composite membrane for reverse osmosis and nanofiltration have smaller pores than the pores on conventionally used microfiltration membrane substrates, and consequently the number of polyelectrolyte multilayer required to achieve adequate selectivity is expected to be less, (2) the negatively charged membrane surface is more suitable for LbL self-assembly fabrication than other uncharged substrates where the hydrolysis step is often needed to make the substrate charged, and (3) the mass transport resistance in the resulting membrane can be mainly determined by the polyelectrolyte multilayer, if the interfacially polymerized substrate is highly permeable. This motivated to use thin film composite polyamide membrane as the substrate for polyelectrolyte LbL deposition to form pervaporation membranes [Xu et al., 2010].

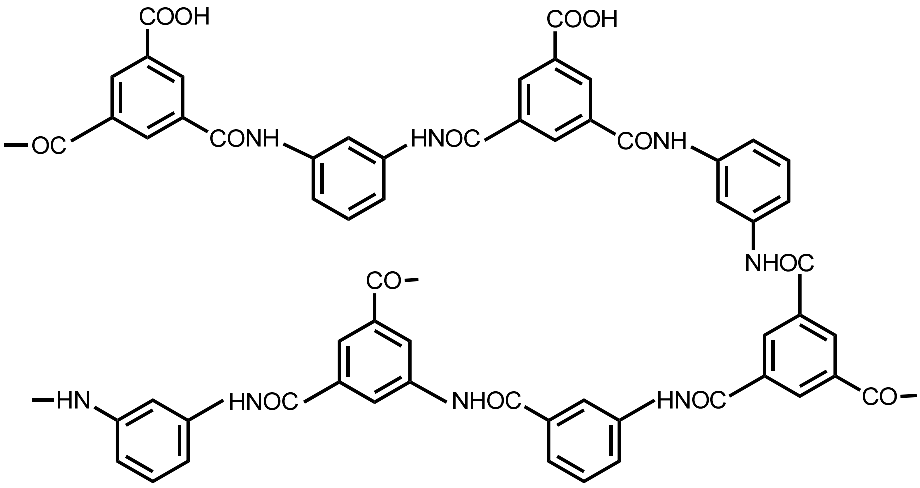


Figure 2.8 Schematic of chemical structure on the surface of aromatic polyamide membrane

2.5 LbL self-assembly membranes for fluid separation

LbL deposition of oppositely charged polyelectrolytes has been proven to be a simple and promising method for membrane fabrication and has received lots of interest for various applications.

Krasemann et al. [1999] used electrostatic deposition onto a porous PAN/PET substrate (a polyethylene terephthalate fleece coated with a thin layer of polyacrylonitrile) and showed that the self-assembled polyelectrolytes separation layer was useful to separate gases, liquid mixtures, and ions in liquid solutions. A poly(4-vinylpyridine)/poly(styrenesulfonate sodium) separation layer was shown to have a high selectivity for CO_2 and N_2 permeation. For the separation of ethanol/water mixtures, the separation factor could reach 80 when a poly(allylamine hydrochloride)/poly(styrenesulfonate sodium) separation layer was annealed at a temperature above 60 ^{o}C. Depending on the polylectrolytes used, the permeation rate of Na^+ could be 15.1 times higher than that of Mg^{2+} in aqueous solutions, which suggested the usefulness of the membranes for ionic separations.

Miller et al. [2004] reported the use of polyelectrolyte multilayers for nanofiltration and dialysis. It was found that because of the thin separation layer, the pure water flux ranged from 1.5 to 3.0 $m^3/(m^2 \cdot day)$ at 4.8 bar. Specifically, to separate sugars, a 42% passage of glucose along with a 98 % rejection of raffinose was obtained, with a pure water flux of 2.4 $m^3/(m^2 \cdot day)$. Poly(styrenesulfonate sodium salt)/poly(diallyldimethyl-ammonium chloride) membranes were found to be capable of separating NaCl and sucrose (selectivity of around 10).

Toutianoush et al. [2002] used polyelectrolyte pairs with a high charge density for separation of alcohol/water mixtures. If a polyvinylamine/ polyvinylsulfate membrane was used for ethanol dehydration, the separation factor could reach 700 at a flux of 0.5 $kg/(m^2 \cdot h)$. The membrane also showed propanol/water and butanol/water selectivities up to 700 and 3,200, respectively.

The LbL self-assembly technique appears to be effective for fabricating polyelectrolyte multilayers. However, Tieke and co-workers [2001] showed that as many as

60 double layers had to be deposited to obtain membranes with sufficient selectivity. This means it is a very time consuming preparation method because one layer will take half an hour to complete. Therefore, it is highly desired to find a suitable procedure to reduce the fabrication time of the polyelectrolyte multilayer.

Zhu et al. [2006] proposed to use a relatively dilute concentration of the polyelectrolytes in the first few cycles of depositions, followed by depositions with more concentrated polyelectrolyte solutions. In addition to the dip coating technique, a single-sided coating process was also proposed to improve the membrane permeability. It was demonstrated that using this technique, a good permselectivity could be achieved with less than 10 cycles of depositions. The membranes showed good performance for separation of water from isopropanol; a permeate concentration of over 99 wt% water was achieved with a permeation flux of about 0.6 kg/($m^2 \cdot h$) at a feed concentration of 90% isopropanol.

Recently, there has been an attempt to develop methods to speed up the multilayer coating process. If the substrate is span while immersed in the polyelectrolyte solution, the mass transport of polyelectrolytes by convection will be accelerated, and the resulting films are expected to be more uniform and smoother [Ji et al., 2008]. Chiarelli et al. [2002] reported spin-assembled multilayers formed by dropping cationic and anionic aqueous solutions onto a spinning substrate. It was claimed that this dynamic technique, to some extent, was better than the traditional method of fabricating multilayers because a good flux could be obtained while keeping the same selectivity by decreasing the number of double layers. Therefore, the dynamic LbL self-assembly deposition is considered to be an effective method to improve the properties of multilayered pervaporation membranes. Zhang et al. [2006] deposited poly(acrylic acid) and polyethylenimine alternatively onto a polyethersulfone ultrafiltration support membrane under a pressure of 0.1 MPa and a relatively high separation factor was obtained with only 4 polyelectrolyte double layers by using the dynamic LbL deposition for isopropanol dehydration. The separation factor and the permeate flux of the polyelectrolyte multilayer membranes were reported to be 1,207 and 140 g/($m^2 \cdot h$), respectively, at a feed temperature of 40 ^oC and concentration of 10 wt% water in the feed.

In the work of Yin et al. [2010], vibrations were employed to enhance the formation of polyelectrolyte multilayers using positively charged poly(diallyldimethylammonium chloride) and negatively charged poly(sodium-p-styrenesulfonate) on a modified polyamide reverse osmosis membrane. The multilayer films built up under vibration exhibited a high selectivity and high permeation flux compared to a membrane prepared under the normal deposition conditions. This was attributed to the polymer chains being deposited orderly, and the films formed being thus dense and smooth under the vibration conditions. Therefore, vibration may be an effective way to improve the performance of multilayer membranes.

Zhang et al. [2008] proposed another method for dynamic multilayer deposition using an electric field to enhance the fabrication of polyelectrolyte multilayer membranes from poly(diallyl dimethylammonium chloride)/poly(styrenesulfonate sodium salt), poly(diallyl dimethylammonium chloride)/poly(acrylic acid sodium salt) and polyethylenimine/poly(acrylic acid sodium salt) on a reverse osmosis membrane. The pervaporation performance of the polyelectrolyte multilayers for separating isopropanol/water mixtures was better than that of membranes prepared under the static self-assembly conditions. With four polyethylenimine/poly(acrylic acid sodium salt) double layers, a separation factor of 1,075 and a permeation flux of 4.05 kg/ ($m^2 \cdot h$) were reported at 70 ^oC.

Table 2. 2 A comparison of polyelectrolyte multilayer membranes by LbL technique [Zhang et al. 2008]

Method	Bilayer Number	Support membrane	Polylectrolyte pair	Feed solution	Temperature (℃)	Separation factor	Permeate Flux (g/(m^{2}h))
Static	60	PAN/PET	PVA/PVS	93.8 wt% ethanol/water	58.5	700	500
Static	60	PAN/PET	PVA/PVS	80 wt% ethanol/water	58.5	1,000	1,500
Static	20	Polyimide	PEI/Alginate	88 wt% isopropanol/water	50	10,000	300
Static	10.5	Alumina Supports	BPDA-DABA/PAH	90 wt% ethanol/water	50	78	1,500
Static	3+7	PAN	PEI/PAA	91.4 wt% isopropanol/water	70	233	989
Dynamic	4	PES	PAA/PEI	95 wt% ethanol/water	40	1,207	140
Dynamic	2.5	PAN	PEI/PAA	95 wt% ethanol/water	70	604	314
Dynamic	2.5	PAN	PEI/PAA	95 wt% isopropanol/water	70	833	338

Table 2.2 shows the performance of membranes formed under static and dynamic conditions. Obviously, using dynamic deposition methods, polyelectrolyte membranes with only 2.5 double layers could achieve reasonable selectivity and flux comparable to those of membranes formed under static depositions with over 10 double layers.

2.6 Stability of polyelectrolyte multilayer membranes

Membrane stability is the ability of a membrane to maintain both the permeability and selectivity under specific operating conditions for an extended period of time. Membrane stability is determined by the chemical, mechanical, and thermal properties of the membrane. When considering polymeric membranes for the separation of organic/organic mixtures, the membrane stability is of prime importance [Feng and Huang, 1997].

It is well known that high degrees of swelling occur in composite membranes [Xu et al., 2003; Matsui and Paul, 2002; Matsui and Paul, 2003]. If the active skin layer and the supporting substrate underneath do not swell in a coordinated manner, a significant stress can be produced at the interface; if the interfacial stress surpasses a “critical point”, which depends on the overall complex interaction between the two neighboring materials, the composite structure could disintegrate, and the membrane would become useless. When polyelectrolyte membranes are in contact with aqueous solutions, membrane swelling may occur because the polymer-polymer intermolecular forces are overcome by strong polymer-solvent interactions which lead to membrane instability in these solvents. However, if the polymer-polymer intermolecular forces are high enough due to crosslinking, crystallinity or strong hydrogen bonding, then membrane swelling will not be significant.

It is well known that water molecules can enter hydrophilic polymer membranes due to their strong affinities, and this generally leads to swelling of the polymer. Similar to water, ethanol and isopropanol are also quite hydrophilic and thus these alcohols may swell polyelectrolyte multilayers as well. As discussed previously, the solubility parameter also could be used to estimate the interaction between a polymer and a solvent. However, the hydrophilicity or hydrophobicity of a membrane is not the only criterion to determine its swelling behaviour in solvents.

Membrane swelling has opposite effects on the membrane performance. While it is favourable for permeability of the membrane, it generally affects the membrane selectivity negatively because membrane swelling makes the polymer chains more flexible, causing large molecules to diffuse through the membrane more easily as well. This lowers the selectivity of the membrane, and sometimes the membrane may become non-selective in pervaporation if excessive swelling of the membrane occurs.

There are some studies on the stability of polyelectrolyte multilayer membranes in different solvents and the membrane performance is shown to change considerably depending on the external conditions. Carrière et al. [2004] showed that the swelling of poly(styrene sulfonate)/ poly(allylamine hydrochloride) films was related to the capping layer. When the capping layer is poly(allylamine hydrochloride), the films swell 25% less than those capped with poly(styrene sulfonate) [Miller et al., 2005]. In addition, Harris and Beuening [2000] reported that the thickness of a membrane with 10 double layers of poly(styrene sulfonate)/ poly(allylamine hydrochloride) increased by 40% if immersed into a pH 6.3 buffer water solution, and the membrane thickness was further increased when soaked in pH 10 buffer water solution due to the swelling of poly(styrene sulfonate)/ poly(allylamine hydrochloride) multilayer [Hiller et al. 2003; Sukhorukov, 1996]. Even worse, Burke and Barrett [2005] found that poly(allylamine hydrochloride)/hyaluronic acid films can reach a degree of swelling as high as 800% in some cases. The degree of swelling of polyelectrolyte multilayers depends on both the solvent and the hydrophilicity of the polyelectrolyte [Miller et al., 2005]. Poptoshev et al. [2004] found that when polyethylenimine/poly(styrene sulfonate)/ poly(allylamine hydrochloride) film was immersed into ethanol solutions, the membrane swelling caused damage in membrane integrity. However, another study showed that there was little difference in the swelling of poly(styrene sulfonate)/ poly(allylamine hydrochloride) films in ethanol and water [Kim et al., 2005].

Several methods have been adopted to improve the structural stability of composite membranes, including the crosslinking of the top layer [Huang et al., 1999; Huang and Yeom, 1990; Yeom and Lee, 1997; Yeom and Lee, 1998 a, b, c; Yeom et al., 1996], the multilayer structure strategy [Huang et al., 1999; Cabasso and Lundy, 1986; Chiou, 1994], and the integrally skinned structure approach [Huang and Feng, 1993]. The crosslinking treatment suppresses the top layer membrane swelling by reducing the mobility of the polymer chains, and therefore a better compatibility between the two “unlike” materials can be achieved. The multilayer approach is to coat the support with one or multiple additional material(s) showing compatibility to both the skin and support materials. Huang et al. [1999]

inserted a slightly crosslinked hydroxylethylcellulose layer between the chitosan top layer and the readily available but relatively hydrophobic polysulfone substrate. The inserted layer was found to serve as a buffer, which bridges the gap in the degrees of swelling of the skin layer and the substrate, and the structural stability of the resulting composite membrane was considerably improved. In the case of the integrally skinned membrane, because the skin layer and the substrate are made of the same material, structural stability is normally not a problem, but unfortunately intergrally skinned membranes can hardly be formed from polyelectrolytes.

Crosslinking is generally used to enhance membrane stability for pervaporation applications. As the polymer chains are restricted, crosslinking often leads to an increased selectivity and a lowered permeation flux. The membrane becomes more compact with an increase in the crosslinking density, and the polymer chains become more rigid. Therefore, the membrane is more discretional to the permeation of penetrant molecules, which favors the selectivity of the membrane, while permeability is compromised [Huang et al., 1999]. Depending on the polymers, many crosslinking agents may be used, including glutaraldehyde [Uragami et al., 1994; Suto and Ui, 1994; Goto et al., 1994], sulfuric acid [Ren and Jiang, 1998; Lee et al., 1997], sulfosuccinic acid [Rhim and Kim, 2000] and trimesoyl chloride [Xiao et al., 2007].

Sullivan and Bruening [2005] suggested that incorporation of additional carboxylic acid groups in poly(amic acid) to crosslink the amines of a polycation was an effective method to improve the membrane performance for pervaporation separation and a reasonably high flux together with a high selectivity could be achieved.

Nawawi and Huang [1997] reported that using hexamethylene diisocyanate to crosslink chitosan membranes improved the permselectivity of the membranes. The separation factor increased and the total permeation flux decreased with an increase in the crosslinking time. At 30 ^oC, the separation factor increased to 1,964, while the total permeation flux decreased to 82 g/($m^2 \cdot h$) for the pervaporation of 95 wt% isopropanol feed solution when a homogeneous chitosan membrane was crosslinked for 24 h.

Finally, Hilmioglu et al. [2001] modified poly(vinyl alcohol) with two different crosslinking agents (glutaraldehyde and formaldehyde) for dehydration of acetic acid. The membrane that crosslinked with glutaraldehyde had a higher selectivity and a lower permeation flux. For both membranes, the chemical crosslinking reaction effectively increased the membrane selectivity, and the swelling of the membrane decreased with an increase in the degree of crosslinking.

Chapter 3

Studies of PEI/PAA LbL self-assembly on interfacially polymerized polyamide membrane for ethylene glycol dehydration

3.1 Introduction

Ethylene glycol has broad applications. It is widely used as a coolant and antifreeze due to its low freezing point, and this also makes it an important component of vitrification mixtures for low temperature preservation of biological tissues and organs. It has also become increasingly important in the plastics industry for the manufacture of polyester, fibers and resins. The characteristics of high boiling point (197 ^{o}C) and good affinity to water also make it an ideal dehydrator for natural gas production, where water vapor is removed by glycol and the glycol/water mixtures are separated by multi-stage evaporation distillation [Du et al., 2008; Bravo et al., 1986]. The thermal process for glycol dehydration is energy intensive because of the high boiling point. Therefore, pervaporation is considered to be a favorable alternative technology for ethylene glycol/water separation. Du et al. [2008] prepared poly(N,N-dithehylaminoethylmethacrylate)/polysulfone composite membranes for ethylene glycol dehydration and a permeation flux of 1 mol/(m^2·h) and a permeate water concentration of 99.7 mol% were achieved at 1 mol% feed water concentration. Nam and Lee [1999] studied an ionically surface-crosslinked chitosan composite membrane for ethylene glycol dehydration, and at 80 ^{o}C and 80 wt% feed ethylene glycol concentration, a permeate flux of 1.13 kg/(m^2·h) and water concentration of permeate greater than 99.5 wt% were achieved.

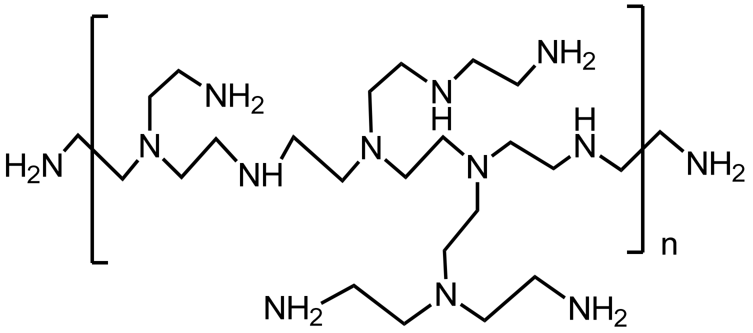
In this chapter, the LbL self-assembly technique was used to modify the aromatic polyamide substrate and the modified membranes were used for ethylene glycol dehydration. The effects of the number of polyelectrolyte double layers, feed water concentration and operating temperature on the separation performance were investigated. In addition, the reproducibility and long term stability of the polyelectrolyte multilayer membranes were also investigated.

3.2 Experimental

3.2.1 Materials

The polyamide membrane was produced by interfacial polymerization of *m*-phenylenediamine and trimesoyl chloride on a microporous polysulfone support reinforced by a nonwoven fabric. It was supplied by the Development Center of Water Treatment Technology (Hangzhou, China) as a commercial membrane for nanofiltration and low-pressure reverse osmosis. The original polyamide membrane exhibited a permeation flux of 50.3 L/(m^2·h) and a salt rejection of 91.0% for a feed solution containing 1500 mg/L NaCl at 0.8 MPa [Xu et al., 2011]. This membrane was used as the substrate for fabricating multilayered polyelectrolyte membranes. PEI (Mw 750,000, in a 50 wt% aqueous solution) and PAA (Mw 250,000, in a 35 wt% aqueous solution) were supplied from Sigma-Aldrich. Ethylene glycol, isopropanol and ethanol were all purchased from Fisher Scientific, and their aqueous solutions used as feeds in pervaporation experiments were prepared by blending with de-ionized water at pre-determined concentrations. De-ionized water was used as the solvent to prepare the polyelectrolyte solutions and for membrane rinsing during self-assembly of the polyelectrolytes. Figure 3.1 shows the chemical structures of the polyelectrolytes used in this study.

PEI:



PAA:

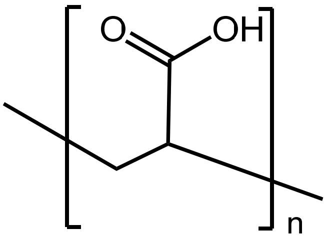


Figure 3. 1 Chemical structures of polyethyleminine and poly(acrylic aicd)

3.2.2 Membrane preparation

The polyamide substrate was soaked in de-ionized water overnight, followed by thorough rinsing to remove any preservatives. Because of its negatively charged surface, in preparing the polyelectrolyte multilayer membrane by LbL self-assembly, the substrate surface was allowed to contact a cationic polyelectrolyte solution for 30 min, and then rinsed thoroughly with de-ionized water for 10 min. This was followed by the same procedure for the deposition of an anionic polyelectrolyte to form one self-assembled bilayer or double layer from a pair of the polyelectrolytes with opposite charges. These steps were repeated to form multiple polyelectrolyte bilayers. Caution was exercised to ensure that any excess polyelectrolyte on the membrane surface during a deposition step was fully washed away prior to subsequent deposition of the oppositely charged polyelectrolyte. Note that polyelectrolyte depositions were carried out in a double-sided surface deposition fashion as a preliminary stage. The concentrations of polyelectrolyte solutions used during membrane fabrication were 0.02 monomol/L (monomol=mole of a monomer unit) for both PEI and PAA.

3.2.3 Pervaporation

The pervaporation setup consisted of a feed tank, a circulation pump, a vacuum pump and a permeation cell, as shown schematically in Figure 3.2. The permeation cell was made of stainless steel and had an effective membrane area of 16.6 cm^2. The membrane was mounted in the permeation cell so that the active surface of the membrane was faced with the feed solution. The liquid feed at a controlled temperature was admitted to the permeation cell, and the residue stream was pumped back to the feed tank, while vacuum (ca. 5 mmHg absolute) was applied to the permeate side. The permeate vapor was condensed and collected in a cold trap immersed in liquid nitrogen. To analyze the compositions of the feed and permeate, a Hewlett-Packard gas chromatograph (HP 5890 series II) equipped with a thermal conductivity detector and a packed column Porapak Q was used. The GC configuration and conditions are: oven temperature: 190 ℃, injector and detector temperature: 220 ℃. The pervaporation experiments focused on a feed water concentration of less than 25 wt%, which was the concentration range of industrial interest.

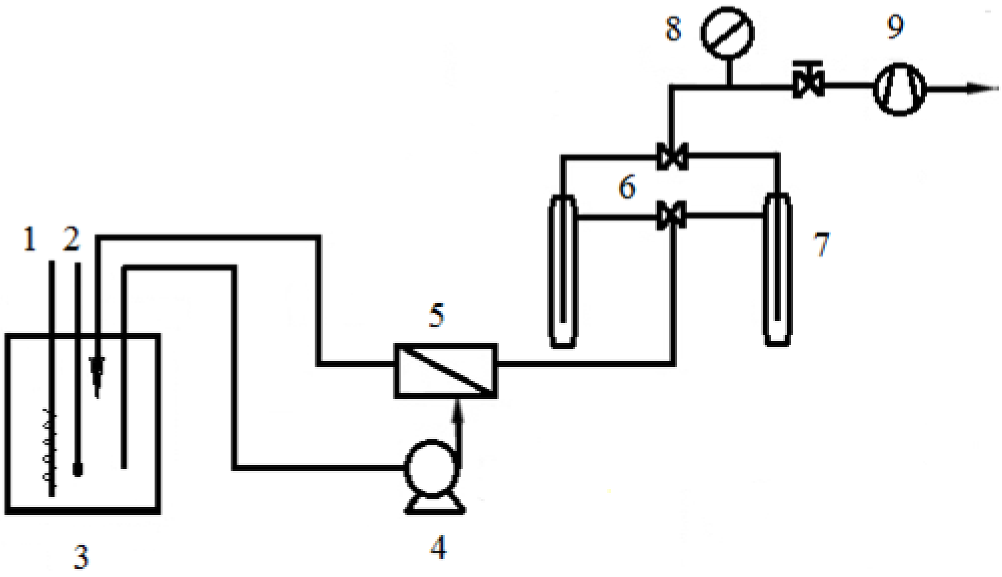


Figure 3. 2 Schematic diagram of pervaporation setup.

(1) Thermometer, (2) Heater, (3) Feed tank, (4) Circulation pump, (5) Permeation Cell, (6) Switch valves, (7) Cold Trap, (8) Vacuum gauge (9) Vaccum pump.

3.3 Result and discussion

3.3.1 Effects of number of polyelectrolyte double layers

To study the effect of the number of polyelectrolyte double layers on the performance of the membranes, membranes with different numbers of double layers were prepared and tested for ethylene glycol pervaporation at 25 ^{o}C at feed water contents of 5.5 and 10.6 wt%. As shown in Figure 3.3, with an increase in the number of double layers, the total permeation flux decreased, while the water concentration in the permeate increased. For instance, the total permeation flux decreased dramatically from 0.085 to 0.01 kg/ ($m^2 \cdot h$) and permeate water concentrations increased from 94.12 to 98.05 wt%, at a feed water concentration of 10.6 wt%. As the number of double layers increases, the effective thickness of the membrane increases. According to the solution-diffusion model for mass transfer in pervaporation, the fact that the membrane preferentially favors the permeating components is due to the differences of both solubility through the membrane and the sorption onto the membrane [Xu et al., 2010]. Therefore, the diffusion path for the permeant molecules to pass through the membrane also increases. On the other hand, the polyelectrolyte/polyamide composite membrane becomes more hydrophilic due to deposition of polyelectrolyte multilayers and consequently water molecules are adsorbed onto the surface of the membrane more easily, which leads to an increase in water concentration in the permeate. Note that the concentration of water in the permeate could reach more than 90% with only 3 double layers. However, adding 2 more double layers did not significantly increase the membrane selectivity. This is presumably due to the defects and pores on the membranes which need to be filled at the first few double layers. A significant increase in the selectivity was observed when the membrane contained more than 5 double layers. Therefore, it appeared that 3 double layers of the polyelectrolytes would be sufficient to cause a significant change in the performance of the composite membrane for ethylene glycol dehydration.

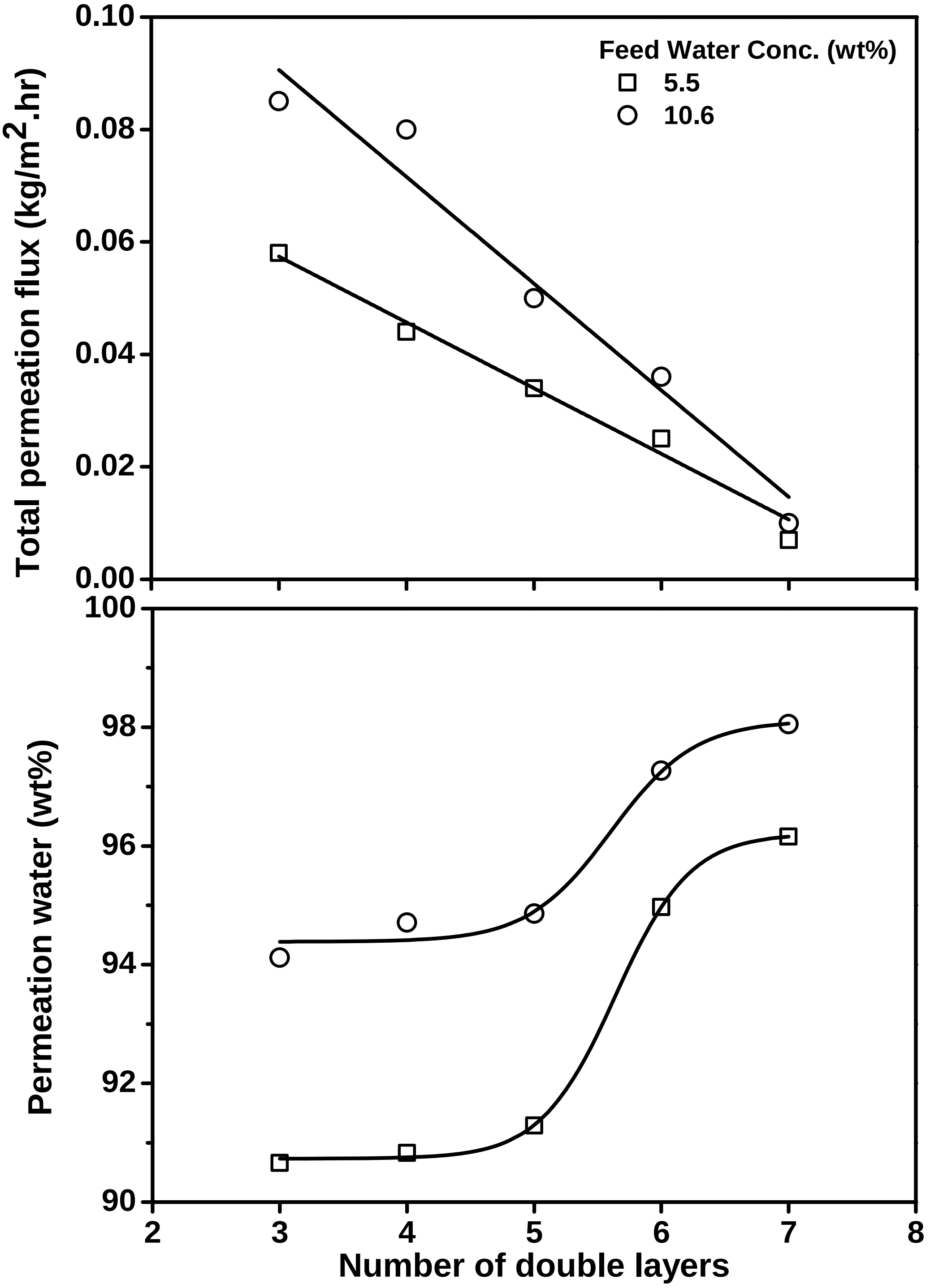


Figure 3. 3 Total permeation flux and permeate water concentration for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 °C.

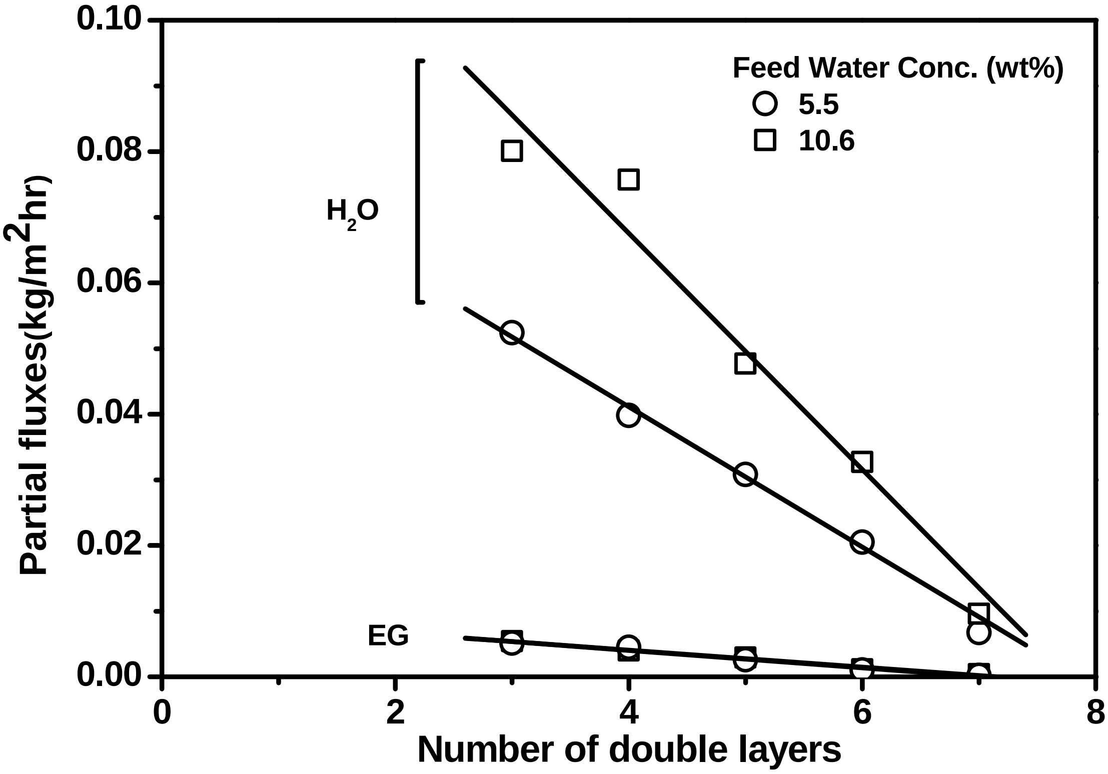


Figure 3. 4 Partial permeation flux for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 °C.

Figure 3.4 shows the effect of the number of double layers on the partial fluxes of water and ethylene glycol. The results showed a similar trend as the total permeation flux. However, the partial flux of ethylene glycol remained almost constant when the feed water concentration changed from 5.5 to 10.6 wt%. This is believed to be due to the larger molecular size of ethylne glycol. As expected, the separation factor, shown in Figure 3.5, increased with an increase in the number of double layers. Water molecules are more permeable than ethylene glycol due to the use of a hydrophilic substrate and the polyelectrolyte in the membrane.

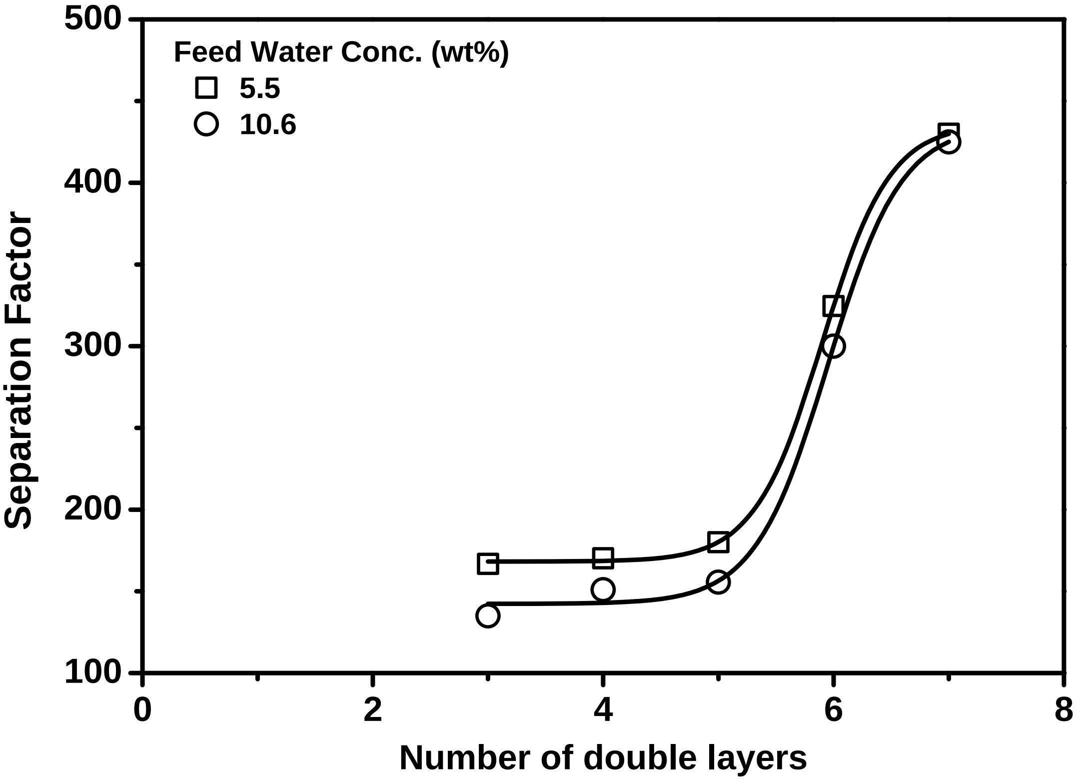


Figure 3. 5 Separation factor for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 ^oC.

Note that the substrate used in this work is a commercial membrane intended for use in nanofiltration, and it is too microporous for direct use in pervaporation. Surface coating with only one or two double layers of polyelectrolyte was found to be not sufficient to fill or plug the big pores in order to achieve a high selectivity. Therefore, all subsequent experiments were performed with at least 3 polyelectrolyte double layers.

3.3.2 Effects of feed concentration

In order to investigate the effects of feed concentration on the performance of the polyelectrolyte/polyamide composite membranes, pervaporation tests were carried out at room temperature while the feed concentration was varied from 2 to 20 wt%. Note that a feed water concentration of less than 25 wt% of water was used in the tests because this is the concentration range of industrial interest.

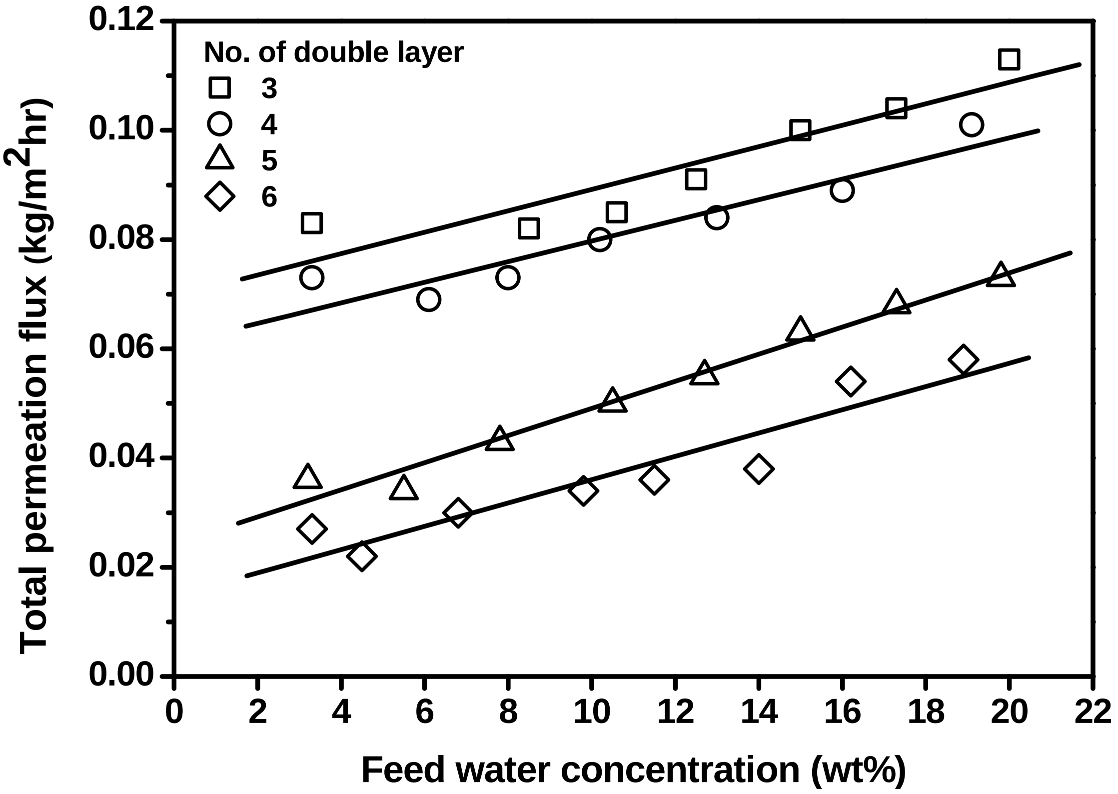


Figure 3. 6 Total permeation flux for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 °C

Figure 3.6 shows that the total permeation flux increases with an increase in water concentration in the feed and follows approximately a linear relationship. The membrane with 5 double layers exhibited a flux of 0.037 and 0.074 kg/(m^2·h), respectively, at feed water concentrations of 3 and 20 wt%. Figure 3.7 shows the partial permeation flux of water, which has a similar trend as the total permeation flux, because of the substantially low permeation flux of ethylene glycol. As the water concentration in the feed increases, more water molecules will be sorbed in the hydrophilic polyelectrolyte separating layer, resulting in an increase in the water permeation rate. Figure 3.8 shows the effect of feed water concentration on ethylene glycol permeation flux. With an increase in the water concentration in the feed, the permeation flux of ethylene glycol tends to decrease. At a feed water concentration of 3 and 20 wt%, the permeation fluxes of ethylene glycol are 0.004 and 0.002 kg/(m^2 · h), respectively, for the membrane with 5 double layers. By comparing the data above, it can be concluded that the total permeation flux was mainly determined by the water permeation flux. Another reason for the high permeation flux of water is that water molecules are smaller than ethylene glycol molecules, and thus water molecules are easier to diffuse through the membranes.

Generally speaking, an increase in permeation flux is often accompanied with a reduction in selectivity. Figure 3.9 shows this is indeed the case as the separation factor tends to decrease with an increase in the feed water concentration. It can be seen that below 5 double layers, the selectivity of the membrane does not change considerably when additional double layers are incorporated in the membrane. 5 double layers appear to be just enough to fill in the defects in the membrane to make it permselective for the separation of the ethylene glycol/water mixtures.

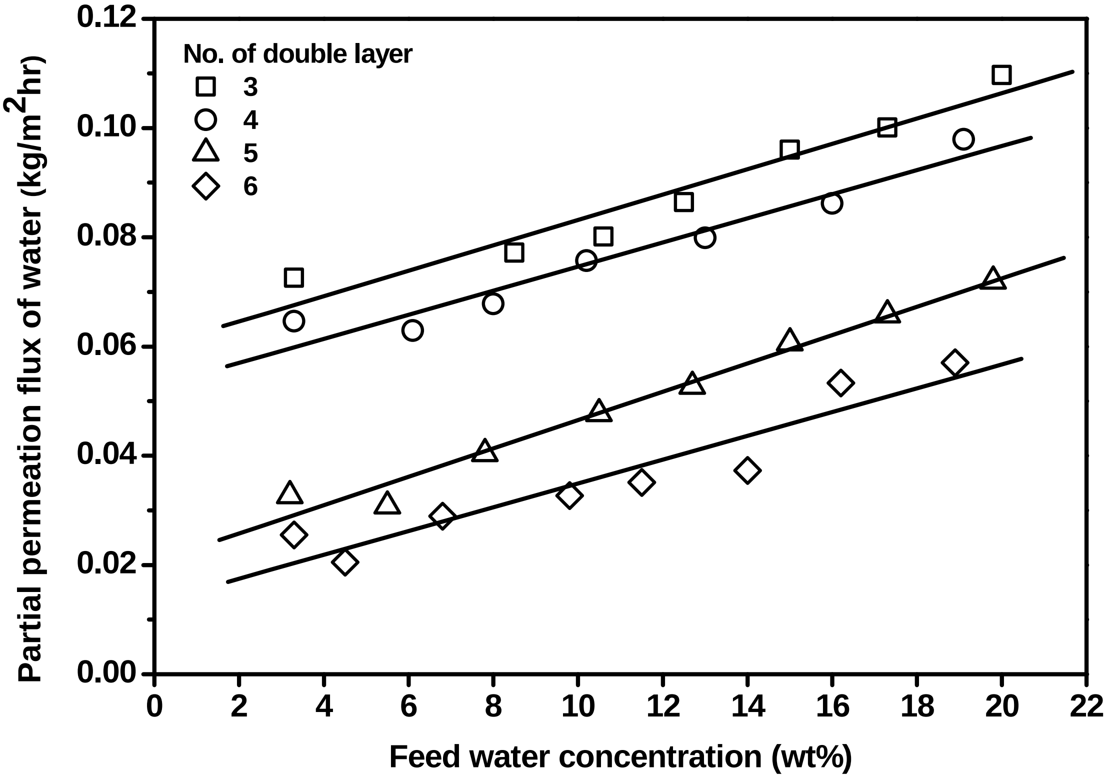


Figure 3. 7 Partial permeation flux of water for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 °C.

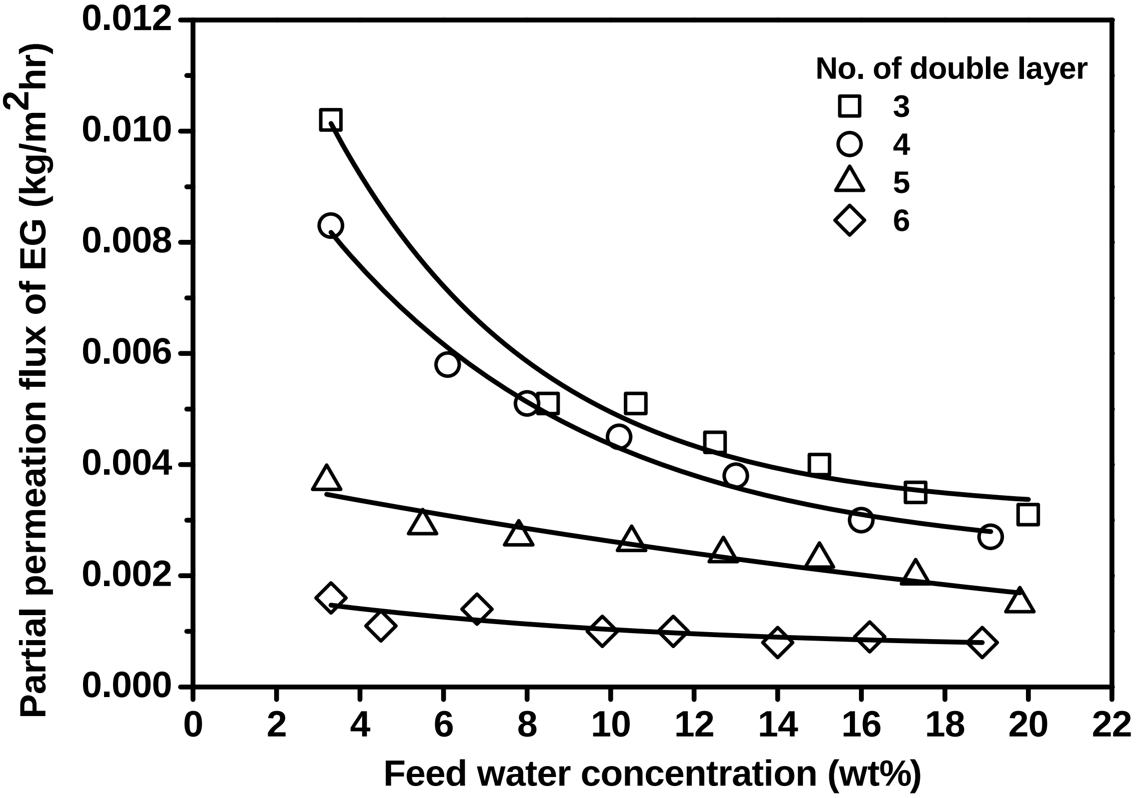


Figure 3. 8 Partial permeation flux of ethylene glycol for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 ^{o}C.

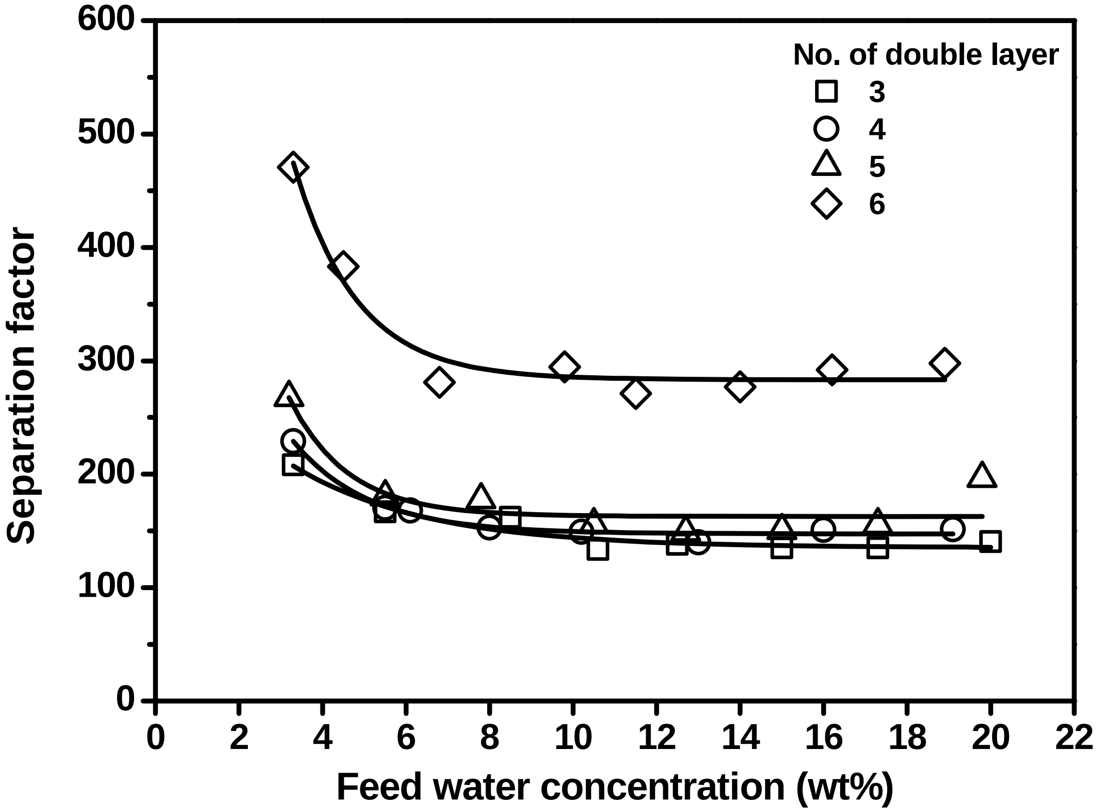


Figure 3. 9 Separation factor for separation of ethylene glycol/water. Operating temperature of pervaporation, 25 ^{o}C.

3.3.3 Effects of feed temperature

The operating temperature is an important factor because it has direct impact on the solubility and permeability of the permeating species in the membrane. To evaluate the effect of feed temperature on the pervaporation performance, membranes with 5 double layers were chosen in the pervaporation experiments at various temperatures: 30, 40, 50, 60 and 70 ^{o}C for given feed concentrations.

According to the solution-diffusion model, the membrane permeability is determined by the solubility and diffusivity of the permeant in the membranes. As the feed temperature increases, the permeating molecules are more energetic and the polymer chain movement is intensified in terms of frequency and amplitude, resulting in a higher diffusivity in the membrane. On the other hand, sorption is generally an exothermic process, which means the solubility is reduced with an increase in temperature. Because of the above two opposite effects, if the increase in diffusivity is more than the decrease in solubility, the permeability will increase when increasing the temperature.

The total and partial permeation fluxes are found to increase with temperature, as shown in Figures 3.10 and 3.11, which exhibit a linear relationship between log of flux and reciprocal temperature. That is, the temperature dependence of permeation flux follows an Arrhenius-type relationship.

At a feed concentration of 13.2 wt% water, the partial flux of ethylene glycol varied from 0.002 to 0.007 kg/(m^2·h), while the partial water flux varied from 0.045 to 0.07 kg/(m^2·h) when the temperature increased from 30 to 70 ^{o}C. Increasing temperature also increases vapor pressure, resulting in a greater driving force for permeation [Reineke et al., 1987]. The separation factor, on the other hand, decreases with an increase in feed temperature, as shown in Figure 3.12. An increase in temperature will increase the diffusivity of both water and ethylene glycol molecules. The positive dependence of temperature appears to suggest that the increased diffusivity is sufficient to compensate for the decreased solubility. However, water permeation flux is increased less significantly than the glycol flux, resulting in an overall decrease in the membrane selectivity as temperature increases.

Furthermore, the temperature-dependencies of both the flux and the permeance follow the Arrhenius relationship. If one considers the 5 wt% feed water, for example, from the slope in Figure 3.10, the apparent activation energies for the permeation of ethylene glycol and water are 37.34 and 13.04 kJ/mol, respectively. However, as shown in Figure 3.13, the activation energy of permeation based on permence is shown to be negative, which means that the increase in diffusion is not enough to outweigh the decrease in solubility, resulting in a decrease in overall permeability.

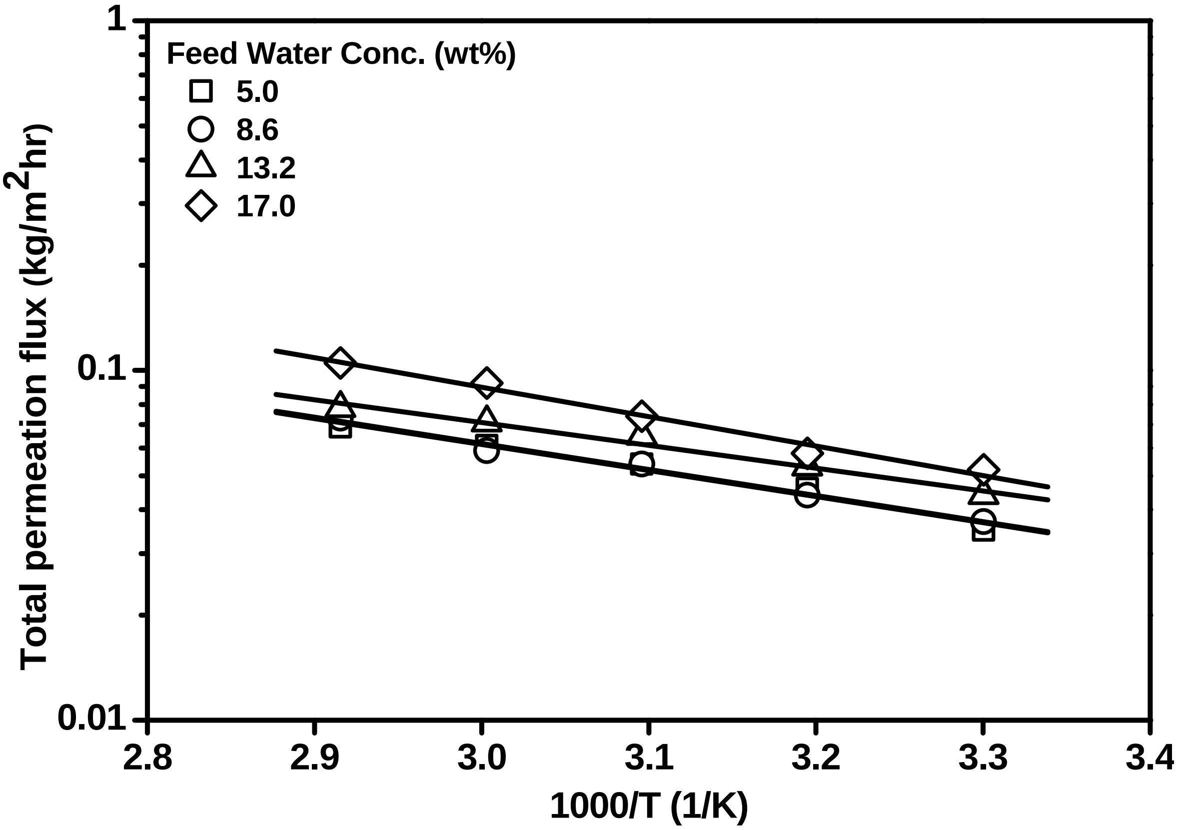


Figure 3. 10 Total permeation flux for separation of ethylene glycol/water with membranes comprising of 5 double layers.

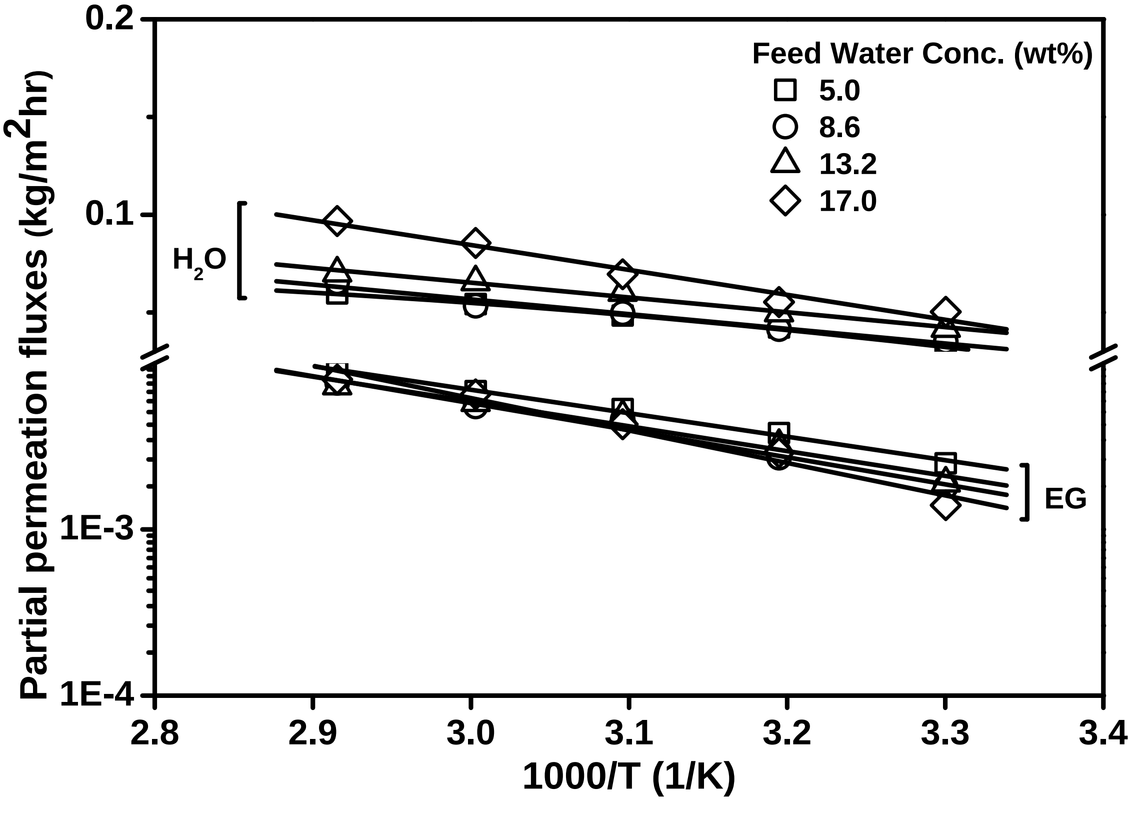


Figure 3. 11 Partial permeation flux for separation of ethylene glycol/water with membranes comprising of 5 double layers.

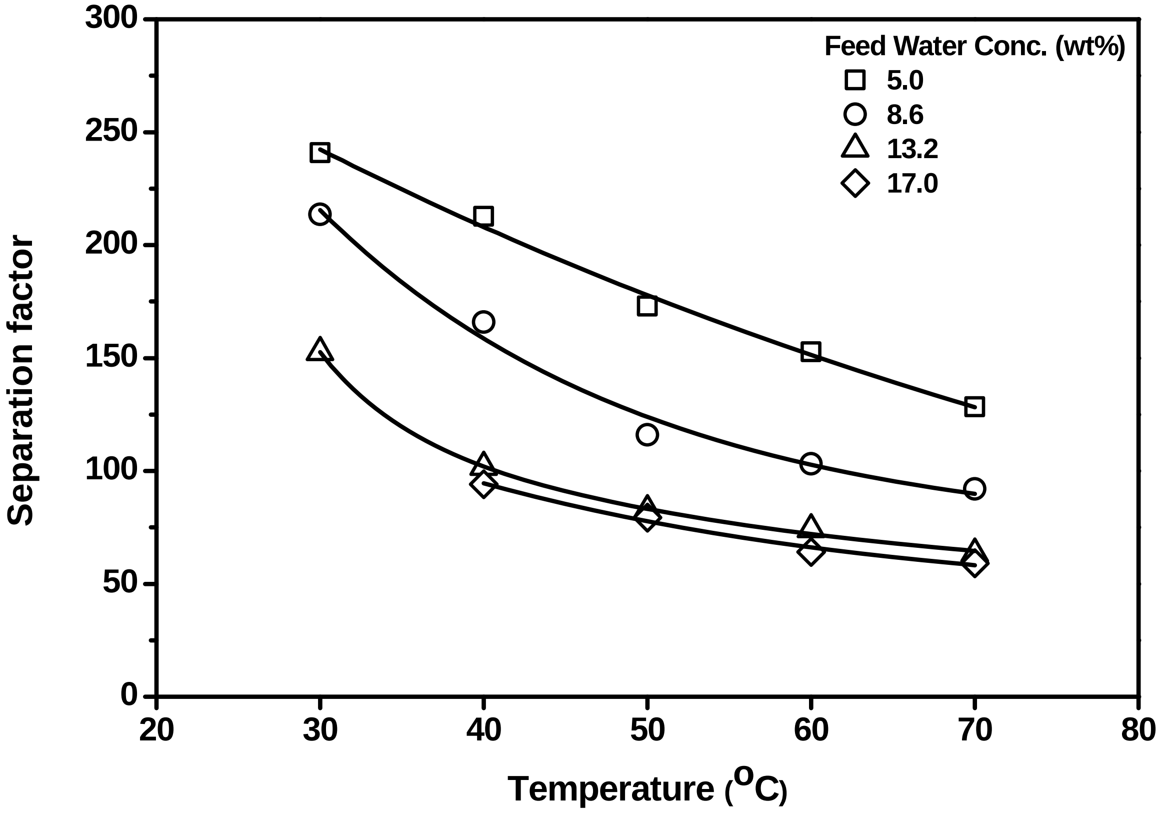


Figure 3. 12 Separation factor for separation of ethylene glycol/water with membranes comprising of 5 double layers.

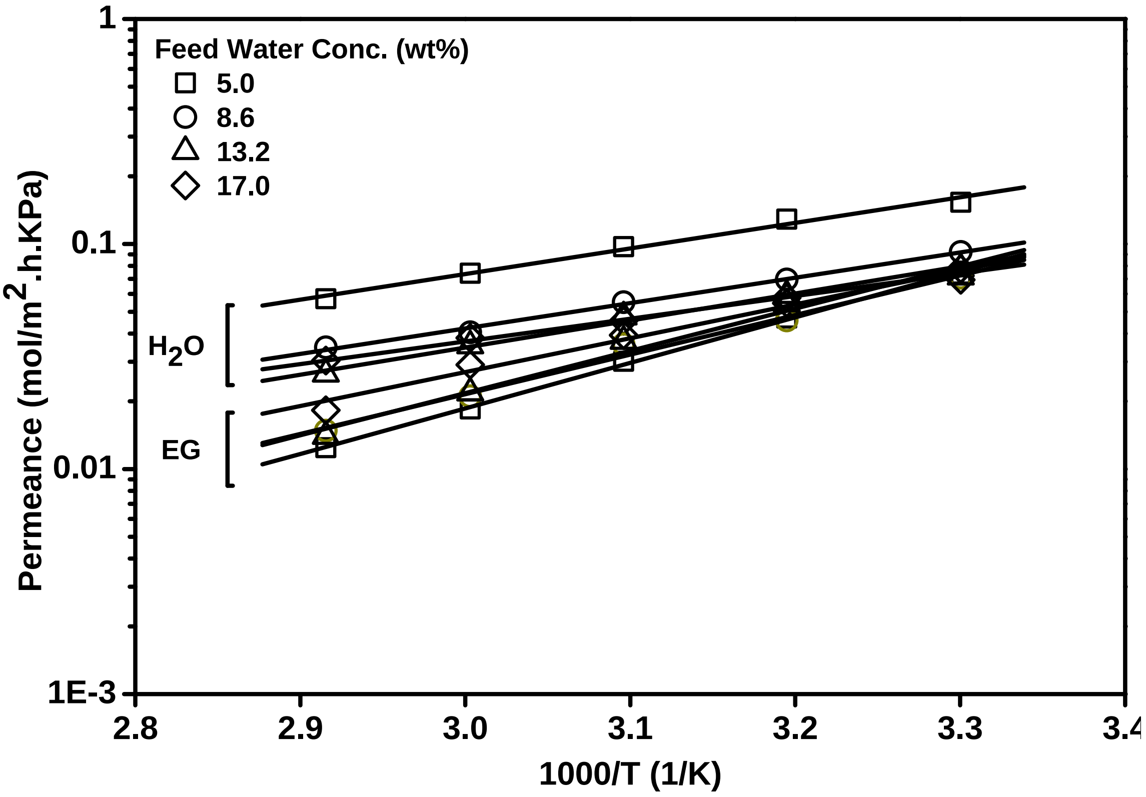


Figure 3. 13 Permeance for separation of ethylene glycol/water with membranes comprising of 5 double layers.

3.3.4 Reproducibility and long term stability of the membrane

The reproducibility and stability of the membrane are essential to practical applications. In this section, the dehydration performance of the membranes will be studied and compared to investigate the reproducibility and stability of the membranes. It can be seen in Figure 3.14 that the different composite membranes prepared separately but under the same conditions showed small variances in the permeation flux, especially at low water concentrations in the feed. The maximum error can be calculated for the total flux of permeation to be 10.9% for three membrane samples of 5 double layers of polyelectrolytes. When a porous substrate is used for the construction of a polyelectrolyte separating layer form a composite membrane, the polyelectrolyte molecules may partially enter the pores on the substrate which makes it difficult to clearly define the effective thickness of the membrane. Consequently, the flux and the selectivity of the composite membrane obtained would vary from one membrane to another. For 3 double layers of polyelectrolyte membranes, also as shown in Figure 3.14, the largest deviation can be 13.5%. The reproducibility is getting better with a large number of polyelectrolyte double layers due to the self-repairing function of the polyelectrolyte multilayers.

To test the long term stability of the membrane, a prvaporation run was carried out continuously with the membrane containing 5 double layers for 15 days and the results are shown in Figure 3.15. It can be seen that there were no obvious changes both in permeation flux and permeate water concentration over the test period. It indicates that the polyaide/poyelectrolyte membrane shows good long term stability.

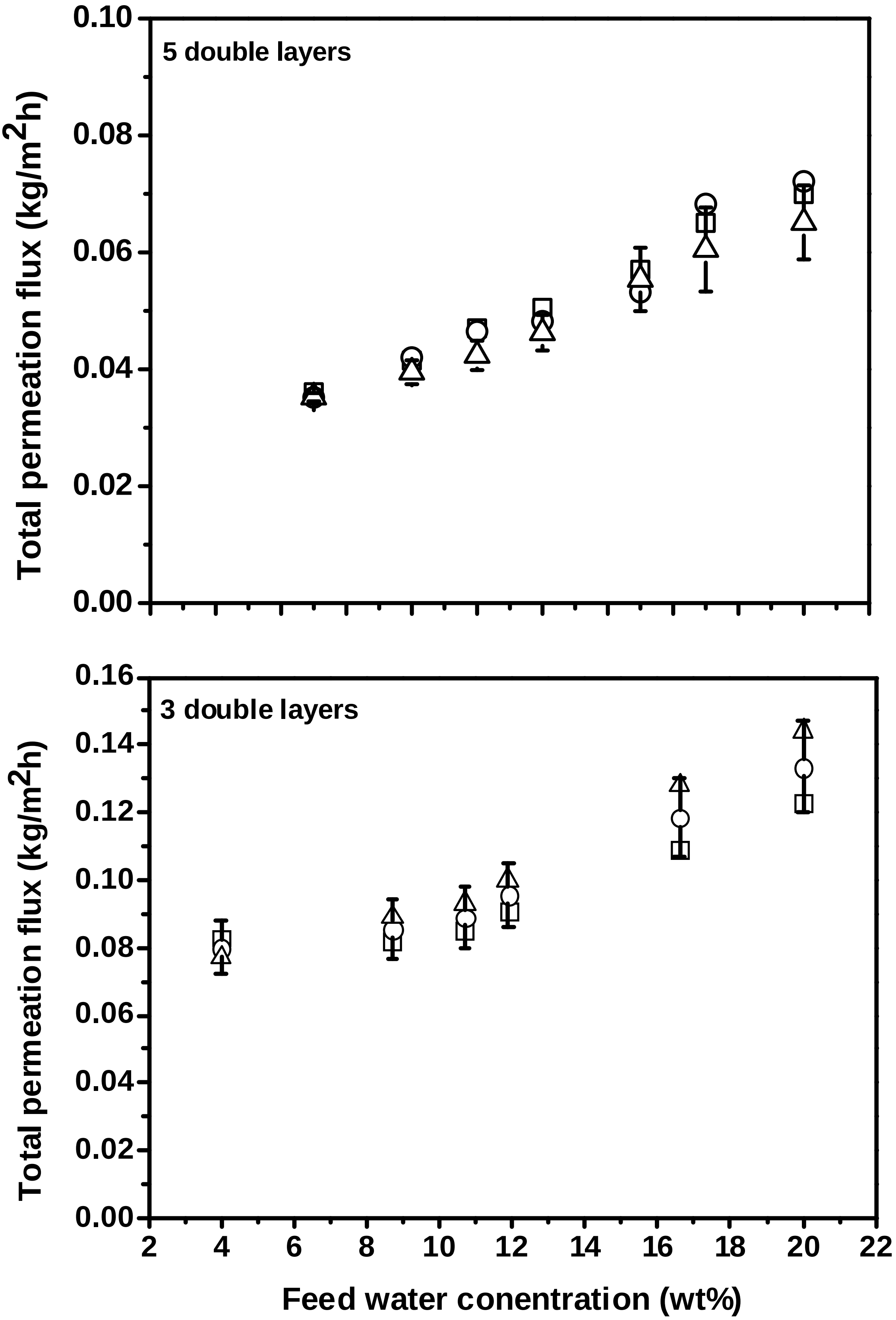


Figure 3. 14 The reproducibility of the separation performance of 3 and 5 double layers composite membranes. Operating temperature of pervaporation, 25 °C.

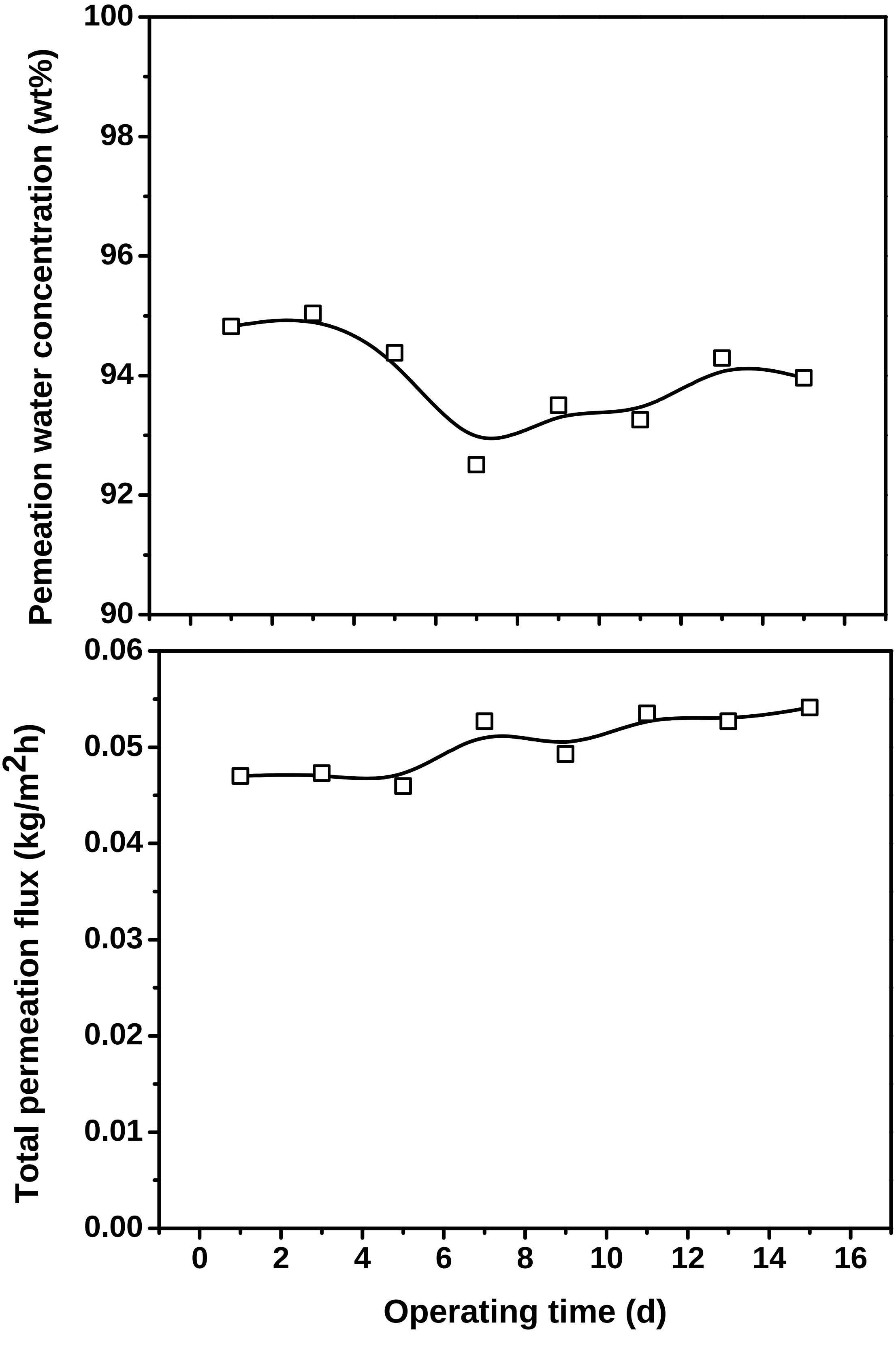


Figure 3. 15 Membrane stability for continuous pervaporation, (a) Permeate water concentration, and (b) permeation flux. 5 double layers; feed water concentration, 10.6 wt%; operating temperature of pervaporation, 25 °C.

3.4 Conclusions

In this chapter, PEI and PAA were used to fabricate LbL self-assembly polyelectrolyte/polyamide composite membranes for ethylene glycol dehydration. The following conclusions can be drawn:

(1) 3 double layers of polyelectrolytes appeared to be sufficient for pervaporative separation of ethylene glycol/water, and the permeation flux and separation factor could reach 0.085 kg/(m^2·h) and 140, respectively. By increasing the number of polyelectrolyte double layers, the permeation flux decreased while the selectivity increased.

(2) The feed water concentration affects the membrane performance of pervaporation significantly. In the range of the feed water concentrations (0~20 wt%) that are of the industrial interest, increasing feed water concentration will lead to an increase in the permeation flux.

(3) Temperature played an important role in the pervaporation separation. An increase in temperature would increase permeation flux, and decrease the separation factor. The temperature dependence of permeation flux followed an Arrhenius relationship.

(4) The reproducibility of the membrane performance was evaluated. 5 double layered composite membranes showed better reproducibility than 3 double layered membranes due to the self-repairing function of polyelectrolyte multilayer.

(5) The polyamidepolyelectrolyte composite membrane showed good long term stability for continuous pervaporation.

Chapter 4

Formation of polyelectrolyte multilayers monitored by UV-Vis spectrophotometer

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4.1 Introduction

Formation of polyelectrolyte multilayers is the basic step of LbL self-assembly of composite membranes. As mentioned in Chapter 2, the growth of polyelectrolyte multilayers by LbL self-assembly is affected by such factors as molecular weight [Yin et al., 2010; Sui et al., 2003], pH [Kim and Bruening, 2003], charge density [Steitz et al., 2001], and electric field [Zhang et al.,2008; Zhang et al., 2009; Zhang et al., 2008]. However, there are not many studies available on other factors such as concentration of polyelectrolyte deposition solutions, deposition time and deposition temperature, all of which can directly affect the adsorption process and hence the overall membrane performance.

In this chapter, the LbL self-assembly technique was used to prepare polyelectrolyte multilayers on an aromatic polyamide substrate, and the formation of polyelectrolyte multilayers was monitored by UV-Vis spectrophotometer. The effects of the concentration of polyelectrolyte deposition solutions, deposition time, and deposition temperature were considered both on the formation of polyelectrolyte multilayers and the performance of ethylene glycol dehydration. In addition, the effects of the sequence of the polyelectrolyte pairs during LbL assembly were studied as well in order to better understand the factors involved in the self-assembly process. This will help establish a correlation between membrane performance and the composite/layered structure of the membrane.

4.2 Experimental

4.2.1 Membrane prepation

The materials (i.e., polyamide substrate membrane and the polyelectolytes) and the procedure used for fabricating polyelectrolyte/polyamide composite membranes were the same as mentioned in chapter 3. Note that single-sided deposition was used for the LbL self-assembly to form polyelectrolyte/polyamide membranes and unless specified otherwise all polyelectrolyte/polyamide membranes used for pervaporation tests consisted of 5 polyelectrolyte double layers.

4.2.2 LbL growth of polyelectrolyte multilayer

To have a better understanding of the LbL growth, the polyelectrolyte multilayer formation was monitored using a UV-Vis spectrophotometer. Basically, a quartz cuvette was first filled with a PEI solution so that the inner walls of the cuvette would be in contact with PEI. After 30 min of contact, the PEI solution was emptied and the cuvette was rinsed with de-ionized water for 10 min. Then a PAA solution was poured into the cuvette for 30 min, followed by water rinsing for 10 min. These processes were repeated to form polyelectrolyte multilayers on the inner walls of the cuvette. This process was essentially the same as that used for fabricating self-assembled polyelectrolyte membranes on the polyamide substrate. After a double layer was formed, the cuvette was filled with deionized water and the absorbance was measured using a Shimaden UV-Vis spectrophotometer (UV mini-1240). Because the polyelectrolyte deposition occurred on all four walls of the cuvette, the absorbance reading was divided by two to obtain the absorbance in order to account for the polyelectrolyte film which formed on the surface of the wall, because the light passed through the 2 walls of the cuvette in the absorbance measurements. All the absorbance measurements were conducted at a wavelength of 210 nm. Figure 4.1 is a typical plot of absorbance at different wavelengths.

4.2.3 Contact angle measurement

To investigate how the surface hydrophilicity of the membrane changed with an increase in the number of polyelectrolyte double layers, the contact angle was measured using a contact angle meter (CAM-Plus Micro, supplied by TANTEC). The polyelectrolyte/polyamide membrane was cut into pieces randomly and the membrane sample was fixed on a glass plate using a double-sided adhesive tape. Then, a drop of distilled water (5 μl) was placed on the membrane surface, and the contact angle was measured. Three different spots on each membrane sample were used to measure the contact angle, and the reported values represented the average values measured.

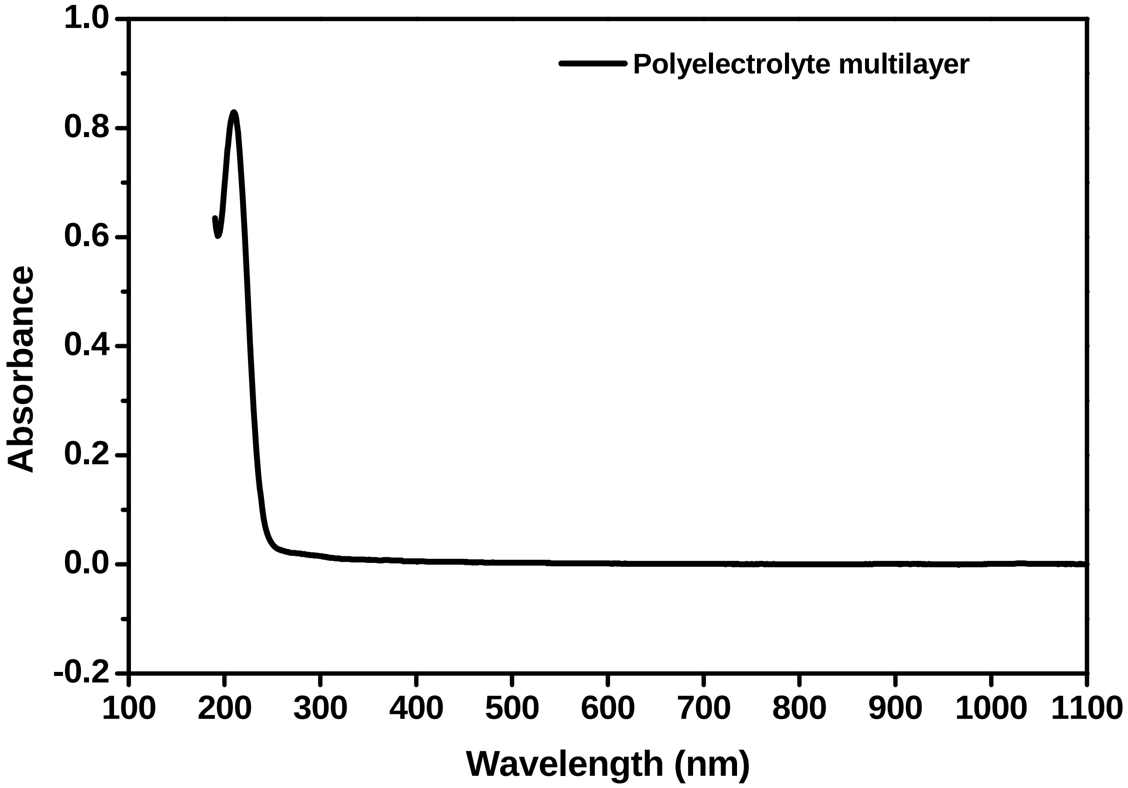

Figure 4. 1 Full wavelength scanning of polyelectrolyte multilayer with UV-Vis spectrophotometer (9 polyelectrolyte double layers; both concentrations of PEI and PAA are 0.02 monomol/L; fabricating temperature, 25 °C)

4.3 Results and discussion

4.3.1 Growth of LbL self-assembly

Figure 4.2 shows the absorbance of polyelectrolyte multilayers in the inner walls of a quartz cuvette coated with different numbers of polyelectrolyte multilayers. It can be seen that there was no obvious increase in the absorbance with the increase of number of double layers in the beginning of deposition, which indicated that the LbL growth was slow primarily due to the uncharged smooth surface of the cuvette. Because the driving force for LbL self-assembly is electrostatic, the polyelectrolyte double layer could not be formed easily on the uncharged walls of cuvette, and the polyelectrolyte deposited can be washed away during water rinsing in the first few cycles of polyelectrolyte deposition. Thereafter, there was a quick increase in the absorbance. This is easy to understand because after polyelectrolytes were adsorbed on the cuvette surface, the double layer formed more easily due to the charged surface during subsequent depositions of oppositely charged polyelectrolyte. After 8-9 cycles of polyelectrolyte deposition, the absorbance showed a linear increase with a further increase in the number of double layers. Zhao et al. [2010] also observed a quick growth in the multilayers initially, followed by a linear growth. Presumably uniform double layer formation started to occur after a certain number of double layers.

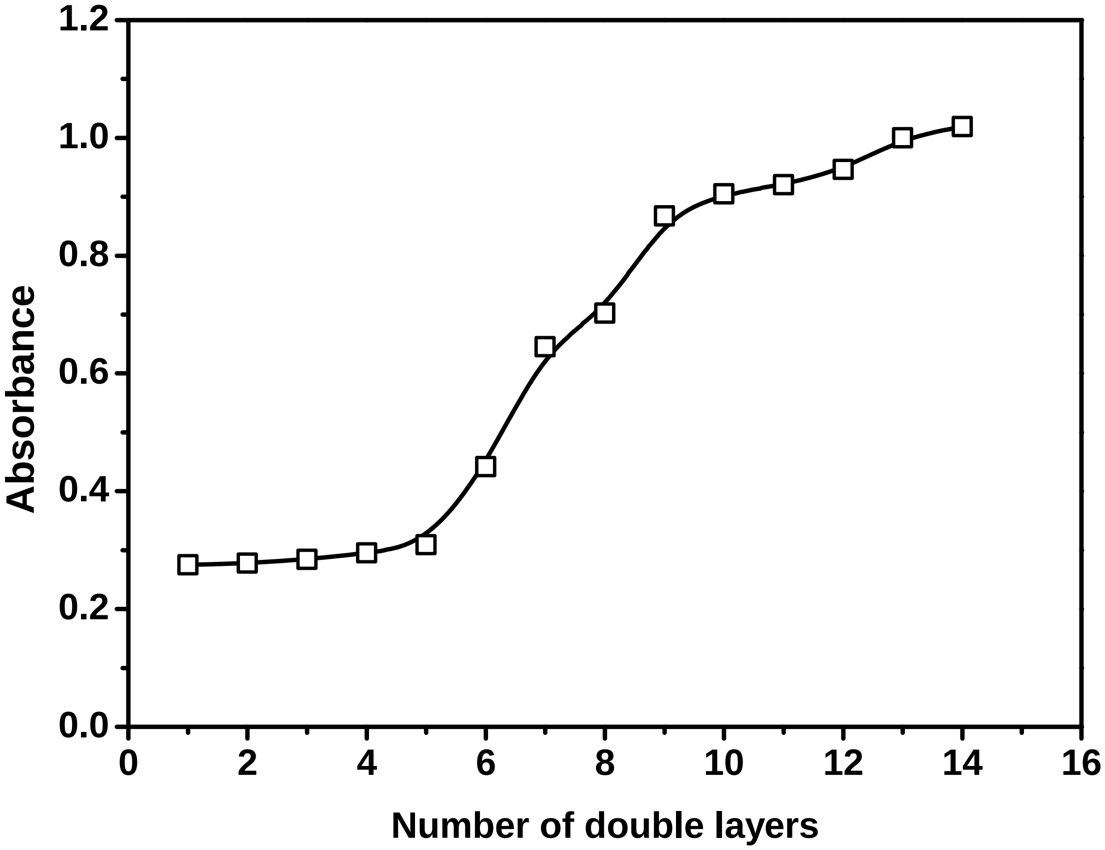

Figure 4. 2 Effect of number of polyelectrolyte double layers on absorbance (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min; deposition temperature, 25 °C)

4.3.2 Effect of deposition time

The deposition time is one of the important factors for fabrication of polyelectrolyte double layers both on the inner walls of cuvette and the surface of polyamide substrate.

Figure 4.3 shows the absorbance as a function of the number of polyelectrolyte double layers with a deposition time of 30, 60, 90, 120, 180 min, respectively. Polyelectrolyte multilayers were fabricated with concentrations of PEI and PAA of 0.02 monomol/L at room temperature of 25 ^{o}C. With an increase in the deposition time, the absorbance also tended to increase, as shown in Figure 4.3. For example, the absorbance with 8 double layers increased by 8.4% when the deposition time changed from 30 to 60 min. However, the increase in absorbance became less significant if the deposition time is sufficiently long. During the deposition step, the polyelectrolyte molecules need time to diffuse from the bulk solution to the vicinity of the charged surface and it also takes time for the polyelectrolytes to rearrange structurally on the charged surface until equilibrium is reached [Chen et al., 2007; Lenk and Meier-Haack, 2002]. A long deposition time will let more polyelectrolyte to diffuse to the opposite charged surface, and this will help repair any defects on the membrane surface during the deposition process. However, it is found that the increase in absorbance was not apparent as the deposition time increased further from 90 to 180 min, because the adsorption and rearrangement of the polyelectrolyte chains would have been completed to achieve equilibrium [Zhu et al., 2007]. Deposition time longer than 60 min is not necessary for effective LbL growth. Therefore, a 60 min can be regarded as an optimum of deposition time for LbL self-assembly.

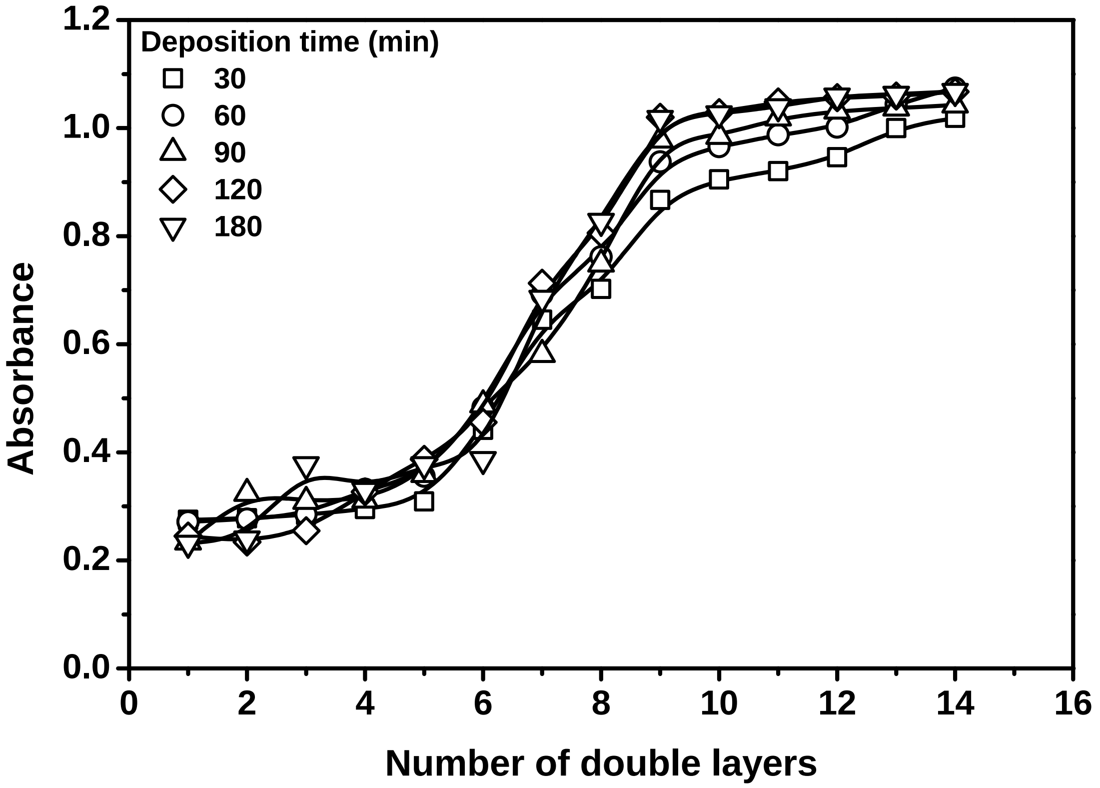

Figure 4. 3 Effect of number of polyelectrolyte double layers on absorbance at different deposition times (polyelectrolyte concentration, 0.02 monomol/L; deposition temperature, 25 ^oC)

The effects of polyelectrolyte deposition time on the separation performance of the self-assembed polyelectrolyte/polyamide composite membranes are shown in Figures 4.4-4.6. The substrate used in this work was a commercial membrane intended for use in nanofiltration, which was too microporous for direct use in pervaporation. Surface coating with only 1 or 2 double layers of polyelectrolytes was not sufficient to fill or plug the big pores in order to achieve a high selectivity. Therefore, the pervaporation experiments were performed with membranes comprising of 5 double layers.

It is shown in Figure 4.4 that the total that permeation flux decreased with an increase in the deposition time of polyelectrolyte during membrane formation. As mentioned before, a long deposition time is favorable for the diffusion and rearrangement of polyelectrolyte chains for the formation of the self-assembled separation layer, however, reduction in the flux is expected because of the tighter structure and/or thicker polyelectrolyte layers. For example, the total permeation flux decreased from 0.107 to 0.0683 kg/ ($m^2 \cdot h$) at 12.6 wt% feed water concentration when the polyelectrolyte deposition time increased from 10 to 60 min. In general, a decrease in permeation flux is accompanied with an increase in selectivity. The separation factor, shown in Figure 4.5, increased with an increase in the deposition time. Increasing the deposition time from 10 to 60 min increased the separation factor by 37.9% for the dehydration of ethylene glycol containing 12.6 wt% water in the feed. Similar observations have been reported by Lenk and Meier-Haack [2002]. Figure 4.6 shows the effects of the polyelectrolyte deposition time on the partial permeation fluxes of water and ethylene glycol, both of which decreased with an increase in the polyelectrolyte deposition time. This means that the total permeation flux is mainly determined by the water permeation flux because water molecules are more permeable than those of ethylene glycol due to the application of hydrophilic substrate and the polyelectrolyte double layers in the membrane [Xu et al., 2010].

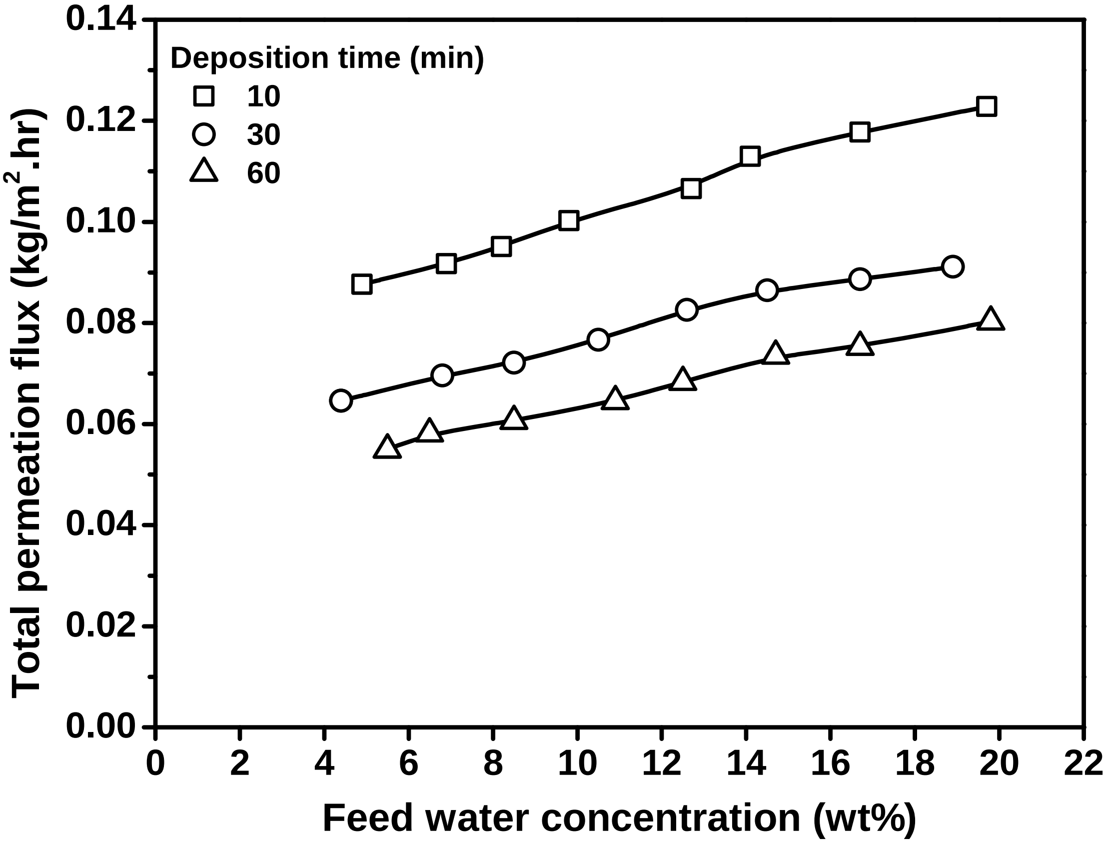

Figure 4. 4 Total permeation flux for separation of ethylene glycol/water with membranes comprising of 5 double layers formed at different deposition times (polyelectrolyte concentration, 0.02 monomol/L; deposition temperature, 25 °C). Operating temperature of pervaporation, 25 °C.

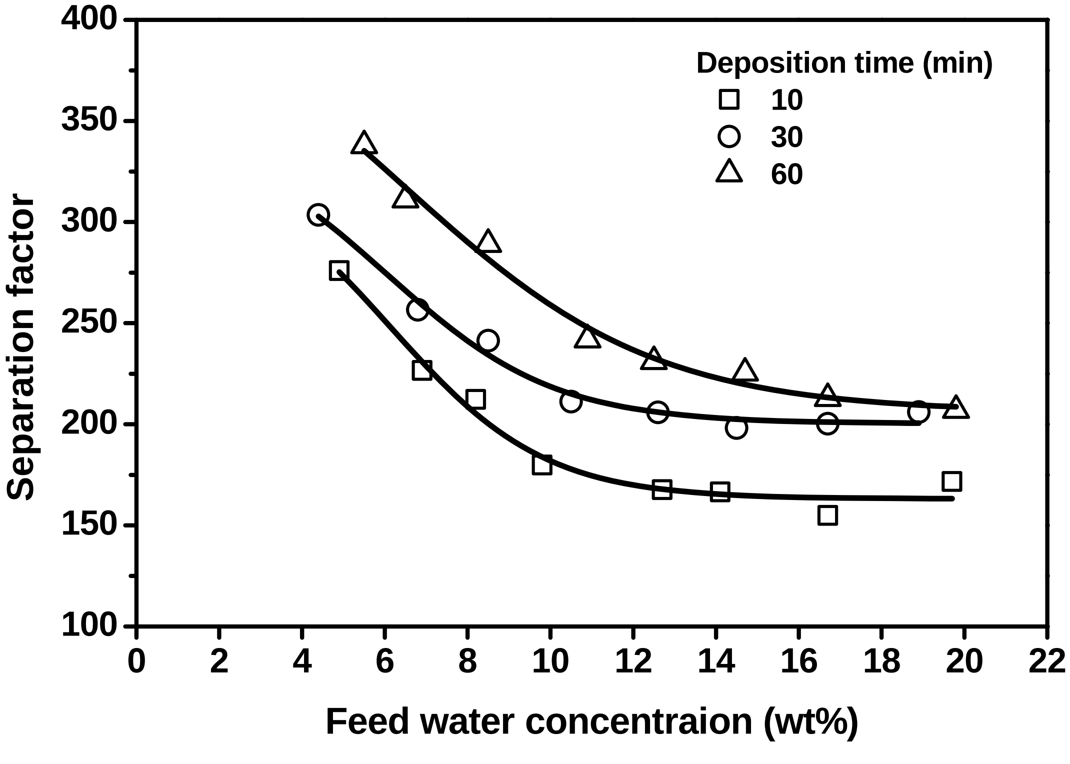

Figure 4. 5 Separation factor for separation of ethylene glycol/water with membranes comprising of 5 double layers formed at different deposition times (polyelectrolyte concentration, 0.02 monomol/L; deposition temperature, 25 °C). Operating temperature of pervaporation, 25 °C.

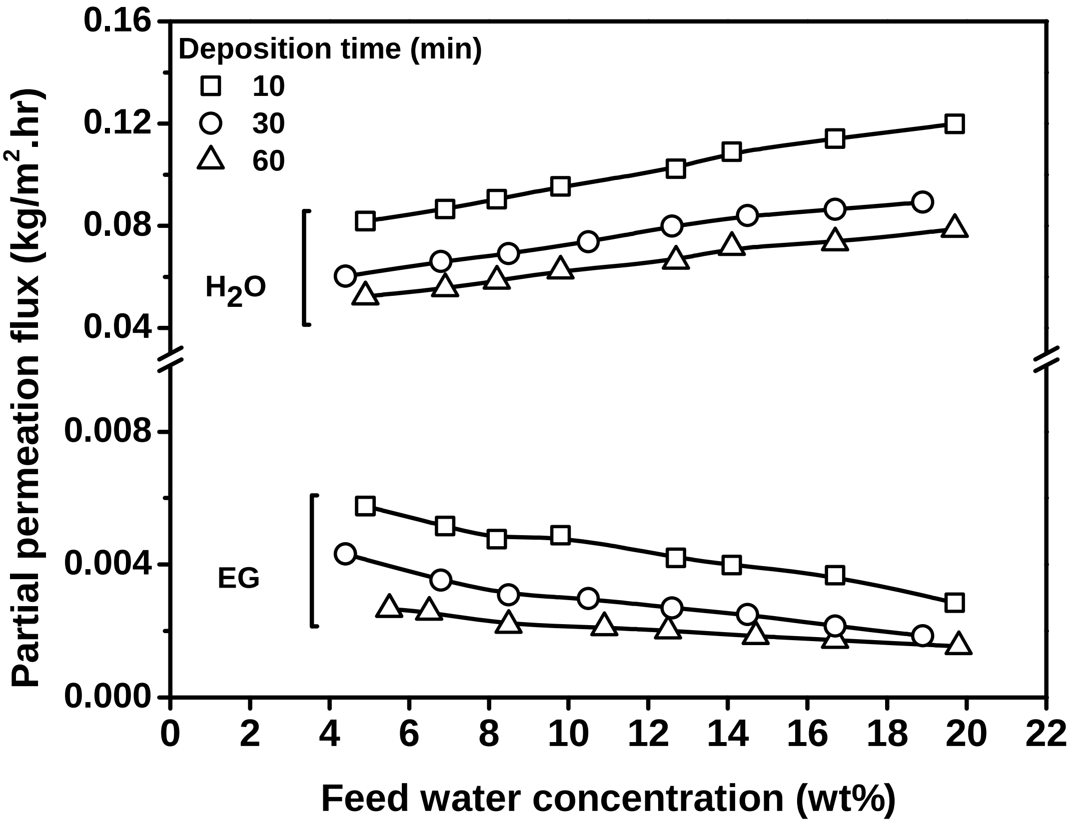

Figure 4. 6 Partial permeation fluxes for separation of ethylene glycol/water with membranes comprising of 5 double layers formed at different deposition times (polyelectrolyte concentration, 0.02 monomol/L; deposition temperature, 25 °C). Operating temperature of pervaporation, 25 °C.

4.3.3 Effect of concentration of polyelectrolyte deposition solution

To study the effects of polyelectrolyte concentration in the deposition solutions, a constant deposition time of 30 min and a fabricating temperature of 25 °C were used. Figure 4.7 illustrates the change in absorbance with the number of double layers using different concentrations of polyelectrolyte (0.01, 0.02, 0.04, 0.06 and 0.08 monomol/L) in the deposition solution. With fewer double layers, the absorbance changes significantly with the polyelectrolyte concentration. For example, the absorbance with 2 double layers formed using a polyelectrolyte concentration of 0.02 monomol/L is more than twice the absorbance with 2 double layers formed with a polyelectrolyte concentration of 0.01 monomol/L. In general, the higher the concentration of the polyelectrolyte solutions, the greater the absorbance of polyelectrolyte multilayers. However, after the first few layers, the absorbance levels of the double layers formed with different concentrations of polyelectrolyte solutions become closer, except for the double layers formed at the concentration of 0.01 monomol/L. This can be attributed to the fact that the initial concentration of polyelectrolyte solutions is an important factor for polyelectrolyte deposition, and a higher concentration provides a platform for rapid formation of polyelectrolyte double layers; however, the polyelectrolyte deposition is primarily based on electrostatic interactions and the polyelectrolyte concentration is not particularly critical in the beginning. The absorbance of double layers formed at a polyelectrolyte concentration of 0.01monomol/L seems to indicate that this concentration is too low to fabricate defect-free membranes. The polyelectrolytes adsorbed on the walls of the cuvette do not appear to form a compact structure since there is no sharp change in the absorbance when the number of double layers increased.

Figure 4.8 shows a schematic diagram of the formation of polyelectrolyte multilayers formed with a low, a medium and a high polyelectrolyte solution. At a low polyelectrolyte concentration, the polymeric chains are isolated and extended, and the polyelectrolyte multilayers have loose structures and even some defects and voids if the concentration of the polyelectrolyte is low enough (Figure 4.8 (a)). With an increase in the concentration of the polyelectrolyte solution, the polyelectrolyte polymeric chains are slightly coiled and defects are reduced on the polyelectrolyte multilayers, as shown in Figure 4.8 (b). The polyelectrolyte macromolecules at a meduim concentration have more chances to interact with the polyelectrolyte that has been adsorbed onto the surface of the substrate. However, when concentration increases to a certain extent (≥ 0.2 monomol/L, shown in Fig. 4.8 (c)), polyelectrolyte polymeric chains will be highly coiled and polyelectrolyte multilayers become thicker due to disorder of the array of polymer chains [Zhu et al., 2007].

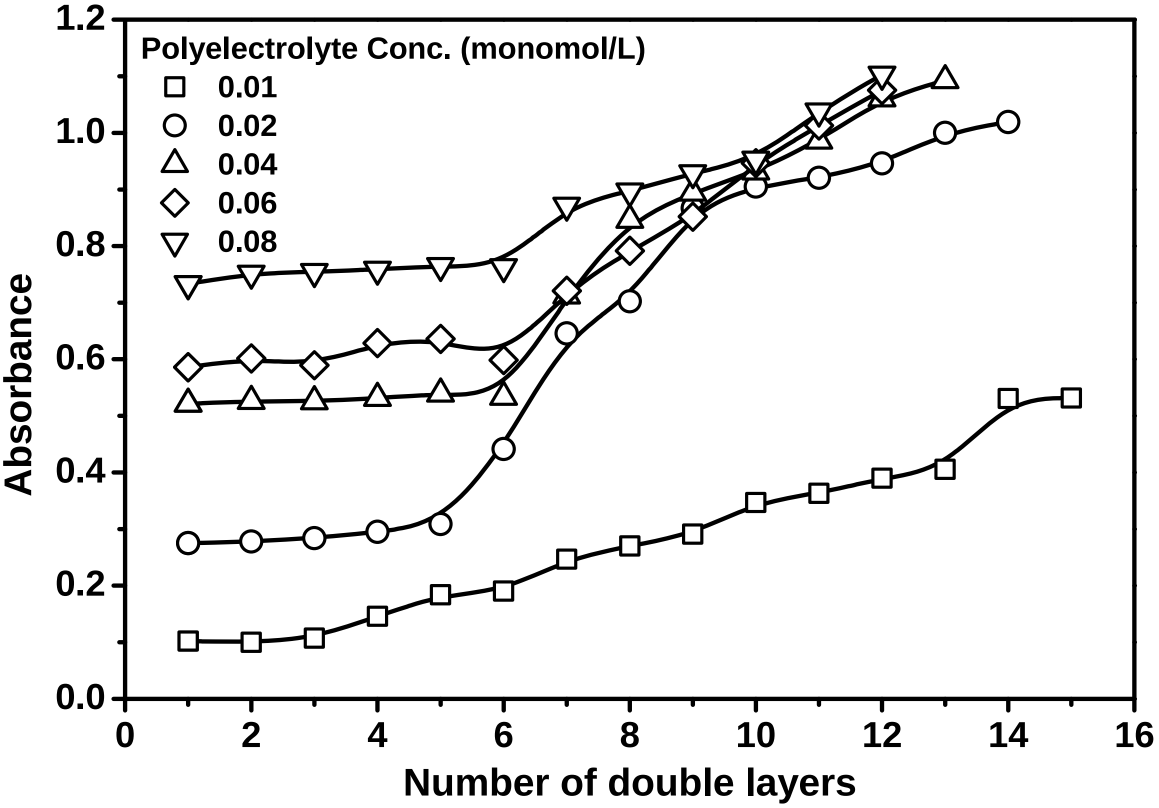

Figure 4. 7 Effect of number of double layers on absorbance at different concentrations of polyelectrolyte solution (deposition time, 30 min; deposition temperature, 25 °C).

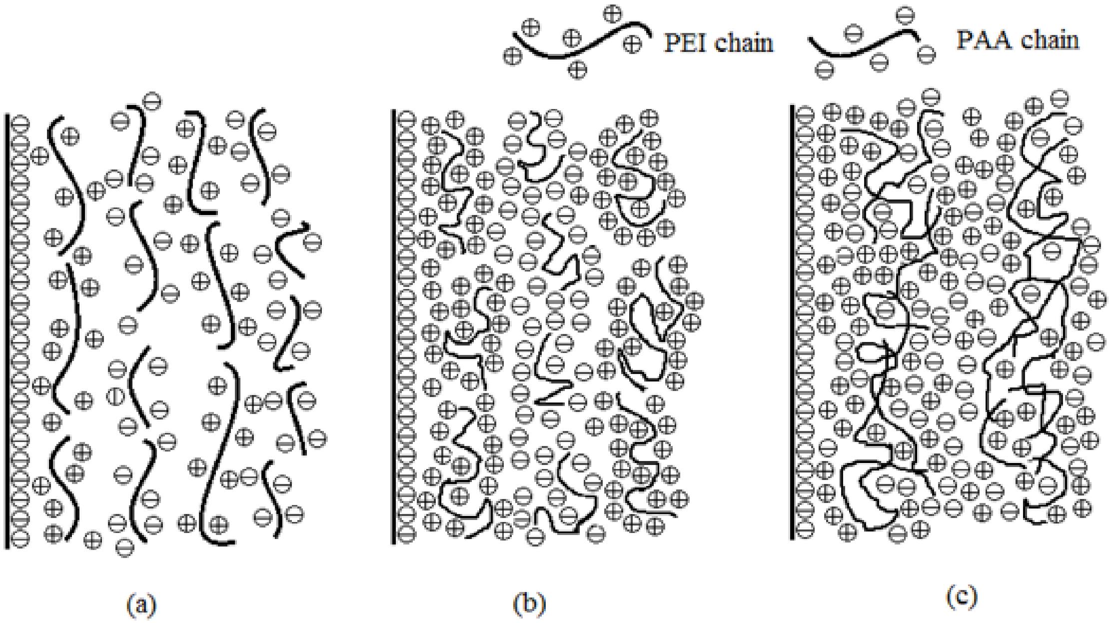

Figure 4. 8 Schematic diagram of the formation of polyelectrolyte multilayers using a low (a), a medium (b) and a high (c) concentration of the polyelectrolyte deposition solutions.

The effects of polyelectrolyte concentration in the deposition solution on the membrane performance are shown in Figures 4.9-4.11, where the pervaporation performance of polyelectrolyte/polyamide composite membranes fabricated at different polyelectrolyte concentrations for dehydration of ethylene glycol at different feed concentration is presented. The total permeation flux decreased while the separation factor increased with an increase in the polyelectrolyte concentrations in the deposition solutions. Both partial permeation fluxes of water and ethylene glycol decreased with an increase in the concentration of the polyelectrolyte solution. This is consistent with the physical reasoning that the polyelectrolyte multilayer becomes thicker with an increase in polyelectrolyte concentration [Dubas and Schlenoff, 1999]. At a water content of 5.5 wt% in the feed, a total permeation flux and separation factor of 0.043 kg/($m^2 \cdot h$) and 453 were obtained for the membrane fabricated at 0.06 monomol/L polyelectrolyte solution.

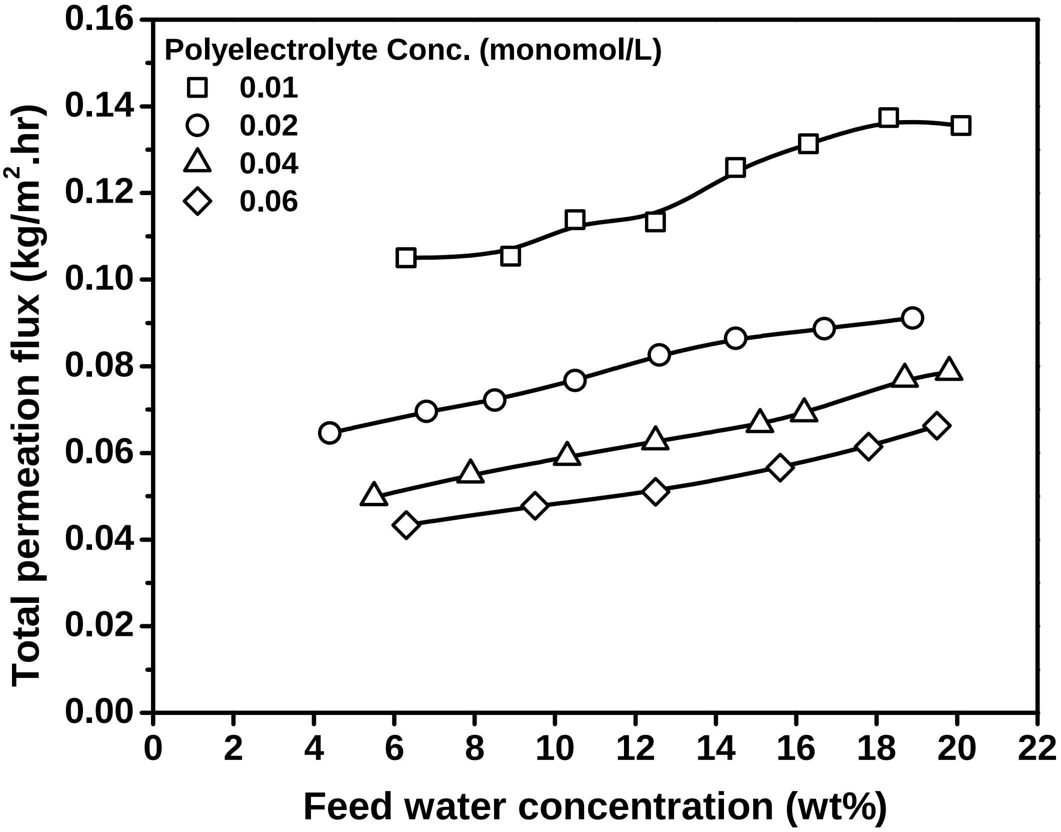

Figure 4. 9 Total permeation flux for separation of ethylene glycol/water with membranes comprising of 5 double layers formed at different polyelectrolyte concentrations (deposition temperature, 25 ^{o}C; deposition time, 30 min). Operating temperature of pervaporation, 25 ^{o}C.

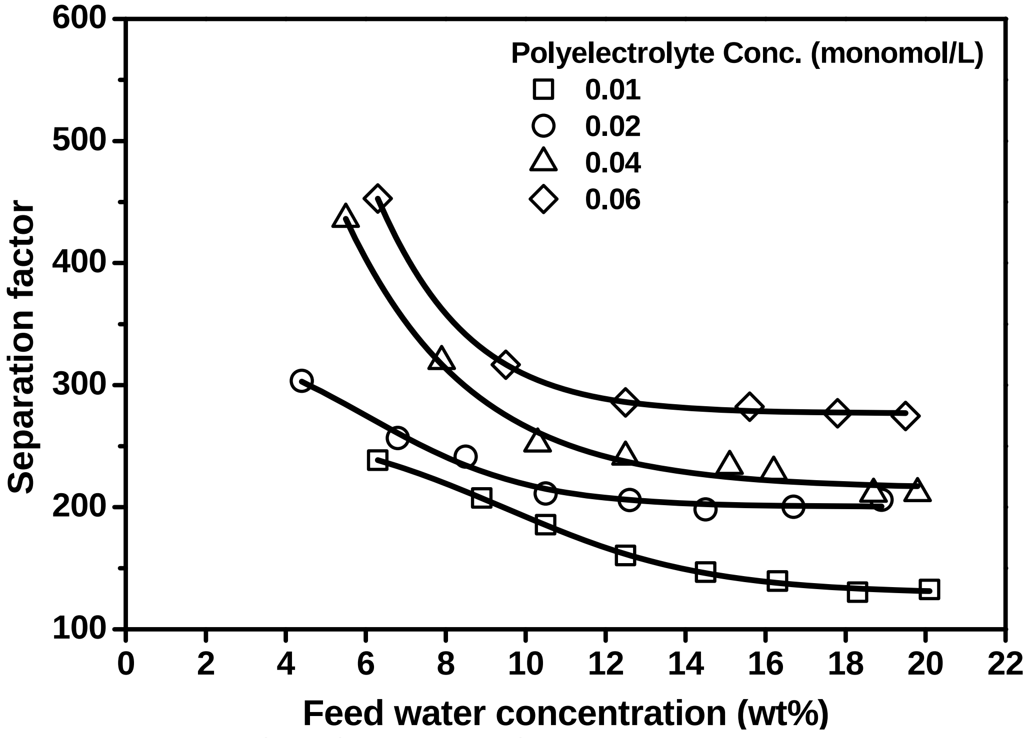

Figure 4. 10 Separation factor for separation of ethylene glycol/water water with membranes comprising of 5 double layers formed at different polyelectrolyte concentrations (deposition temperature, 25 ^{o}C; deposition time, 30 min). Operating temperature of pervaporation, 25 ^{o}C.

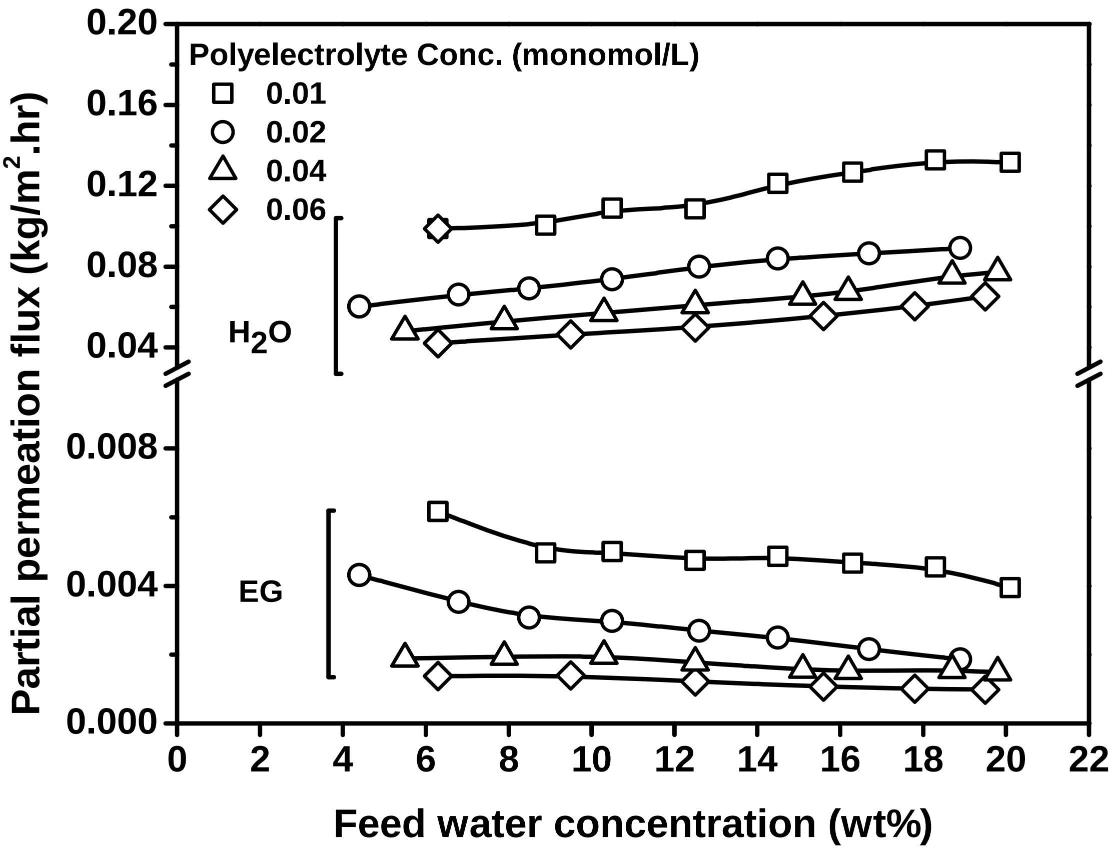

Figure 4. 11 Partial permeation flux for separation of ethylene glycol/water water with membranes comprising of 5 double layers formed at different polyelectrolyte concentrations (deposition temperature, 25 °C; deposition time, 30 min). Operating temperature of pervaporation, 25 °C.

4.3.4 Effect of deposition temperature

In general, the deposition of polyelectrolyte to form multilayers is a diffusion-related process. With an increase in the deposition temperature, the polyelectrolyte macromolecues will become more dynamic in the polyelectrolyte solutions and their diffusion will be faster and consequently the polyelectrolyte molecues will be absorbed on the substrate faster. Increasing the deposition temperature also can accelerate the rearrangement of adsorbed polyelectrolytes during deposition. Therefore, a high deposition temperature is preferred for the formation of polyelectrolyte multilayers from a diffusion point of view [Zhu et al., 2007; Lenk and Meier-Haack, 2002]. However, on the other hand, adsorption is normally an exothermic process, and increasing deposition temperature will have a negative effect on the formation of polyelectrolyte multilayers. In view of the two opposite effects, it is difficult to predict a suitable depodition temperature for the formation of polyelectrolyte multilayer. As a result, an appropriate deposition temperature for the formation of polyelectrolyte layers is often determined experimentally.

To study the effects of deposition temperature, a constant deposition time (i.e., 30 min) and polyelectrolyte concentration (i.e., 0.02 monomol/L) were used. Figure 4.12 shows the absorbance of polyelectrolyte multilayers fabricated at different deposition temperatures. It can be seen that increasing the deposition temperature increased the absorbance. This supports the reasoning that a high deposition temperature causes a rapid diffusion of polyelectrolytes and rearrangement of the deposited polyelectrolyte macromolecules on the substrate.

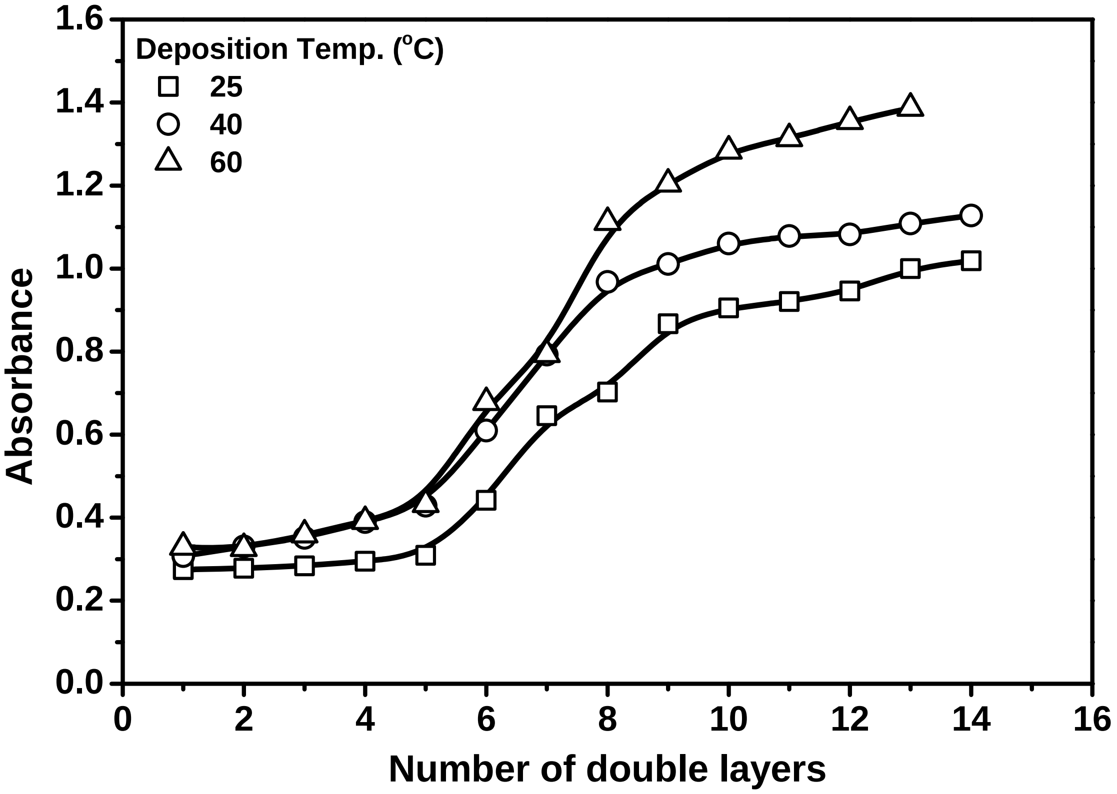

Figure 4. 12 Effect of number of double layers on absorbance at different deposition temperatures (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min).

This is also supported by the pervaporation data with the membranes fabricated at different deposition temperatures. Figures 4.13 and 4.14 show the separation performance of the composite polyelectrolyte membranes with 5 self-assembled double layers produced at different polyelectrolyte deposition temperatures. The total permeation flux decreased from 0.072 to 0.049 kg/(m^2·h) as the deposition temperature increased from 25 to 60 °C for the dehydration of ethylene glycol at a 8.5 wt% feed water concentration, and the corresponding separation factor increased by 20.7% to reach 304 at 60 °C. Lenk and Meier-Haack [2002] found that a large number of interpolyelectrolyte bonds are formed at high temperatures, resulting in a tight network that results in low permeability and high selectivity.

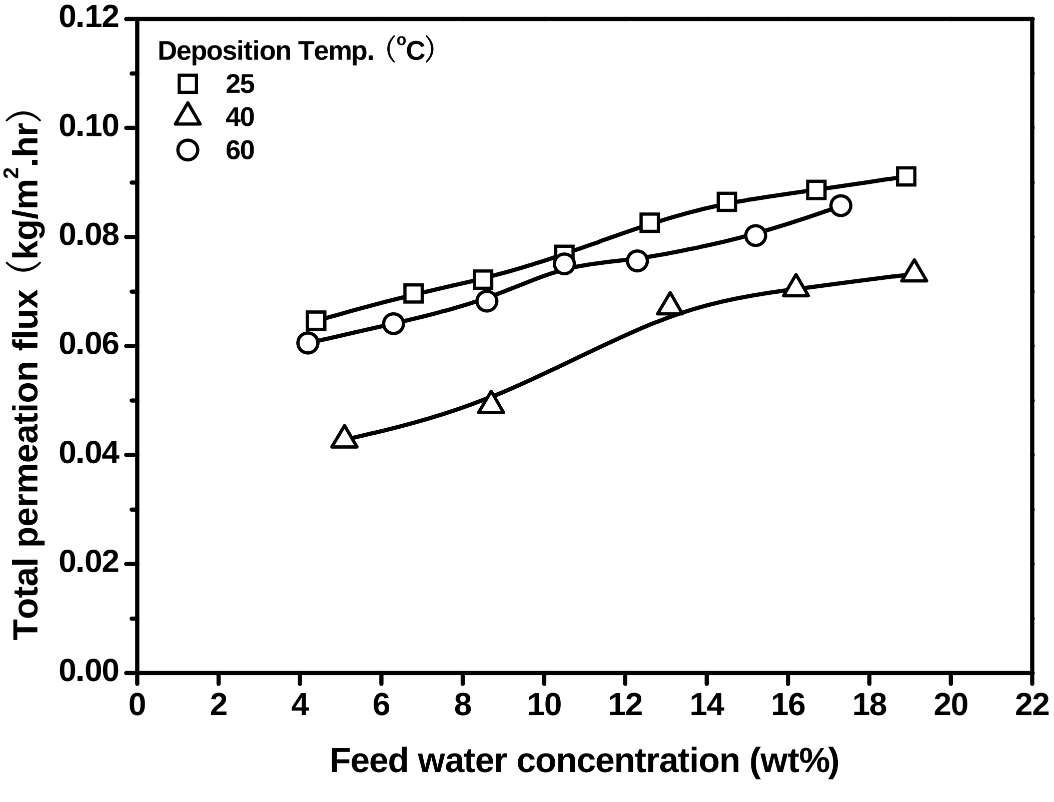

Figure 4. 13 Total permeation flux for separation of ethylene glycol/water with membrane comprising of 5 double layers formed at different deposition temperatures (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min). Operating temperature of pervaporation, 25 °C.

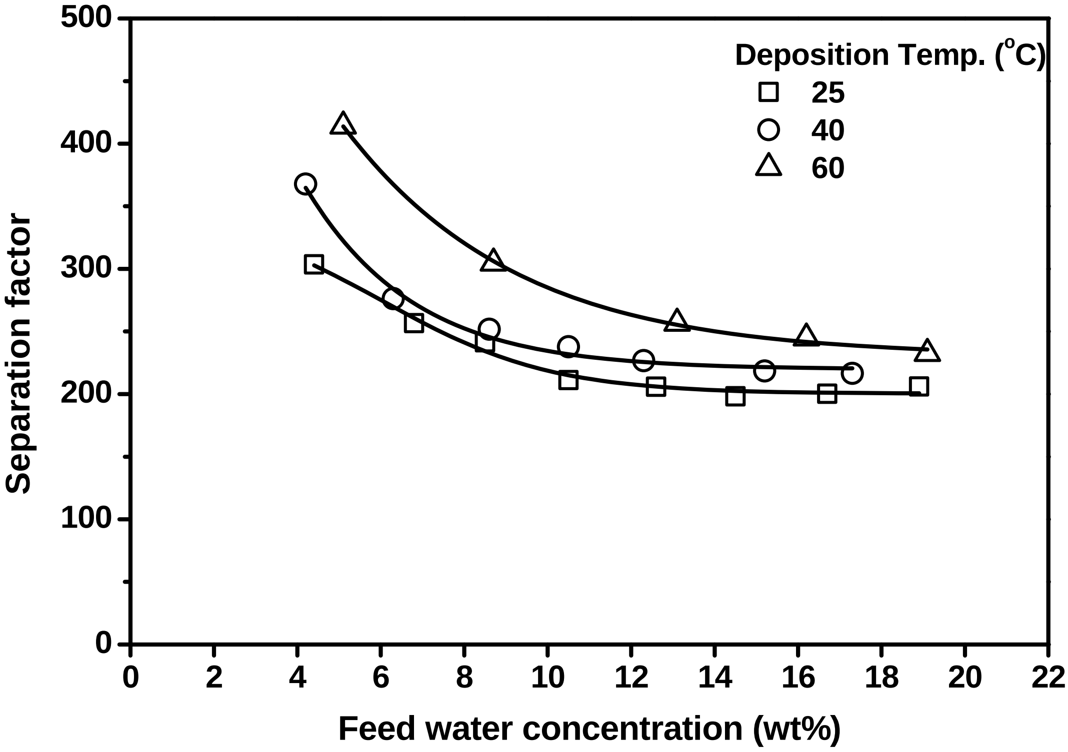

Figure 4. 14 Separation factor for separation of ethylene glycol/water water with membrane comprising of 5 double layers formed at different deposition temperatures (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min). Operating temperature of pervaporation, 25 ^{o}C.

4.3.5 Effect of changing sequence of polyelectrolyte

Figure 4.15 shows the effect of sequence of polyelectrolyte deposited on the absorbance of polyelectrolyte multilayers. As expected, there is no considerate difference in the absorbance when the sequence of deposition of cationic and anionic polyelectrolytes is reversed because of the uncharged walls of the cuvette. However, for polyelectrolyte deposition on a charged substrate, the effect of the sequence of polyelectrolyte deposition is expected to be important and the first polyelectrolyte to be deposited should have a charge opposite to that of the substrate. In this case, PEI, positively charged, should be used for the first cycle of deposition because of the negatively charged polyamide substrate. Otherwise, there will be electrostatic repulsion between the substrate and the polyelectrolyte, which will prevent the deposition of the polyelectrolyte as well as charge overcompensation for subsequent deposition of oppositely charged polyelectrolyte.

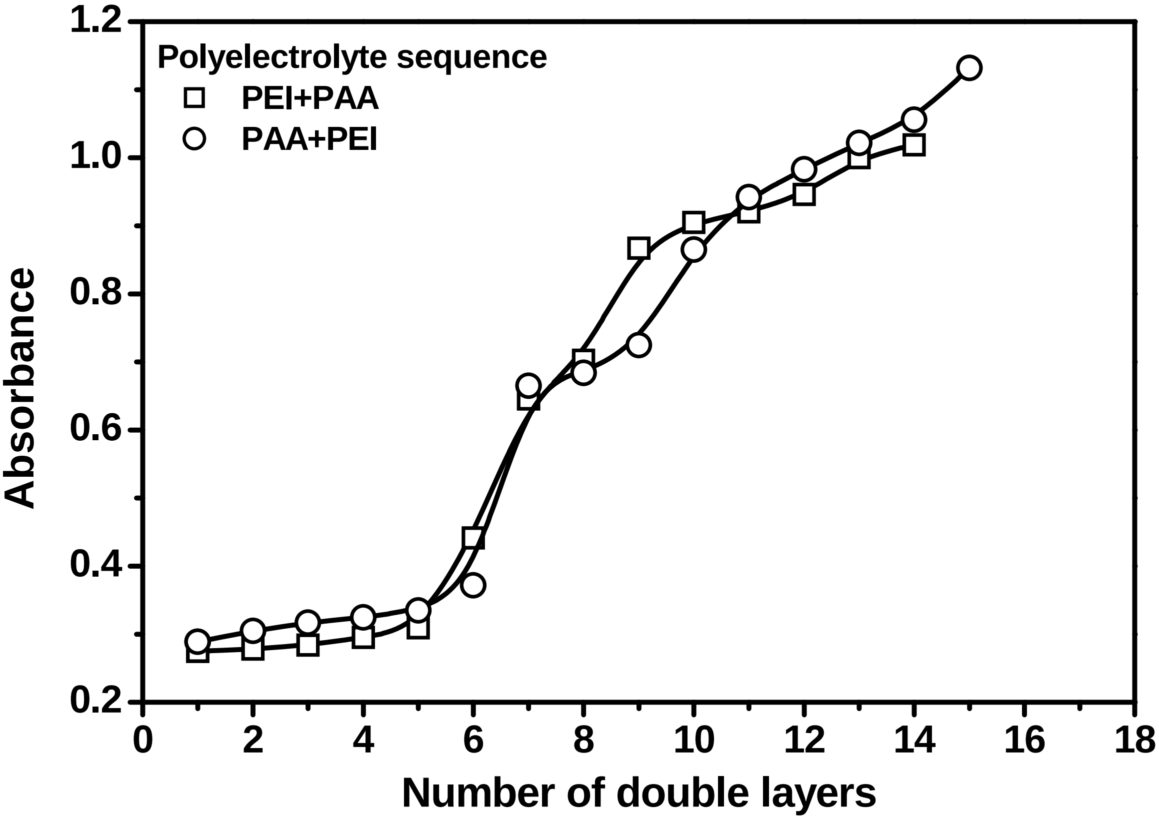

Figure 4. 15 Effect of polyelectrolyte sequence deposition on absorbance (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min; deposition temperature, 25 °C).

4.3.6 Contact angle on the polyelectrolyte layer

Contact angle measurements have been used in studies of surface energy, wettability and adhesion of low surface energy materials. A contact angle less than 90° indicates that the wetting of the surface is favorable; while a contact angle greater than 90° generally means the wetting of the surface is not favorable. For example, completely wetting occurs when the contact angle is 0°, as the droplet turns into a flat puddle. For superhydrophobic surfaces, water contact angles are usually greater than 150°. Therefore, the measurement of water contact angle on the surface could provide the measure/indicator for evaluating whether the surface is hydrophilic or hydrophobic.

For pervaporation dehydration processes, hydrophilic membranes are used. The hydrophilic groups or hydrophilic deposition layers are introduced into the membranes to increase the selectivity for water permeation. In this work, the polyamide substrate is hydrophilic and the deposited polyelectrolyte multilayer is more hydrophilic than the substrate. Therefore, the resulting composite membrane is effective to separate water from organic solutions. The contact angles of the polyamide substrate and polyelectrolyte multilayer membranes fabricated on polyamide substrate are shown in Figure 4.16. The polyamide substrate showed a water contact angle of 68^o. After surface deposition of the polyelectrolyte multilayers, the water contact angle decreased quickly within 3 double layers, reaching 20^o. Thereafter, the water contact angle decreased less significantly as the number of the polyelectrolyte double layers increased further. This proves that the hydrophilicity of the membrane is improved by the deposition of polyelectrolytes on the membrane surface.

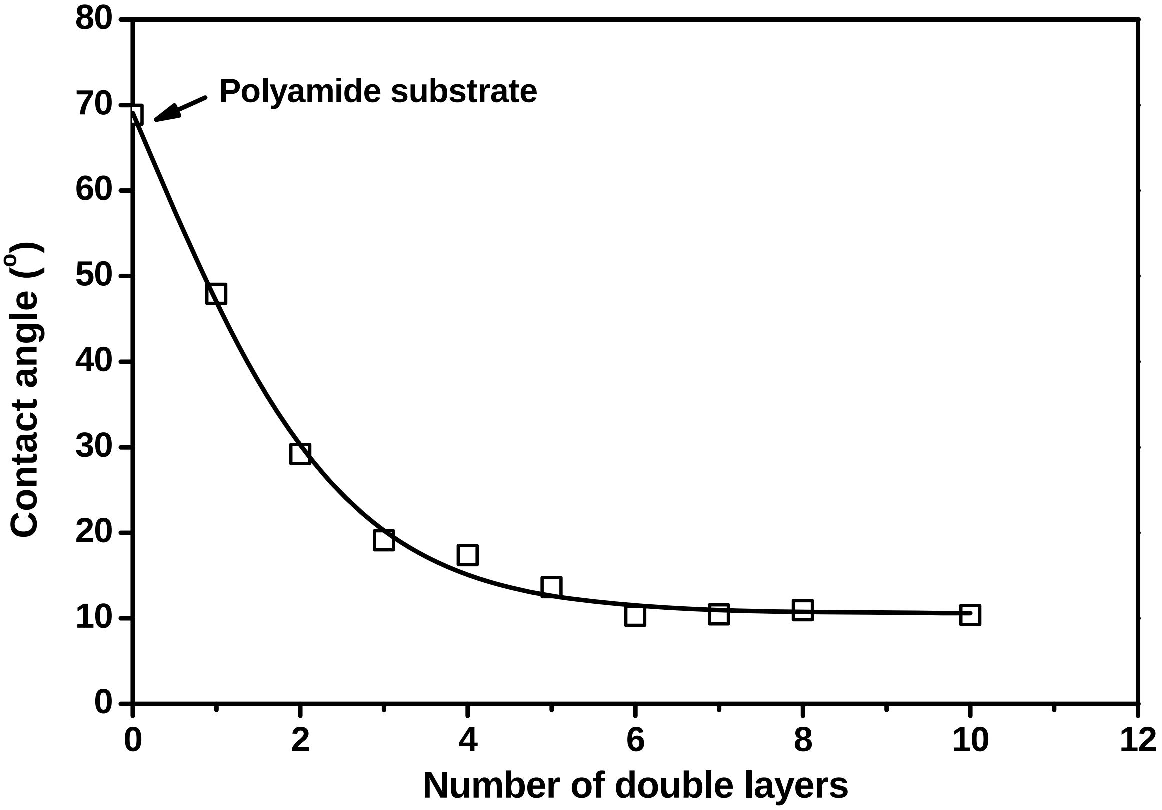

Figure 4. 16 Effect of number of double layers on surface hydrophilicity of the polyelectrolyte/polyamide composite membranes (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min; deposition temperature, 25 °C).

Membranes with different number of double layers were prepared and tested for ethylene glycol pervaporation at 25 °C at feed water contents of 5.5 and 10.6 wt%. As shown in Figure 4.17, with an increase in the number of double layers, the total permeation flux decreases dramatically from 0.085 to 0.01 kg/(m^2·h) at a feed water concentration of 10.6 wt%. This is easy to understand: as the number of double layers increases, the effective thickness of the membrane increases. Therefore, the resistance for the permeant to pass through the membrane also increases. The membrane is more selective as the polyelectrolyte layer becomes thicker and thus the concentration of water in the permeate is increased accordingly. Note that the concentration of water in the permeate could reach more than 90% with 3 double layers. However, adding 2 more double layers did not significantly increase the membrane selectivity. This is presumably due to the polyelectrolyte double layer not dominating the overall permeation for the first few double layers.

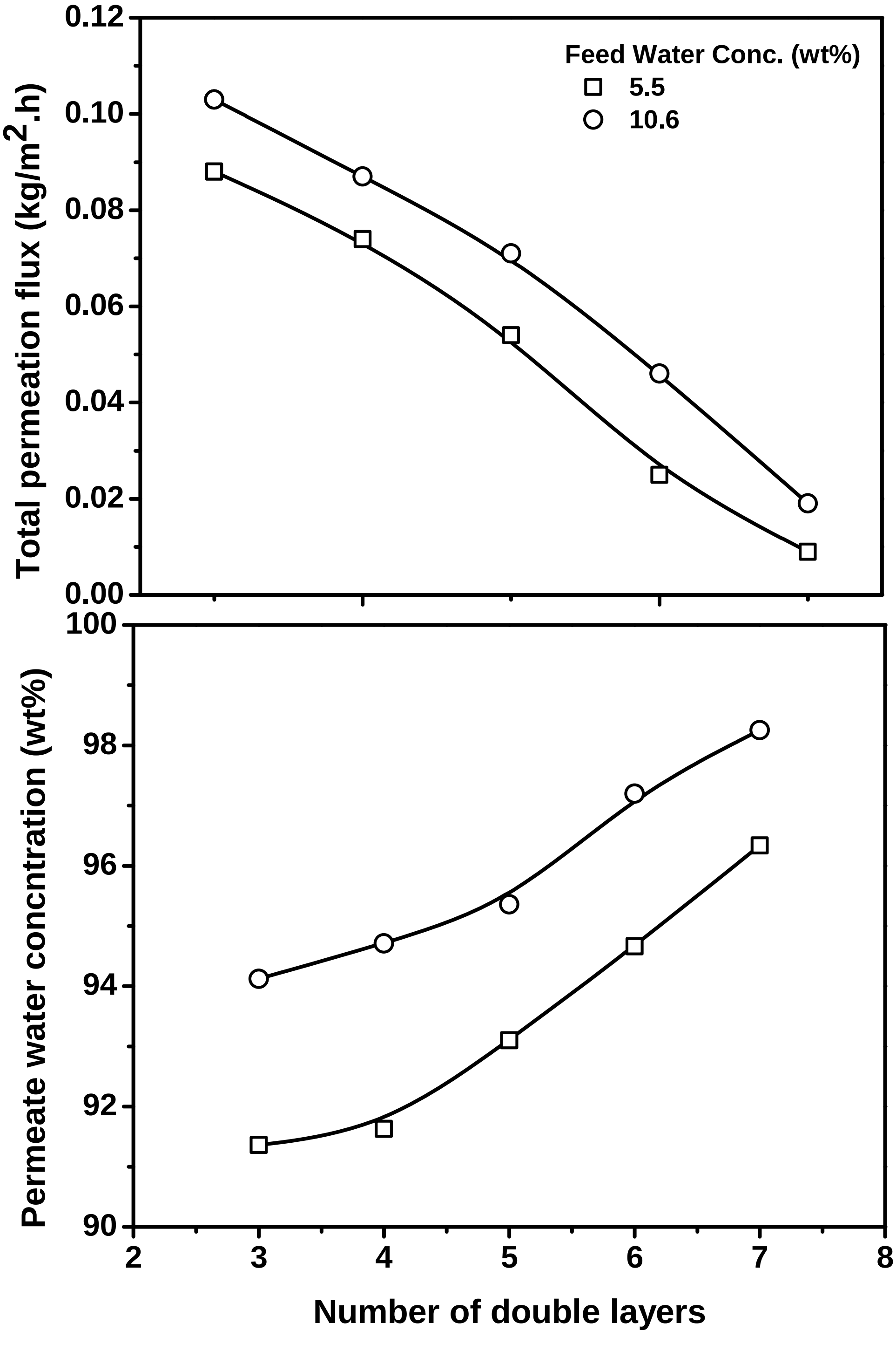

Figure 4. 17 Effect of number of double layers of polyelectrolyte/polyamide membrane on total permeation flux and permeation water concentration (polyelectrolyte concentration, 0.02 monomol/L; deposition time, 30 min; deposition temperature, 25 °C).

4.4 Conclusions

Polyelectrolyte multilayers were fabricated on the inner walls of a cuvette to study the LbL self-assembly growth and polyelectrolyte/polyamide composite membranes were also prepared for dehydration of ethylene glycol. This would allow us to see how the multilayers formed affected the separation performance of the membrane. The effects of LbL fabrication conditions were evaluated, and the following conclusions can be drawn:

(1) A long deposition time was favorable to LbL self-assembly. A deposition time of 60 min was shown to be sufficient to form uniform polyelectrolyte multilayers for use in pervaporative separation of ethylene glycol/water mixtures.

(2) With an increase in the polyelectrolyte solution concentration, the polyelectrolyte multilayer grew more rapidly and the membrane performance was improved. A permeation flux of 0.043 kg/($m^2 \cdot h$) and separation factor of 453 were obtained at a feed water content of 5.5 wt% with for the membrane fabricated at 0.06 monomol/L polyelectrolyte solution.

(3) The LbL self-assembly was formed faster at a higher deposition temperature over the range of deposition temperatures studied.

(4) The sequence of polyelectrolyte deposition had no impact on multilayer formation on the inner surface of the cuvette.

(5) The surface hydrophicility of the polyelectrolyte composite membrane increased with an increase in the number of polyelectrolyte double layers, but no further significant increase in the surface hydrophicility was observed beyond 5 double layers.

Chapter 5

Improving the stability of LbL self-assembed membranes for dehydration of alcohol and diol

5.1 Introduction

Pervaporation has attracted significant attention as an efficient membrane process for liquid separations, especially for dehydration of such organic solvents as alcohol that form azeotropes with water (e.g., ethanol and isopropanol) or diols that have energy intensive with conventional distillation [Neel, 1991; Feng and Huang, 1997; Shao and Huang, 2007; Chapman et al., 2008]. For selective removal of water, hydrophilic membrane are preferred, and composite membranes comprising of a dense skin layer and a micro-porous support are often used to enhance the permeation flux [Bruschke, 2006; Baker, 2012]. From an application standpoint, research efforts to produce a higher flux is almost always more important than to produce a higher selectivity as long as a moderately high membrane selectivity can be maintained. LbL self-assembly of oppositely charged polyelectrolytes is a simple and promising method to fabricate high flux hydrophilic membranes due to the skin layer so formed under electrostatic forces [Toutianoush et al., 2002; Krasemann and Tieke, 1998; Krasemann and Tieke, 2000]. These membranes are shown to be effective for dehydration of organic solvents by pervaporation [Krasemann et al., 2001; Krasemann and Tieke, 1999; Zhu et al., 2006]. For instance, using poly(allylamine hydrochloride) and

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poly(styrene sulfonate sodium) salt as the polyelectrolytes,Krasemann and Tieke [1999] prepared a composite membrane with 60 double layers on a microporous PAN/PET substrate, which showed a separation factor from 4.5 to about 70 for dehydration of 93.8 wt% ethanol when the membrane was annealed at 90 ^{o}C. Using a relatively dilute polyelectrolyte solutions in the first few layer by layer depositions, followed by depositions with more concentrated polyelectrolytes, Zhu et al. [2006] fabricated a membrane with less than 10 double layers of polyelectrolyte and the membranes showed good performance for separation of water from isopropanol.

Besides permeability and selectivity, the stability of the membrane is another important property for pervaporation applications. When the membrane contacts with an aqueous solution, the membrane stability may become compromised if the polycation-polyanion intermolecular forces cannot overcome the polymer-solvent interactions. Especially, water molecules can enter the polymer matrix of the hydrophilic polyelectrolyte membranes due to their strong affinities, causing interchain stretching and membrane swelling. Similar to water, isopropanol and ethanol are also polar solvents and these alcohols may swell the polyelectrolyte multilayer as well. If excessive membrane swelling occurs, the ionic crosslinks in the tethered state of the multilayer will be broken. As a result, the membrane selectivity will be lowered and the membrane may even become non-selective. There are studies on the stability of polyelectrolyte multilayer membranes in different solvents, and the membrane performance is shown to change considerably depending on the external conditions [Miller and Bruening, 2005]. As one may expect, the stability of polyelectrolyte multilayers depend on both the solvent and the hydrophilicity of the polyelectrolyte. Poptoshev et al. [2004] demonstrated that highly charged polyelectrolytes can precipitate in polar solvents (e.g., ethanol) and waterwet polyelectrolyte films can shrink or collapse in an aqueous ethanol solution. Another study

[Kim et al., 2005] showed that polyelectrolyte multilayers behave differently in different organic solvent/water mixtures, and the polymer coils in the multilayers can be contracted or softened, depending on the organic solvent. This will ultimately affect the membrane permeability for pervaporative separation of water from organic solvents.

Crosslinking is generally used to enhance membrane stability for pervaporation applications. As the polymer chains are restricted, crosslinking often leads to an increased selectivity and a lowered permeation flux. The membrane becomes more compact with an increase in the crosslinking density, and the polymer chains become more rigid. Therefore, the membrane is more discretional to the permeation of penetrant molecules, which favors the selectivity of the membrane, while the permeability is compromised [Huang et al., 1999]. Depending on the polymers, many crosslinking agents have been used in pervaporation membranes, including glutaraldehyde [Uragami et al., 1994; Suto and Ui, 1996; Goto et al., 1994], sulfuric acid [Ren and Jiang, 1998; Lee et al., 1997], sulfosuccinic acid [Rhim and Kim, 2000] and trimesoyl chloride [Xiao et al., 2007].

In this study, polyelectrolyte membranes were self-assembled onto an interfacially formed polyamide composite membrane that was developed for low-pressure reverse osmosis applications. The polyamide membrane was chosen as a substrate here because of the following considerations: (1) it has a negatively charged surface, which favors initial deposition of a polycation during electrostatic self-assembly of the polyelectrolytes; (2) the polyamide membrane itself is a thin-film composite membrane with an ultrathin dense skin layer and a microporous support, and thus a relatively fewer number of polyelectrolyte bilayers are needed to achieve an adequate selectivity as compared to cases where ultrafiltration or microfiltration membranes are used as a substrate; (3) interfacial polymerization to produce thin film composite membranes is a well established technique, and the use of such membranes as a substrate for pervaporation membranes represents an expansion of their scope of applications. Polyethylenimine (PEI) and poly(acrylic acid) (PAA) were used as the polyelectrolytes. For this pair of polyelectrolytes, besides electrostatic attractions, the strong hydrogen bonding is also expected to occur as a reinforcing effect in the polyelectrolyte complex [Molyneux, 1984]. The membranes were investigated for the dehydration of ethylene glycol, isopropanol and ethanol by pervaporation. PEI and PAA were used as the polyelectrolytes because of their suitable charge densities and electrolyte strength for layer-by-layer self-assembly under electrostatic attractive forces, and this has been demonstrated in numerous studies [Toutianoush et al., 2002; Decher, 1997; Zhang et al., 2006; Zhang et al., 2009; Ji et al., 2008; Zhu et al., 2007; Wang et al., 2012]. PAA has a relatively high charge density, which favors overcompensation of the surface charge so as to revere the surface charge of the previously adsorbed polyelectrolyte layer, making it ready for subsequent deposition of oppositely charged polyelectrolyte during the successive layer-by-layer growth.

It was found during this work that while the membranes worked very well for dehydrating ethylene glycol, the membrane selectivity for dehydration of isopropanol and ethanol was relatively low. To pinpoint the cause of the problem so as to improve the membrane accordingly, the stabilities of the polyelectrolyte multilayers, the polyamide substrate and the self-assembled polyelectrolyte/polyamide membranes in these solvents were investigated. This was done by the following: (1) polyelectrolyte multilayers were also built up on the surface of quartz cuvettes, and light absorbance was monitored by means of UV–vis spectrophotometry after the polyelectrolyte layers were exposed to the solvents; (2) the hydraulic permeabilities of water through the polyamide substrate and the polyelectrolyte/polyamide membranes were measured after immersing in isopropanol, ethanol, ethylene glycol and water separately, and (3) the surface morphologies of the polyamide substrate and the polyelectrolyte/polyamide membranes were examined as well after the solvent “treatment”. Based on these results, two remedy approaches were used to enhance the stability and selectivity of the polyelectrolyte/polyamide membranes for dehydration of ethanol and isopropanol. One is controlled cross-linking of the outmost layer of the polyelectrolyte/polyamide composite membrane to shield the interior polyelectrolyte and the polyamide layers, and the other was to replace PEI with protonated chitosan, at least for the last few layers, for stronger electrostatic attractions that help maintain a more stable polyelectrolyte assembly. This was shown to be very effective to improve the stability and selectivity of the membranes for alcohol dehydration. The effects of operating temperature and feed composition on the membrane performance were evaluated.

5.2 Experimental

5.2.1 Materials

The polyamide membrane and polyelectrolytes used for fabriating polyelectrolyte/polyamide composite membrane are same as mentioned in chapter 3. Chitosan flakes (Flonac-N, Mw: 500,000, and 99% N-deacetylation) were supplied by Kyowa Technos Co. Ltd, Japan. Acetic acid, which was used to dissolve chitosan, was supplied from Fisher Scientific. Glutaraldehyde (aqueous solution,25 wt%) from Sigma Chemicals was used as a cross-linking agent.

5.2.2 Membrane preparation

LbL self-assembly membrane prepareation was same as mentioned in chapter 3. Note that single-sided deposition is used for LbL self-assembly polyelectrolyte/polyamide membrane fabrication. The concentrations of polyelectrolyte solutions used during membrane fabrication were 0.02monomol/L for both PEI and PAA, and 0.001monomol/L for chitosan. As mentioned earlier, chitosan was used to substitute for PEI, at least for the formation of last few bilayers, to enhance membrane stability and selectivity for the dehydration of ethanol and isopropanol. For convenience, the membranes produced were designated based on the bilayers of the membrane and the polyelectrolytes used. For instance, Membrane $(PEI/PAA)_4/PEI$ means the membrane had 4 bilayers of PEI and PAA plus another PEI layer on the outmost surface, and Membrane $(PEI/PAA)_3/(CS/PAA)_4$ was formed from 3 cycles of alternative depositions of PEA and PAA, followed by 4 cycles of alternative depositions of chitosan and PAA. Figure 5.1 shows the chemical structure of chitosan.

When crosslinking was used to improve the membrane stability and selectivity, the membrane was deposited with either PEI or chitosan as the outmost layer, which was brought into contact with a 0.3 wt% aqueous glutaraldehyde solution for 2 h at ambient temperature. Afterwards, the membrane was thoroughly washed with de-ionized water.

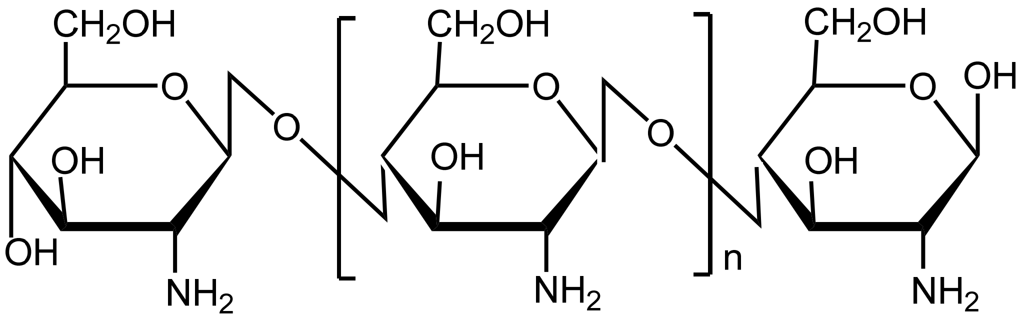

Figure 5. 1 Chemical structure of chitosan

5.2.3 Stability of polyelectrolyte layers against the solvents

To pinpoint the cause of relatively low selectivity of the PEI/PAA polyelectrolyte membranes on a polyamide substrate for dehydration of ethanol and isopropanol, the stability of the polyelectrolyte layers against the solvents was investigated. First, polyelectrolyte multilayers were fabricated on the inner surfaces of quartz cuvettes by 12 cycles of sequential depositions of PEI and PAA, with appropriate water rinses during the process, similar to the membrane formation procedure described above. Then, the cuvettes were filled with isopropanol and ethanol, separately. To see whether there was any dissolution or structural change in the polyelectrolyte bilayers by these solvents, the cuvettes were periodically emptied and filled with water quickly for absorbance measurements using a UV-Vis spectrophotometer. This allowed us to monitor the absorbance as a function of time of the solvent contact with the polyelectrolyte multilayers. As a comparison, another two cuvettes coated with polyelectrolyte multilayers were also allowed to contact ethylene glycol and water separately and the absorbance was monitored as well. In all absorbance measurements, the wavelength was set at 210 nm.

5.2.4 Hydraulic permeability of polyamide substrate and polyelectrolyte/polyamide composite membranes with solvent treatment

The hydraulic permeability of the polyamide substrate and the polyelectrolyte/polyamide composite membranes was measured to assess how the solvent would affect the membrane structure. The membranes were rinsed with de-ionized water, and then immersed in the solvents studied here (i.e., isopropanol, ethanol and ethylene glycol) for 24 h. Then membrane permeability to water was determined at various pressures. The surfaces of the membranes were examined before and after the solvent treatment. This, along with the above stability tests of polyelectrolyte layers, would help identify whether the low selectivity of PEI/PAA membranes for ethanol and isopropanol dehydration was due to the polyelectrolyte skin layers, the polyamide substrate, or both, so as to address the problems accordingly.

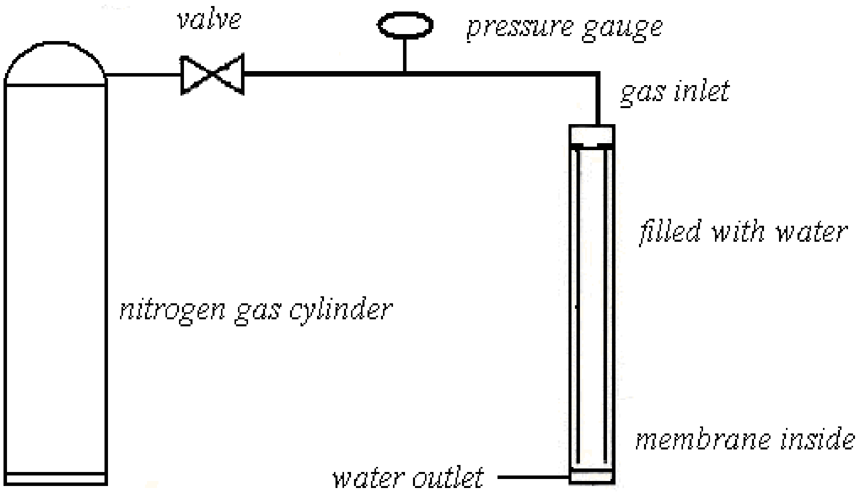

Figure 5. 2 Schematic diagram of the set up for measurement of the water flux

5.3 Results and Discussions

5.3.1 Pervaporation with polyelectrolyte/polyamide composite membranes

Figure 5.3 show the permeation fluxes of a polyelectrolyte/polyamide composite membrane comprising of 7 double layers of PEI and PAA for separation of water from aqueous solutions of ethanol, isopropanol and ethylene glycol at various feed water concentrations. As expected, with an increase in the feed water concentration, the permeation flux increased due to increased driving force for the permeation through the water-selective hydrophilic membrane. However, the total permeation fluxes for the dehydration of isopropanol and ethanol are more than two orders of magnitude higher than the permeation flux for ethylene glycol dehydration. While a high permeation flux is always desired, the membrane selectivity for dehydration of ethanol and isopropanol is rather limited. As shown in Figure 5.4, the separation factors for the separations of binary water/ethanol and water/isopropanol mixture were within 10 to 50 over the feed concentration range studied, which is much lower than that for the dehydration of ethylene glycol where a separation factor of over 410 was achieved.

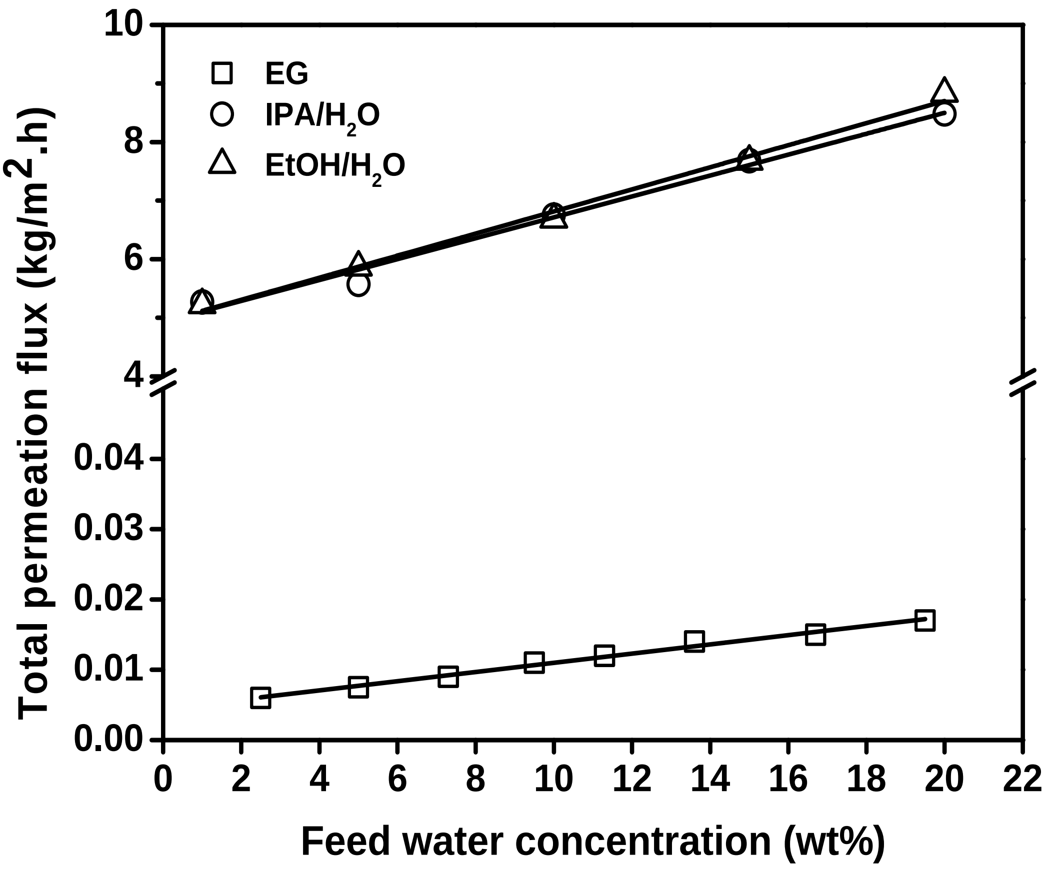

Figure 5. 3 Total permeation flux for separation of water from aqueous solutions of ethanol, isopropanol and ethylene glycol. Operating temperature, 25 °C.

Based on the solution-diffusion model for mass transfer in pervaporation [Feng and Huang, 1997; Bruschke, 2006; Baker, 2012], the mass transport across the membrane is governed by two steps: selective sorption onto the membrane surface and molecular diffusion through the membrane. For a given membrane, the diffusivity and solubility of a permeant are mainly determined by its molecular size and affinity to the membrane.

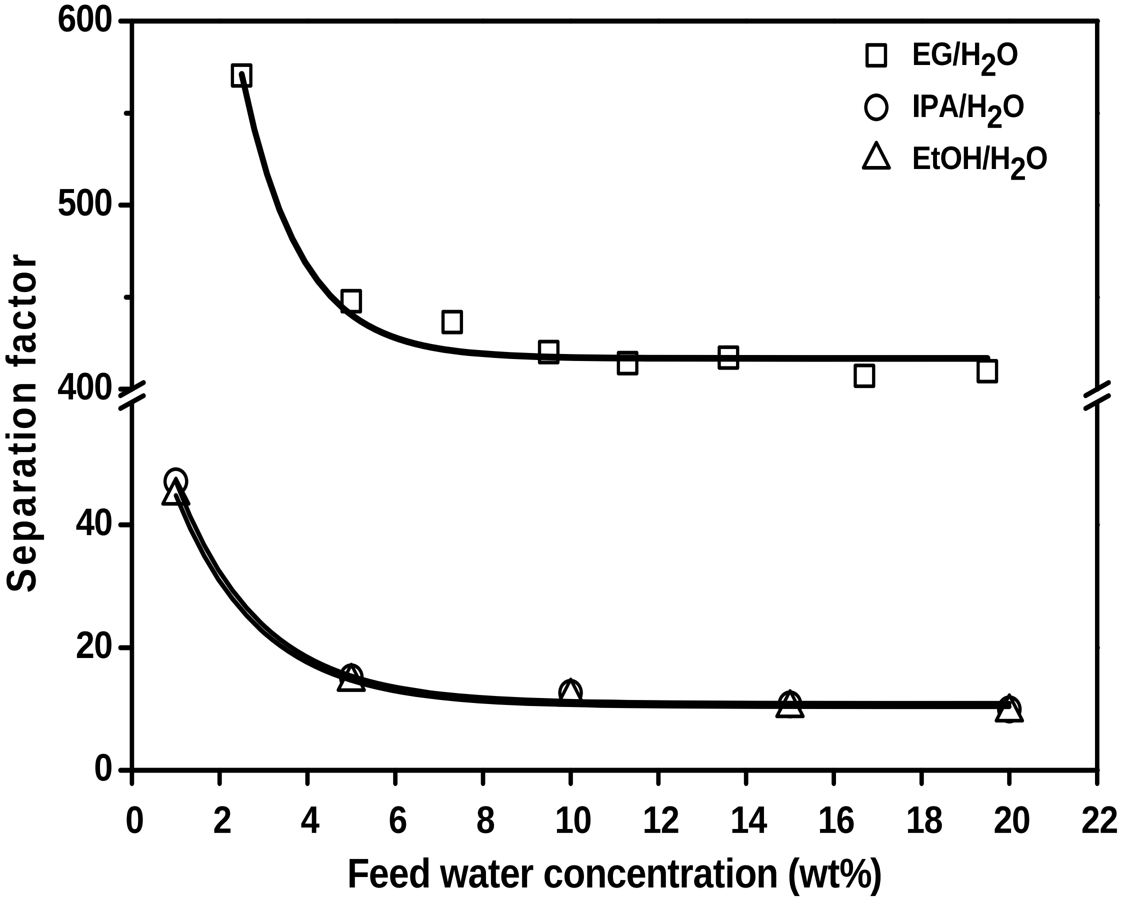

Figure 5. 4 Separation factor for dehydration of ethanol, isopropanol and ethylene glycol. Operating temperature, 25 °C.

Table 5.1 shows the equivalent molecular diameters and hydrogen bonding parameters of the permeating species in this study. Both the diol and alcohols considered (i.e., ethylene glycol, ethanol, and isopropanol) here are polar and hydroscopic solvents, but ethylene glycol has a stronger hydrogen bonding capacity than ethanol and isopropanol due to its two hydroxyl groups. This suggests that ethylene glycol would have a strong affinity to the hydrophilic polyelectrolyte membrane, which favors the solubility aspect of pervaporation transport of ethylene glycol. On the other hand, ethylene glycol and ethanol molecules have similar sizes. Therefore, based on the solubility and diffusivity considerations, the permeation fluxes for the dehydration of ethanol, isopropanol and ethylene glycol are not expected to be different by several orders of magnitude, unless the membrane is impaired by the permeant. In view of the substantially higher fluxes of the polyelectrolyte composite membrane for ethanol and isopropanol dehydration than the permeation flux for dehydration of ethylene glycol, it was reasonable to suspect the stability of the membrane against ethanol and isopropanol.

Table 5. 1 Molecular size and hydrogen bonding parameters of penetrant (25 °C)

	Molar volume (cm^3/mol)[a]	Molecular diameter (nm) [b]	Hydrogen bonding parameter [a] $(MPa)^{0.5}$
Ethanol	58.5	0.570	19.4
Isopropanol	76.8	0.624	16.4
Ethylene glycol	55.8	0.561	26.0
Water	18.0	0.385	42.3

[a] From Reference [Barton, 1983]

[b] Equivalent molecular diameter calculated from molar volume considering the molecules to be spherical

In what follows, the stability of the membrane in the solvents was to be investigated, and appropriate remedies would be developed to improve the separation performance of the polyelectrolyte membranes for ethanol and isopropanol dehydration.

5.3.2 Stability of polyelectrolyte multilayers, polyamide substrate, and polyelectrolyte/polyamide composite membranes against ethanol and isopropanol

5.3.2.1 Stability of polyelectrolyte multilayers against ethanol and isopropanol

Pristine polyelectrolyte multilayers were built up on the surface of cuvettes, which were filled with ethanol, isopropanol and ethylene glycol, respectively, for solvent contact with the films. The cuvettes were intermittently emptied and filled with water quickly for absorbance measurements using a UV-Vis spectrophotometer to monitor the absorbance as a function of the solvent contact time. As a base case for comparison, the polyelectrolyte multilayer was also contacted with water to monitor the absorbance with time. The results are presented in Figure 5.5.

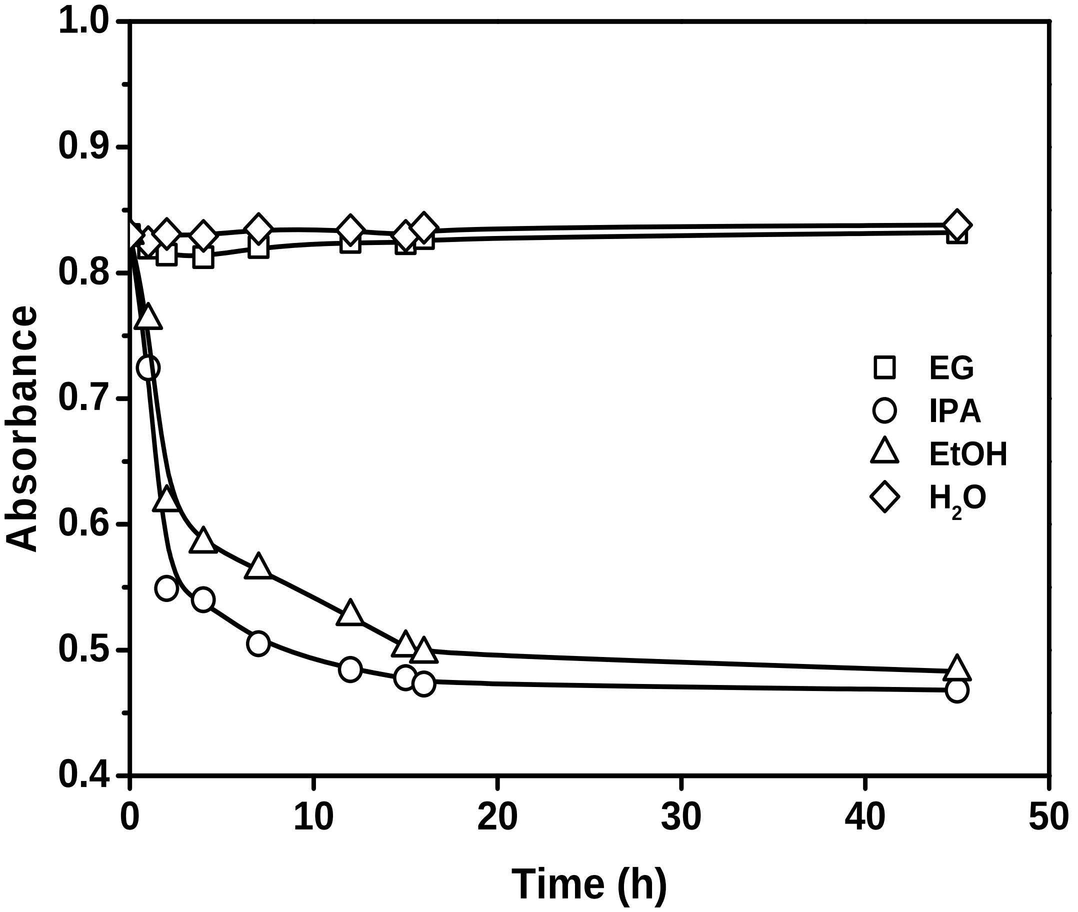

Figure 5. 5 Absorbance of polyelectrolyte multilayers formed on cuvette surfaces as a function of solvent contact time.

Clearly, there was no change in the absorbance when the polyelectrolyte multilayers contacted with ethylene glycol or water, confirming the good stability of the polyelectrolyte multilayers in water and ethylene glycol, in spite of their strong hydrogen bonding effects. However, when the polyelectrolyte multilayers were "treated" with ethanol and isopropanol, the absorbance decreased significantly. This seems to suggest that not all the polyelectrolyte macromolecules were bonded strongly enough by the electrostatic forces to maintain a cohesion of the self-assembly, and some of them were etched away by these solvents. This hypothesis is also supported by the hydraulic water permeabilities of the membranes, as discussed below.

5.3.2.2 Stability of polyamide substrate against ethanol and isopropanol

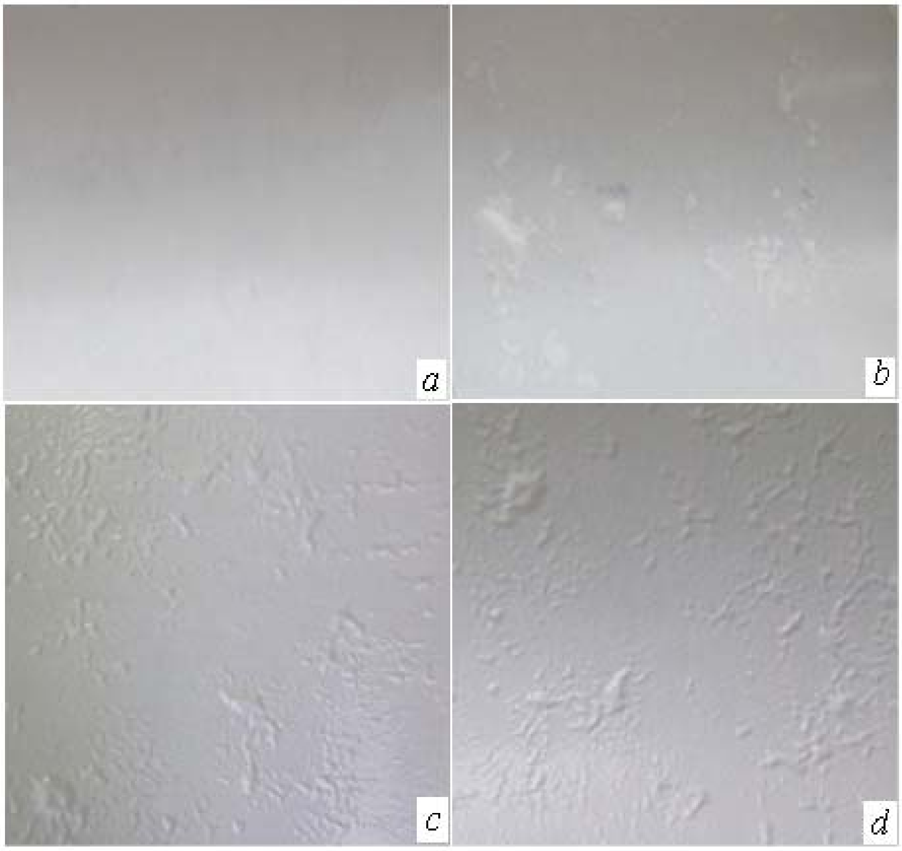

Figure 5. 6 Surface of polyamide substrate membrane after immersion overnight in (a) water, (b) ethylene glycol, (c) ethanol, and (d) isopropanol.

To look at the effects of the solvents on the stability of the polyamide substrate, its surface morphology was examined and hydraulic permeability to water was determined after being immersed in the solvents overnight. As shown in Figure 5.6, the polyamide substrate soaked in de-ionized water overnight had no visible change in the surface morphology, which was expected as the polyamide membrane was intended for uses in water treatment. However, after immersion in ethylene glycol, there were a few bulges on the substrate surface, while most of the substrate surface was still intact. When the polyamide substrate was immersed in ethanol or isopropanol, the membrane surface was seriously affected, with excessive local swelling and blistering occurred on the membrane surface. Isopropanol appeared to be more detrimental than ethanol in this regard. These observations are consistent with the hydraulic permeability of the polyamide membrane after immersion in the solvents overnight, as shown in Figure 5.7. The pure water permeability of the polyamide substrate membrane was increased after exposure to isopropanol, ethanol and, to a lesser extent, ethylene glycol. Here again isopropanol was shown to have the most significant impact on the hydraulic permeability of the membrane, and up to a 45% increase in water permeability was observed after the membrane contacted isopropanol overnight. However, even under the "abusive" conditions of contacting with pure solvents, the membrane structure did not collapse; otherwise a much higher hydraulic permeability would be observed in view of the interfacially polymerized ultrathin surface layer of the polyamide substrate membrane.

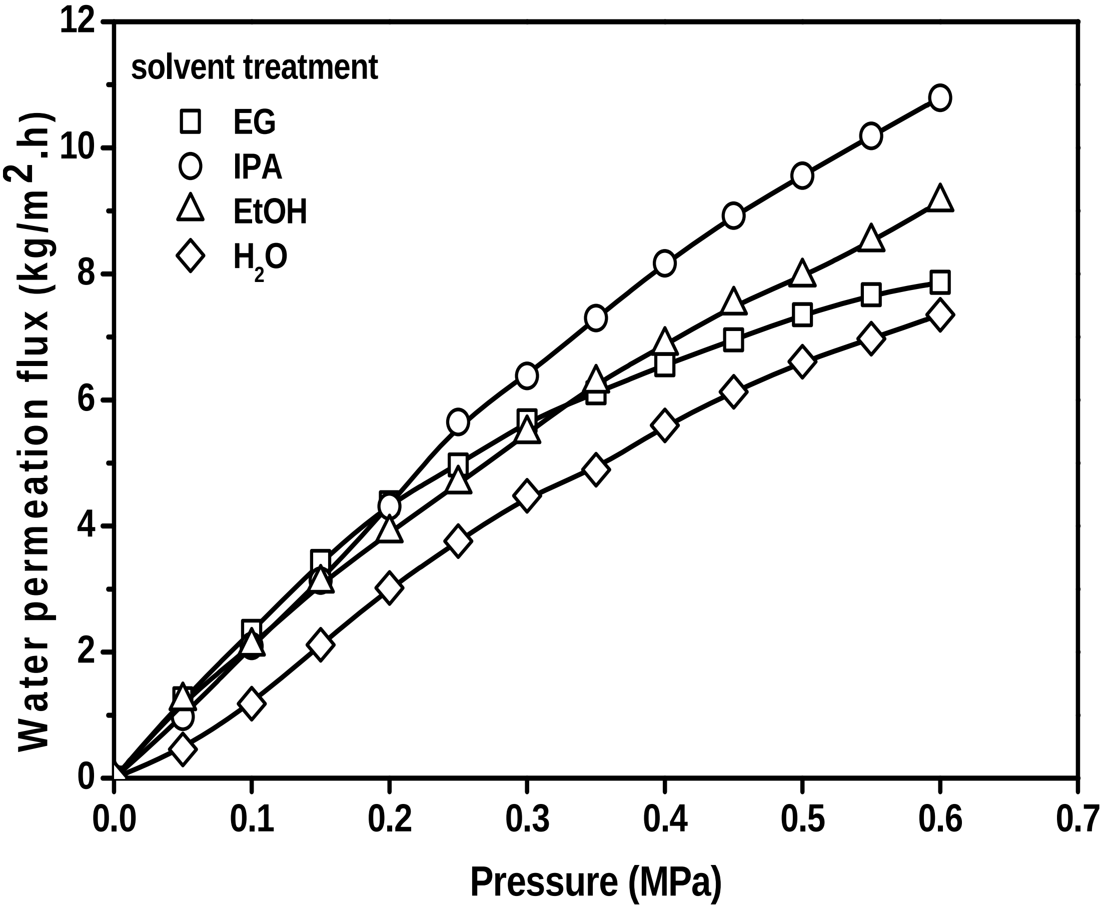

Figure 5. 7 Hydraulic permeability of the polyamide substrate membrane to water after immersion overnight in water, ethylene glycol, ethanol, and isopropanol.

To have a better understanding about the interactions between the solvent molecules and the polyamide substrate, their solubility parameters are presented in Table 5.2. In principle, when the solvent-polymer interaction is dominant over the cohesive force of the polyamide macromolecules, the polymer will swell or dissolve in the solvent. Based on the solubility parameter theory, if the solubility parameter of a solvent and a polymer are close enough, the polymer could be swollen by or dissolved in the solvent. The difference in the solubility parameters between polyamide and isopropanol is the smallest, followed by ethanol, ethylene glycol and water. It is thus unsurprising that the polyamide substrate was adversely affected by isopropanol and ethanol.

Table 5. 2 Solubility parameters (25 °C)

	Solubility Parameter $(\mathrm{MPa})^{0.5}$
Ethanol	26.5 [a]
Isopropanol	23.5 [a]
Ethylene glycol	32.9 [a]
Water	47.8 [a]
Aromatic polyamide	23.1 [b]; 18.4-28.6 [c]

[a] **Reference [Barton, 1983]**
[b] **Reference [Aharoni, 1992]**
[c] **Reference [Arshady, 1989]**

5.3.2.3 Stability of polyelectrolyte/polyamide membrane against ethanol and isopropanol

It may be mentioned that in solvent dehydration by pervaporation, the polyamide substrate does not contact the feed solution (where water is normally the minor component) directly. If the polyelectrolyte skin layer can adequately function as a barrier to the permeation of the solvent, the underneath polyamide substrate will be protected. It has been revealed that the polyamide substrate is not stable in isopropanol, ethanol and ethylene glycol, while the polyelectrolyte multilayer is not resistant to ethanol and isopropanol but stable in ethylene glycol. This explains why the polyamide/polyelectrolyte composite membranes performed well for the dehydration of ethylene glycol but did not work well for the dehydration of ethanol and isopropanol. This was substantiated further with hydraulic water permeability tests on the composite membranes before and after contact with the solvents (i.e., ethanol, isopropanol, and ethylene glycol) overnight, as well as the examinations of the membrane surface.

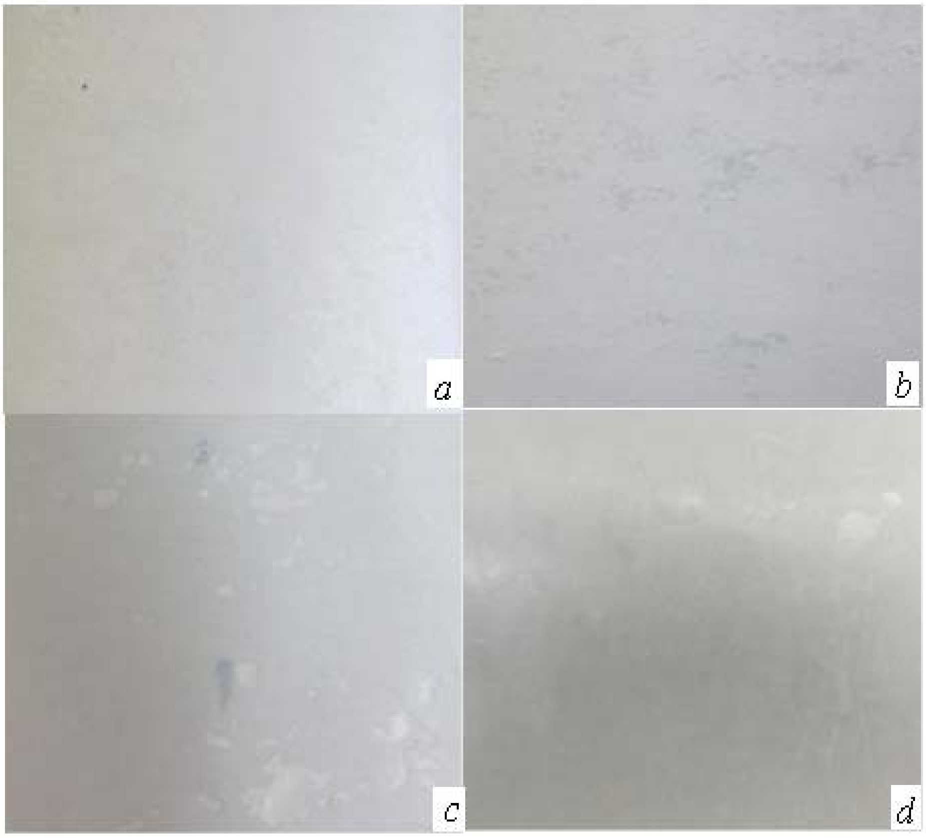

Figure 5. 8 Surfaces of pristine polyamide/polyelectrolyte composite membranes comprising of 5 double layers of PEI/PAA (i.e., membrane $(PEI/PAA)_5$) after contacts with solvents overnight. (a) water, (b) ethylene glycol, (c) ethanol, (d) isopropanol.

Figure 5.8 shows the surface morphologies of the pristine composite membranes after exposure to the solvents. There was no change on the membrane surface after immersion in water. After the membrane was immersed in ethylene glycol, the bulging of the membrane surface was significantly reduced as compared to the polyamide substrate membrane. This suggests that the polyelectrolyte multilayer did help to shield the interior polyamide substrate layer from attack by ethylene glycol. This is consistent with the fact that the polyamide/polyelectrolyte composite membranes can separate ethylene glycol/water effectively by pervaporation. However, when exposed to ethanol and isopropanol, the barrier function provided by the polyelectrolyte multilayer to protect the polyamide membrane was insufficient, and small blisters were still observed on the membrane surface, which would affect the membrane selectivity in pervaporation. Figure 5.9 shows the changes in the hydraulic water permeability of the membranes after immersion in the solvents for single-side and double-side deposition. The pristine composite membrane coated with 5 double polylectrolyte layers exhibited a hydraulic permeability approximately 50% lower than the hydraulic permeability of the polyamide substrate, indicating that the polyelectrolyte surface layer indeed exerted a considerable resistance to permeation. After immersion in ethylene glycol, the hydraulic water permeability of the composite membrane was essentially the same at a pressure below 0.3 MPa, and an up to 20% increase in the membrane permeability was noticed at higher pressures. However, when the membrane was immersed in isopropanol and ethanol, the hydraulic water permeability of the composite membrane was almost the same as that of the polyamide substrate alone. This confirms that the polyelectrolyte multilayer was destroyed by isopropanol and ethanol. As a result, such a membrane in its present form is deemed to be not very selective for removal of water from ethanol and isopropanol by pervaporation at relatively high alcohol concentrations in the feed. Note that composite membranes with two deposition methods showed almost the same tendacy of hydraulic water permeability. However, the membrane with double side-deposition has lower hydraulic water permeability than that of single-side deposition which indicates that double-side deposition provides larger resistance for permeating molecules and permeation flux is consequently reduced.

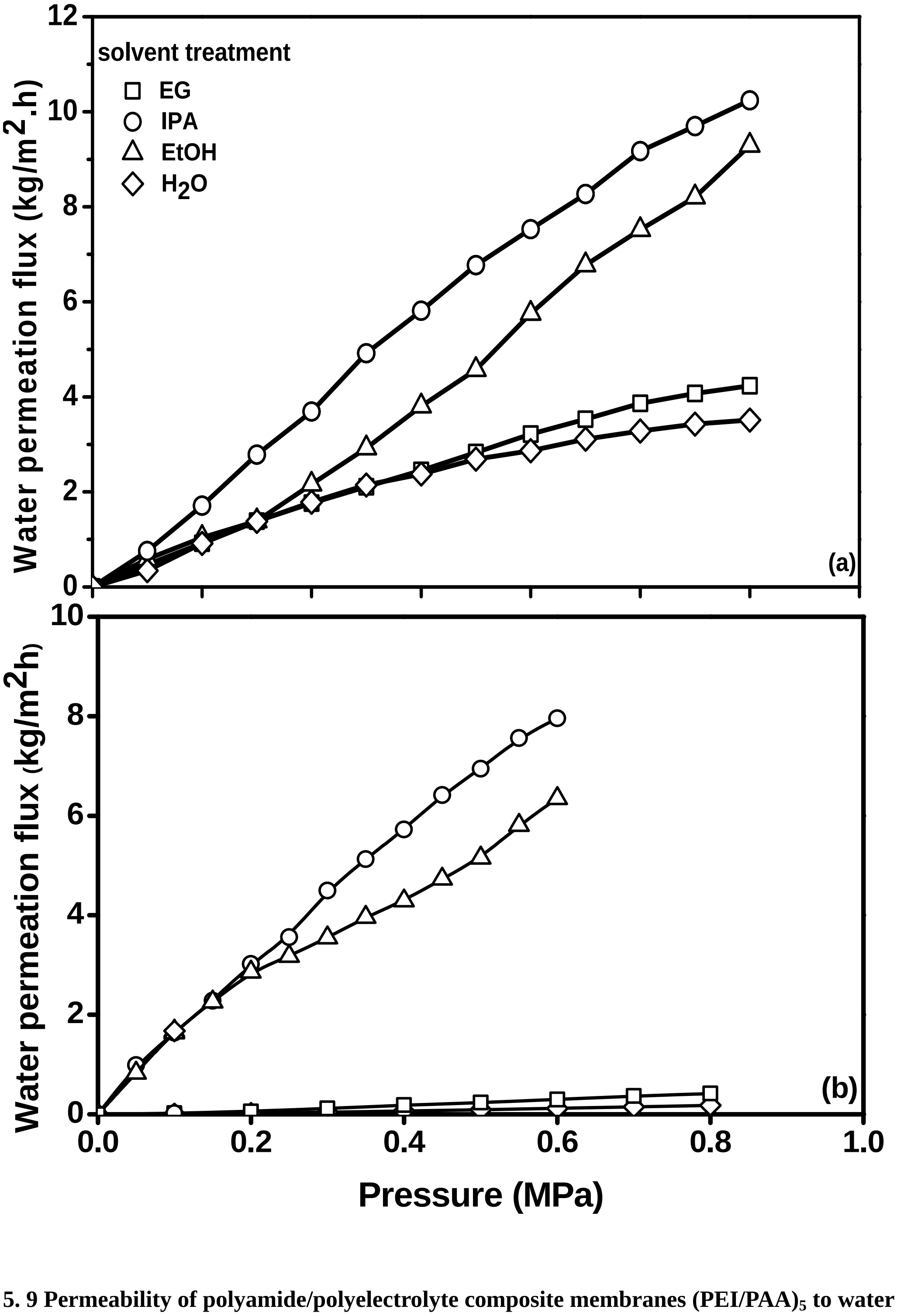

Figure 5. 9 Permeability of polyamide/polyelectrolyte composite membranes $(PEI/PAA)_5$ to water after immersion overnight in water, ethylene glycol, ethanol and isopropanol (for single-side (a) and double-side (b) deposition).

It may be mentioned that the polyelectrolyte macromolecules were attached to the polyamide substrate surface by electrostatic force and hydrogen bonding, and there was no physical anchoring as the macromolecules could not set inside the substrate. Zhu et al. [2006] reported PEI and PAA polyelectrolyte membranes for isopropanol dehydration using a hydrolyzed ultrafiltration polyacrylnitrile membrane (MWCO 20,000-30,000) as the substrate. If the substrate were microporous with proper sizes for the macromolecules to attach on the pore walls, the anchoring effect will be helpful to the membrane stability.

5.3.3 Improvement of polyelectrolyte multilayered membrane for dehydration of alcohols

After the root cause for the relatively low selectivity of the membranes for ethanol and isopropanol dehydration was identified, attempts were made to improve the membrane performance. Two approaches were used to improve the chemical stability of the membranes without a substantial sacrifice in permeation flux: one was to use surface cross-linking to stabilize the surface polyelectrolyte layer and the other was to restructuring the membrane by substituting PEI with chitosan in the outmost polyelectrolyte layers for stronger electrostatic interactions between the oppositely charged polyelectrolytes.

It is well known that PEI, which contains chemically reactive amino groups, can be crosslinked by aldehydes for various applications [Chanda and Rempel, 1995; Chanda and Rempel, 2001; Devi et al., 2007; Farber et al., 2010; Liu and Huang, 2011; Xia et al., 2011]. Figure 5.10 illustrates crosslinking of PEI with glutaraldehyde. Polyelectrolyte/polyamide composite membranes comprising of 7.5 double layers of PEI/PAA where the outmost polyelectrolyte layer was PEI, were surface crosslinked by glutaraldehyde, and the membranes (denoted as $(PEI/PAA)_7PEIx$, where x represents crosslinking of the outmost layer PEI) were tested for alcohol dehydration.

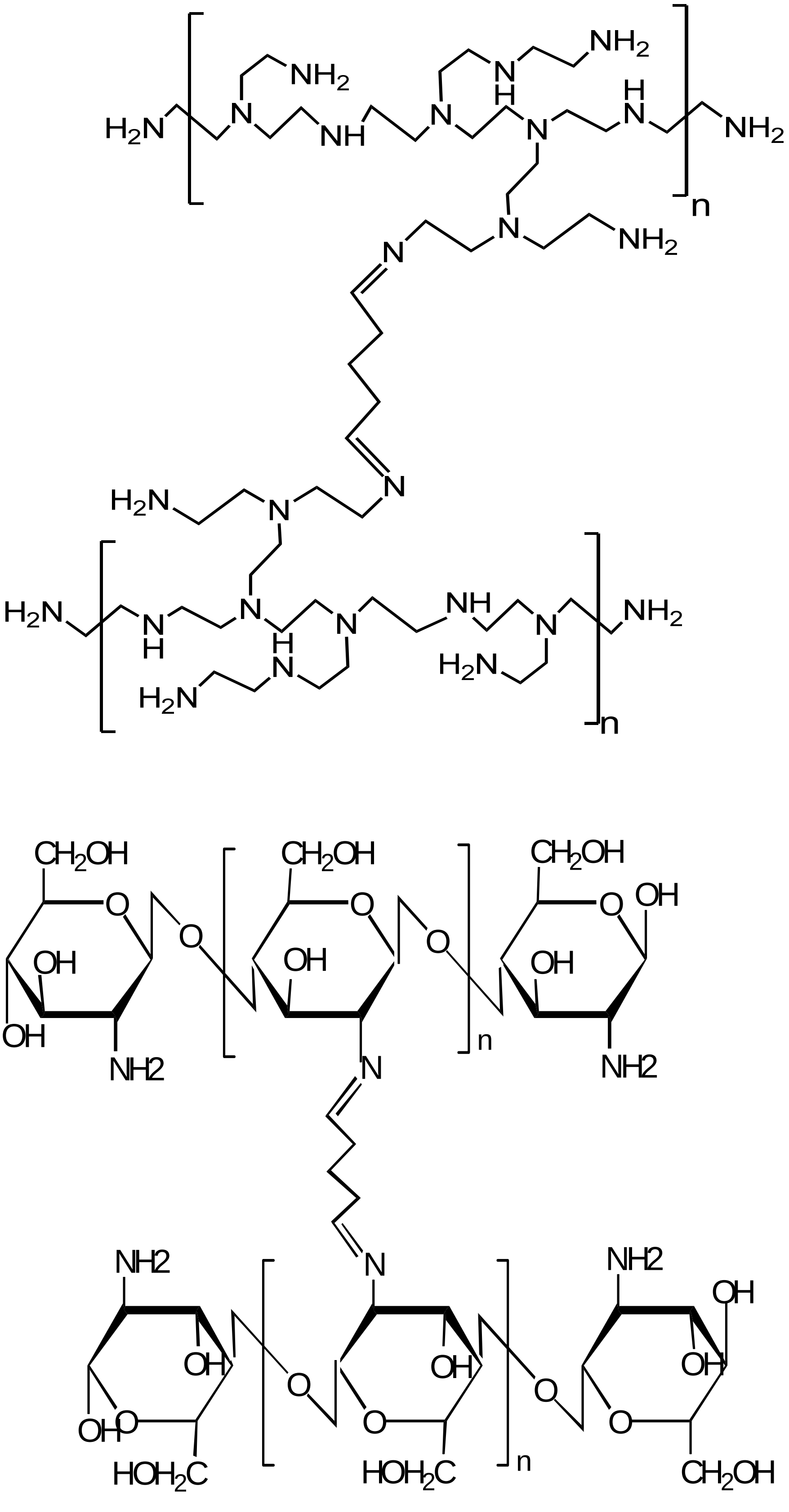

Figure 5. 10 Schematic of crosslinking of PEI and chitosan with glutaraldehyde

The total permeation fluxes and separation factors of the membranes are shown in Figures 5.11 and 5.12 for the dehydration of isopropanol and ethanol, respectively. As a comparison, the performance of membrane $(PEI/PAA)_7$ without crosslinking was also presented in the figures.

The separation factors were almost tripled by the crosslinking for both dehydration of both isopropanol and ethanol. Account should be taken of the fact that cross-linking often reduces the permeation flux, and this loss appears to be necessary to ensure membrane stability. Although there was a 42-57% reduction in the permeation flux over the feed concentration range tested, the crosslinked membrane still had a very high permeation flux (on an order of a few $kg/m^2 \cdot h$). This suggests that surface crosslinking is effective to improve the selectivity of the polyelectrolyte/polyamide composite membranes by forming a stable barrier skin to protect the interior structure of the membrane. In the meantime, the outmost skin layer became more selective after crosslinking, which also contributed to the permselectivity of the membrane. Please note that the crosslinking was not carried out under optimized conditions and these results were mainly for proof of concept purposes. When the crosslinking conditions are optimized, which is a subject of further studies but beyond the scope of this work, a further enhancement in the membrane selectivity is expected.

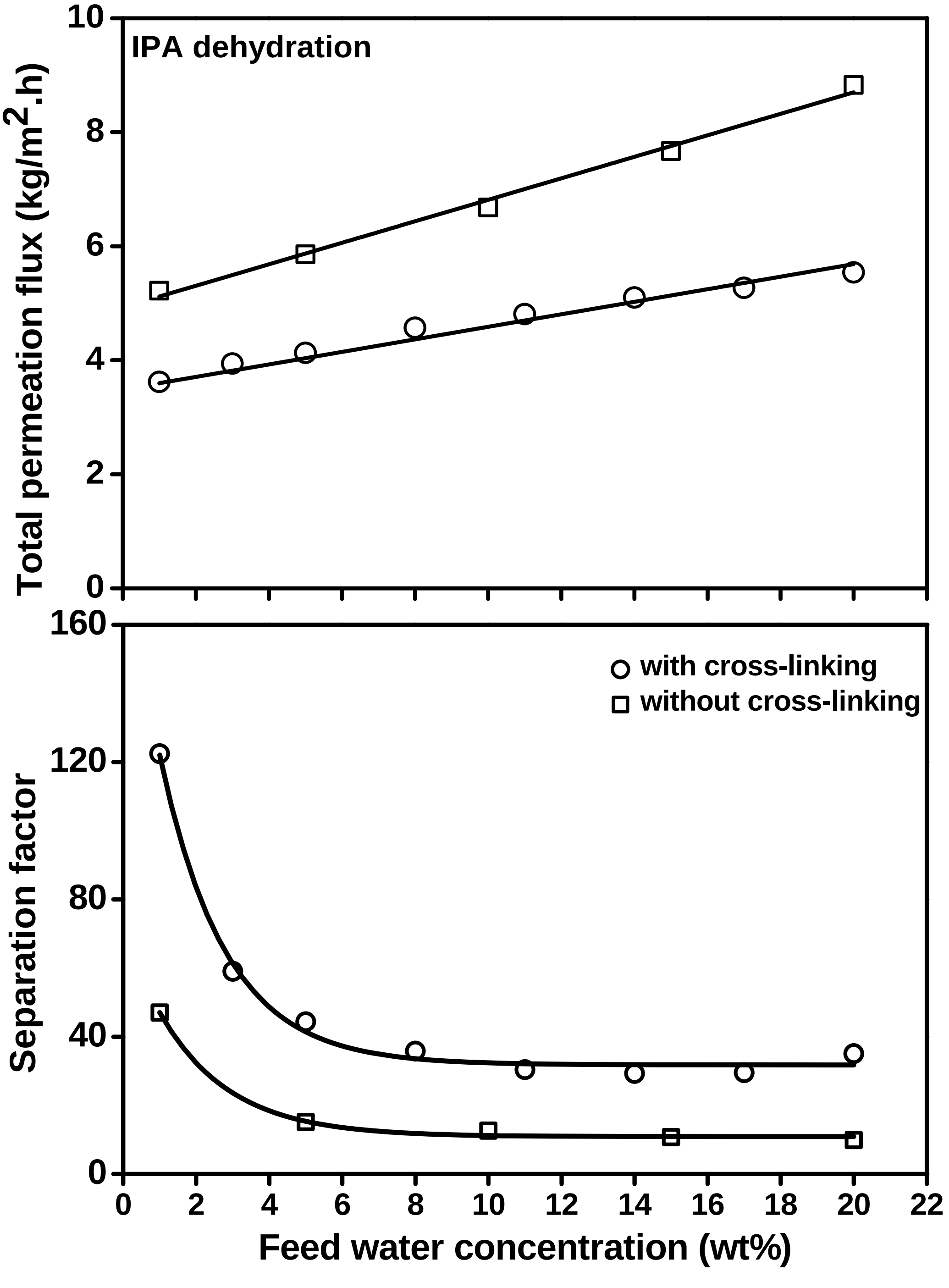

Figure 5. 11 Effect of surface crosslinking on membrane performance for isopropanol dehydration. Operating temperature, 25 °C.

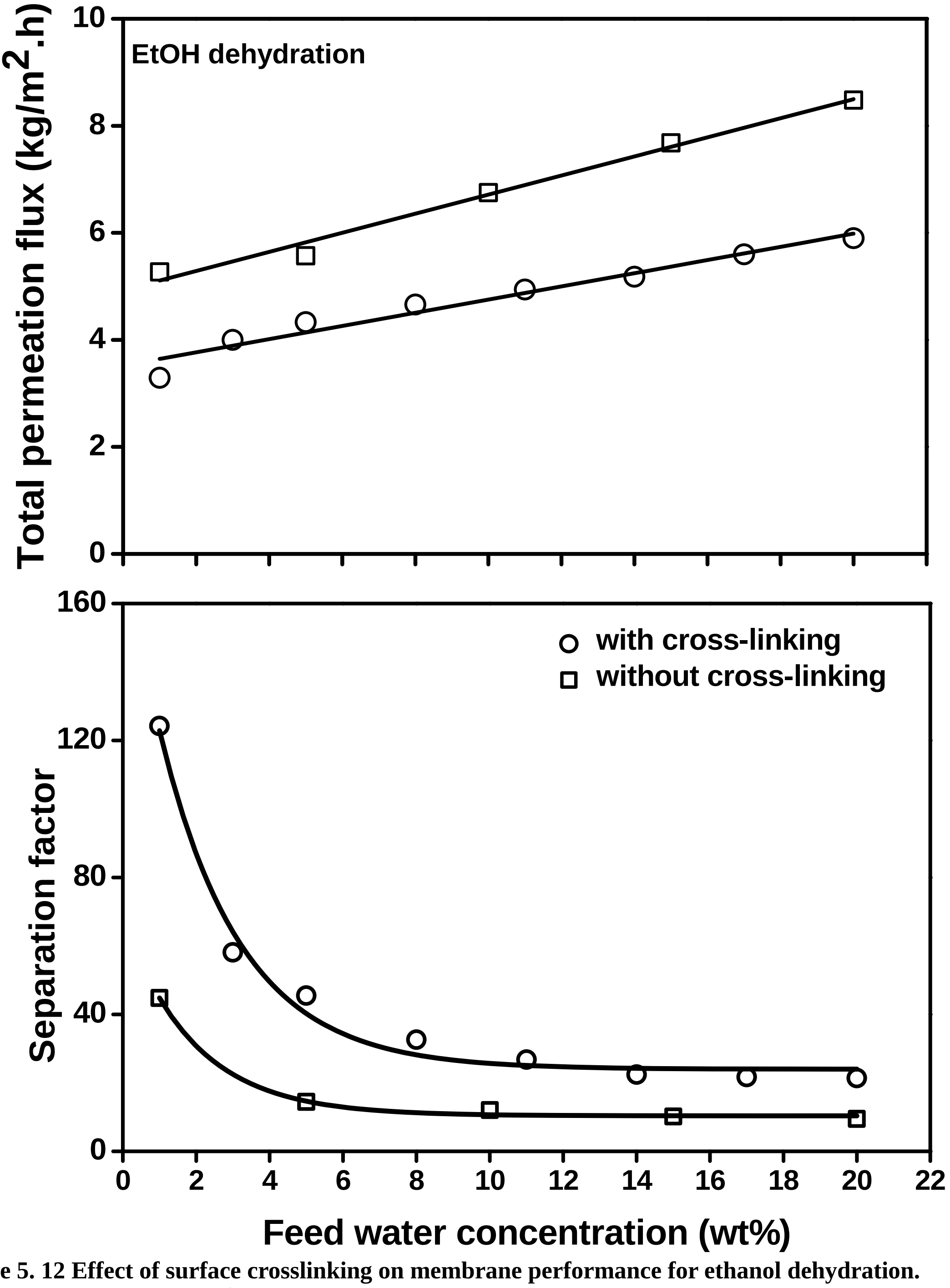

Figure 5. 12 Effect of surface crosslinking on membrane performance for ethanol dehydration. Operating temperature, 25 °C.

Chitosan is a unique polysaccharide with ample amine and hydroxyl groups that offers a high potential for chemical modifications. Chitosan, insoluble in water in its free amine form, can be dissolved in dilute acetic acid solutions through partial protonation of the amine groups on the C-2 position of its D-glucosamine repeat unit, thereby converting to a polyelectrolyte. The protonated chitosan (i.e., chitosanium) is a stronger polycation than PEI. Chitosan (in both protonated and free amine forms) can be crosslinked readily by aldehydes. A schematic of crosslinking of chitosan with glutaraldehyde is also presented in Figure 5.9. There is a great deal of work reported in the literature about crosslinked chitosan for a broad range of applications (see for example, [Zielinska t al., 2011; Dashtimoghadama et al., 2010; Yang and Chiu, 2012; Xiong and He, 2012; Liu et al., 2012; Wang et al., 2010]). This prompted us to progressively substitute PEI with chitosan for the last polyelectrolyte layers in membrane fabrication. To demonstrate the viability of this approach, a series of membranes having different number of chitosan layers (starting from the outmost layer) but with a fixed total of 7.5 double layers were prepared and tested, and the results are shown in Figures 5.13 and 5.14 for the dehydration of isopropanol and ethanol, respectively. Membrane $(CS/PAA)_7CSx$, assembled using chitosan and PAA only, represents an extreme case where PEI is completely replaced with chitosan. As a base case, the performance of membrane $((PEI/PAA)_7PEIx)$ was also presented for easy comparison.

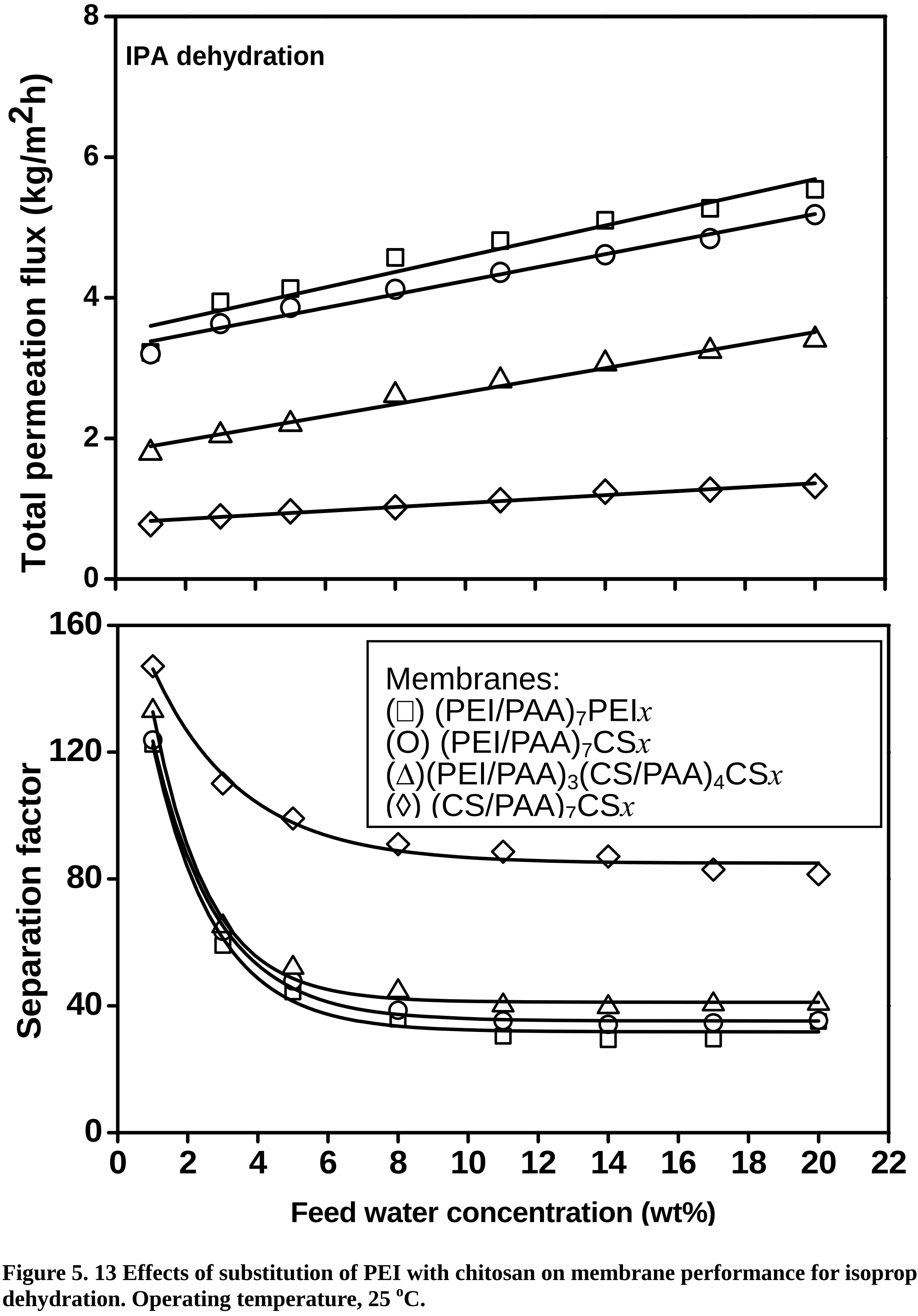

Figure 5. 13 Effects of substitution of PEI with chitosan on membrane performance for isopropanol dehydration. Operating temperature, 25 ^{o}C.

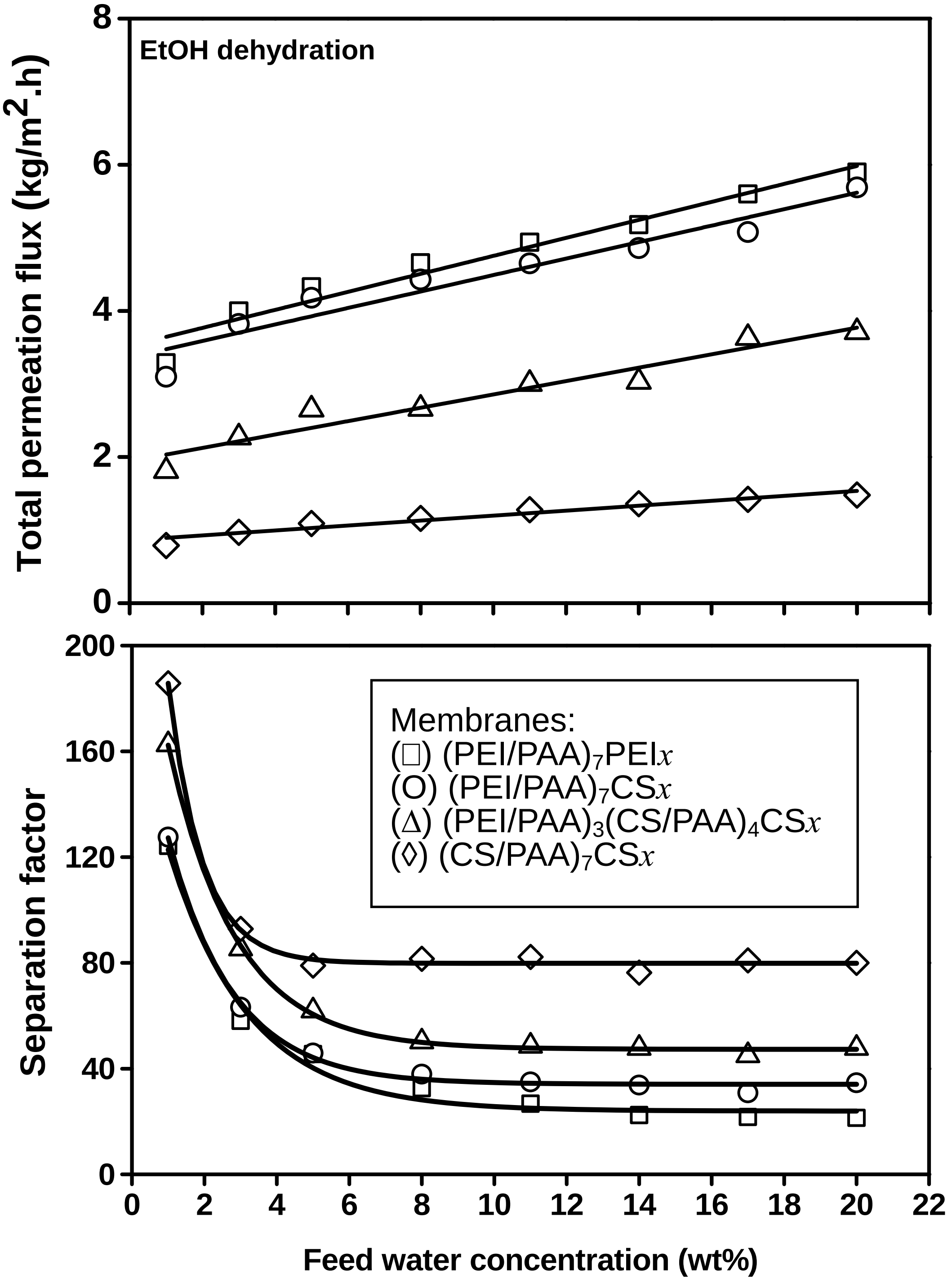

Figure 5. 14 Effects of substitution of PEI with chitosan on membrane performance for ethanol dehydration. Operating temperature, 25 °C.

It is clear that as PEI was gradually substituted with chitosan, the membrane became more permselective, and the membrane selectivity reached a maximum when the PEI/PAA bilayers were all replaced by chitosan/PAA pairs. In the meantime, the permeation fluxes of the membranes showed an opposite trend. That the CS/PAA-based polyelectrolyte/polyamide composite membrane was more selective for isopropanol and ethanol dehydration than the PEI/PAA counterpart can be explained from the following aspects. PEI and PAA are nonionized weak polyacid and polybase, respectively. The PEI/PAA complexes are formed due to transfer of protons to give the polyions [Plate, 1976; Molyneux, 1984], and the polymer pairs in the polyeletrolyte complexes are held together under electrostatic and hydrogen bonding effects. Partially protonated chitosan is a stronger polycation than PEI. In the case of chitosan/PAA system, not only is the intermolecular electrostatic attractions stronger, the presence of the ionic charges will also enhance the strength of the hydrogen bonds formed to reinforce the polyelectrolyte complex [Molyneux, 1984], making the membrane assembly more discretional to diffusion of permeant. On the other hand, the solubility parameters of chitosan and PEI can be estimated from the van Krevelen group contribution method to be 48 $(\mathrm{MPa})^{0.5}$ [Ravindra et al., 1998] and 22 $(\mathrm{MPa})^{0.5}$ [Matsuura, 1994], respectively. The difference in the solubility parameter between chitosan and ethanol (or isopropanol) is a greater than the difference in the solubility parameters between PEI and the corresponding alcohols. This suggests that the chitosan/PAA pairs are less favorable to the alcohol permeation than PEI/PAA pairs from a solubility standpoint, which favors the membrane selectivity for dehydration of alcohols.

These surface crosslinked membranes were found to be stable for the alcohol dehydration, and there was little change in the membrane performance for continuous operation of pervaporation over a period of more than one month. Ideally, in order to achieve a high flux, the chemical crosslinking should occur on the outmost surface layer of the membrane. However, as each self-assembled polyelectrolyte bilayer is very thin (about 0.5-3 nm [Decher, 1997]), it is inevitable that the crosslinking agent will penetrate to the interior as well, and proper control of the crosslinking conditions will thus be important in optimizing the membrane performance. This is especially advantageous from a practical membrane manufacturing point of view as a much larger number of polyelectrolyte depositions (e.g., 60-90) (see [Zhu et al., 2006]) are often needed when conventional microporous substrates are used, which represents substantial time required for membrane formation.

5.4 Conclusions

Thin film composite membranes comprising of LbL polyelectrolyte assembly on top of interfacially polymerized polyamide substrate were prepared using PEI/PAA and chitosan/PAA polyelectrolyte pairs. The membrane performances for the dehydration of ethylene glycol, ethanol and isopropanol were studied. The following conclusions can be drawn from this research:

(1) The composite membranes based on PEI/PAA complexes showed good performance for dehydration of ethylene glycol, but the membrane performance was less satisfactory for the dehydration of ethanol and isopropanol at relatively high feed alcohol concentrations. This prompted us to inverstigate the stability of the PEI/PAA polyelectrolyte bilayers and the polyamide substrate in the solvents so as to develop a remedy to solve the problem.

(2) The polyamide substrate could be swollen significantly by isopropanol and ethanol. When contacting isopropanol and ethanol, the PEI/PAA polyelectrolyte bilayer on top of a polyamide substrate could not function as an effective barrier to the permeation of the alcohols, resulting in a high flux but a low selectivity for dehydrating the alcohols.

(3) The stability and selectivity of the composite membranes for dehydration of ethanol and

isopropanol were improved by crosslinking of the outmost PEI layer. A further improvement in the membrane selectivity was accomplished by substituting PEI with partially protonated chitosan in the last few polyelectrolyte bilayers during membrane fabrication.

(4) It was demonstrated that using interfacially polymerized polyamide membrane as a substrate, self assembled polyelectrolyte composite membranes with less than 8 bilayers can be fabricated for dehydration of ethylene glycol, ethanol and isopropanol, and structuring manipulation of the outer layers and chemical crosslinking are effective to enhance membrane stability.

Chapter 6

Crosslinked chitosan/PAA polyelectrolyte composite membranes for isopropanol and ethanol dehydration

6.1 Introduction

Dehydration of isopropanol is a great challenge not only because of the price of isopropanol and its use in various industries, but also because of the difficulty to separate azeotropes and close boiling liquids, isomers or temperature-sensitive liquid mixtures by distillation [Zhu et al., 2007; Moon et al., 1999]. Isopropanol is one of the important alcohols and has been widely used in the chemical and pharmaceutical industries. It is generally used as solvent and chemical intermediate. It is also used in many everyday products such as paints, inks, general-purpose cleaners, and ingredients in cleaners, especially in modern semi-conductor and electronic industries [Nam et al., 1999; Choudhari et al., 2007; Liu et al., 2005; Logsdon, 2000; Svang-Ariyaskul et al., 2006]. Therefore, fabricating membranes to separate isopropanol/water with a high permeation flux, a high separation factor, and good thermal and mechanical stability is important for industrial applications.

In a previous study, polyelectrolyte/polyamide composite membranes fabricated by PEI/PAA were not very capable of dehydrating isopropanol, which was attributed to the instability of the membranes in isopropanol solvent. Since polyelectrolyte/polyamide composite membranes have poor stability for isopropanol dehydration, the membrane should be insolubilized by modification such as crosslinking to improve the stability of the membrane in aqueous solutions [Zhang et al., 2013]. Generally speaking, chemical crosslinking is a routine method to improve solvent resistance of common polymeric membranes, and the crosslinking can be done by immersing the membrane in a crosslinking reagent [Beppu et al., 2007; Devi et al., 2005; Okamoto et al., 1999; Liu et al., 2011], or by blending the crosslinking agent with the casting solution [Zhang et al., 2007; Huang and Yeom, 1990; Chen et al., 2008; Zielinska et al., 2011].

In these studies, the swelling of crosslinked membranes in solvent was significantly depressed, improving both the stability and selectivity of the membranes. Sullivan and Bruening [2005] used alternating polyelectrolyte depositions with covalent interlayer crosslinking, and a permeation flux of 2 kg/(m^2·h) and a separation factor of 500 were obtained for dehydration of ethanol at a feed water concentration of 10 wt%. Huang et al. [1999] found that structural stability of chitosan/polysulfone composite membranes was improved when using glutaraldehyde and H_2SO_4 as crosslinking agents. In addition, the separation factor increased with a sacrifice in the permeation flux.

In this study, chitosan (CS) was used as the cationic polyelectrolyte to replace PEI for forming polyelectrolyte multilayers with PAA on the polyamide substrate, followed by crosslinking with glutaraldehyde to improve the stability of the membrane for isopropanol and ethanol dehydration. It has been shown in Chapter 5 that by gradually replacing PEI with CS, the resulting membranes became more stable. This motivated us to completely replace PEI with CS in membrane fabrication using LbL self-assembly. The effects of operating conditions such as feed water concentration, number of deposited polyelectrolyte double layers and the operating temperature were investigated. Furthermore, the effects of the concentration of crosslinking agents, the crosslinking reaction time, and the crosslinking reaction temperature on the membrane performance were also investigated in the present work. Unless specified otherwise, the membrane fabrication conditions were: polyelectrolyte concentration in the deposition solution, 0.02 monomol/L; deposition time, 30 min; deposition temperature, 25 °C.

6.2 Experimental

All materials and chemicals were the same as mentioned in Chapter 5.

6.3 Results and discussion

6.2.1 Effect of feed water concentration on membrane performance

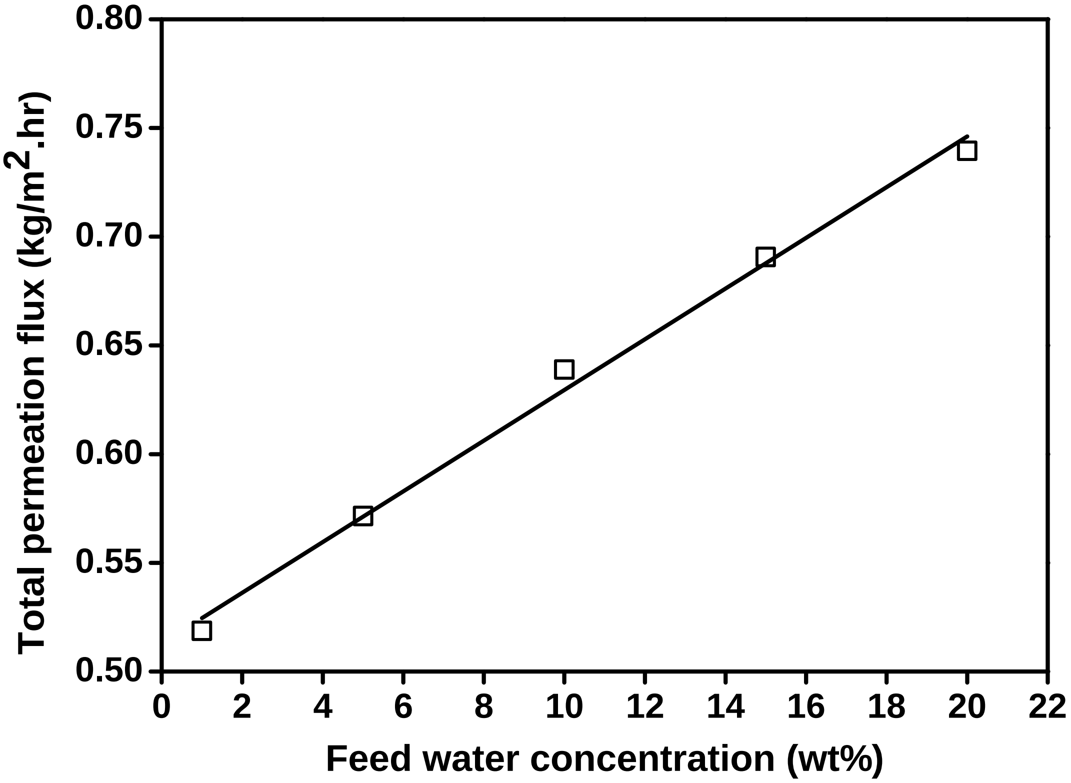

Figure 6. 1 Total permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membrane $(CS/PAA)_7CSx$. Operating temperature, 25 °C.

To study the membrane performance for isopropanol dehydration by pervaporation, glutaraldehyde crosslinked polyelectrolyte/polyamide composite membranes fabricated by CS and PAA with 7.5 double layers ($(CS/PAA)_7CSx$) were prepared. Notice that 7.5 double layers on the membrane mean that the membrane was fabricated with 7 CS/PAA double layers plus one CS layer as the topping layer. It is generally observed that the permeation flux increases with an increase in the concentration of preferentially permeable component in the feed but the selectivity decreases due to high swelling of the membranes [Nguyen et al., 1983; Guan et al., 2006]. As shown in Figure 6.1, with an increase in feed water concentration, the total permeation flux increased. This is consistent with prior work reported in the literature for dehydration of aqueous organic mixtures through hydrophilic membranes [Hyder et al., 2009]. This can be explained in terms of the plasticization effect of water on the membrane. At a higher feed water concentration, the membrane becomes swollen more significantly, and the polymer chains become more flexible, resulting in an increase in the interaction between water molecules and the membranes [Guan et al., 2006].

Figure 6.2 shows the partial permeation fluxes of isopropanol and water through the membrane. For membranes with 7.5 double layers, the partial permeation fluxes of water are 0.35 and 0.70 $kg/(m^2 \cdot h)$ at water concentrations of 1 and 20 wt% in the feed, respectively. However, the permeation flux of isopropanol tends to decrease. For instance, at a feed water concentration of 3 and 20 wt%, the fluxes of isopropanol are 0.169 and 0.035 $kg/(m^2 \cdot h)$, respectively. This is easy to understand because the driving force for isopropanol permeation decreases with an increase in water concentration in the feed [Zhang et al., 2007].

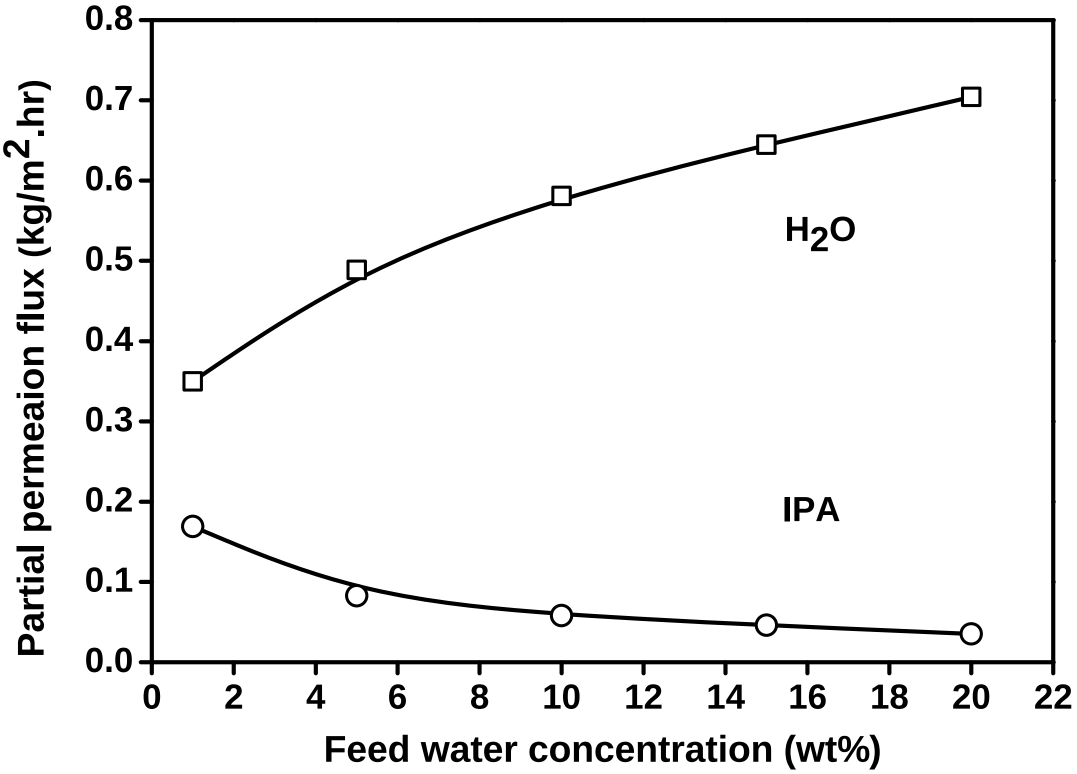

Figure 6. 2 Partial permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membranes $(CS/PAA)_7CSx$. Operating temperature, 25 °C.

Water has a smaller molecular size than isopropanol and can thus diffuse through the membrane easier [Huang et al., 1999; Hyder et al., 2009]. Generally speaking, an increase in permeation flux is often accompanied with a reduction in the selectivity. This is shown in the Figure 6.3, where the separation factor for isopropanol dehydration is found to decrease with an increase in the feed water concentration due to swelling of the membrane by water.

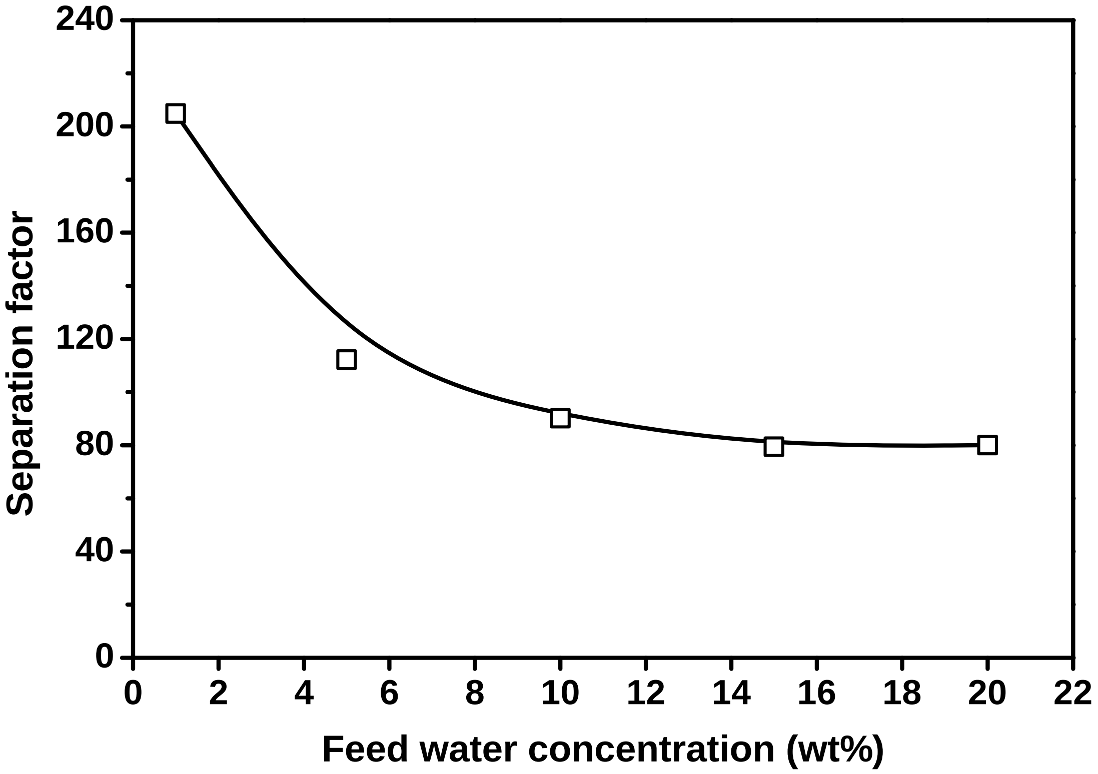

Figure 6. 3 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes (CS/PAA)$_7$CS*x*. Operating temperature, 25 ^{o}C.

6.2.2 Effect of number of double layers on membrane performance

Membranes with different number of double layers (5.5, 7.5, 9.5 and 15.5) were prepared and tested for isopropanol dehydration at room temperature at feed water contents of from 1~20 wt%. As shown in Figure 6.4(a), with an increase in the number of double layers, the total permeation flux decreases dramatically from 3.64 to 0.41 kg/ ($m^2 \cdot h$) when the number of double layers increased from 5.5 to 15.5 for a feed water concentration of 5.0 wt%. This is easy to understand as the number of double layers increases, the effective thickness of the separating layer of membrane increases. Therefore, the resistance for the permeant to pass through the membrane also increases. The membrane is more selective as the polyelectrolyte layer become thicker, and thus the concentration of water in the permeate is increased accordingly [Xu et al., 2010]. Figure 6.4(b) shows the permeate water concentration. It shows that the water concentration in permeate increased with an increase in the number of double layers that were mainly responsible for selective permeation of water. Note that the total permeation flux decreased drastically when the number of double layers increased from 5.5 to 7.5, and then the decreasing trend was less siginificant with a further increase from 7.5 to 15.5. In addition, with 7.5 polyelectrolyte double layers, the water concentration in the permeate could reach 91.63 wt% at a feed water concentration of 11 wt%, and a further increase in the number of polyelectrolyte double layers did not lead to a significant increase in the permeation water concentration [Xu et al., 2010]. The data in Figure 6.4 show that the selectivity of the membrane does not change considerably when additional double layers are incorporated in the membrane beyond 7.5 double layers. All subsequent experiments were performed with 7.5 double layers.

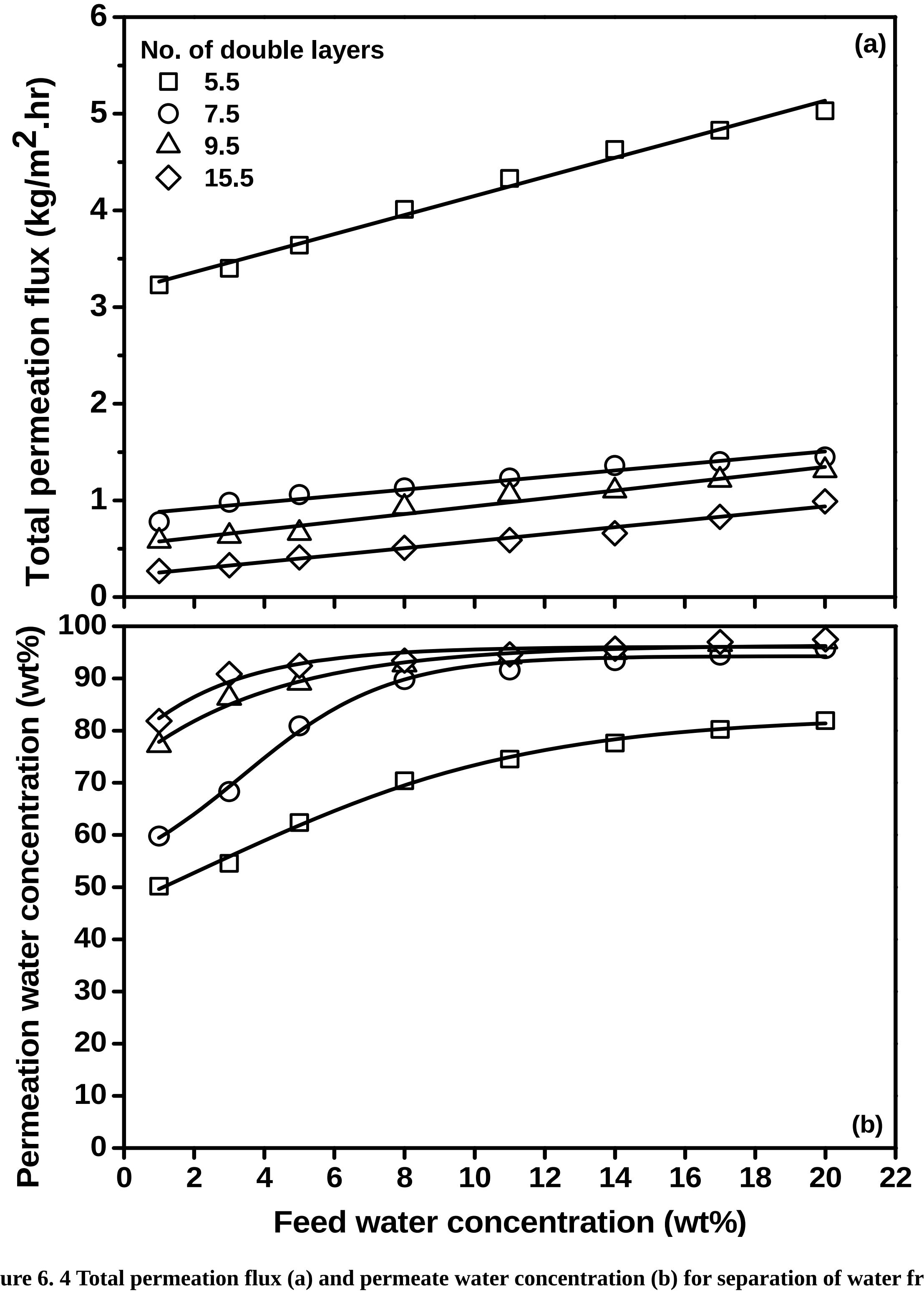

Figure 6. 4 Total permeation flux (a) and permeate water concentration (b) for separation of water from IPA using polyelectrolyte/polyamide composite membranes. Operating temperature, 25 ^{o}C.

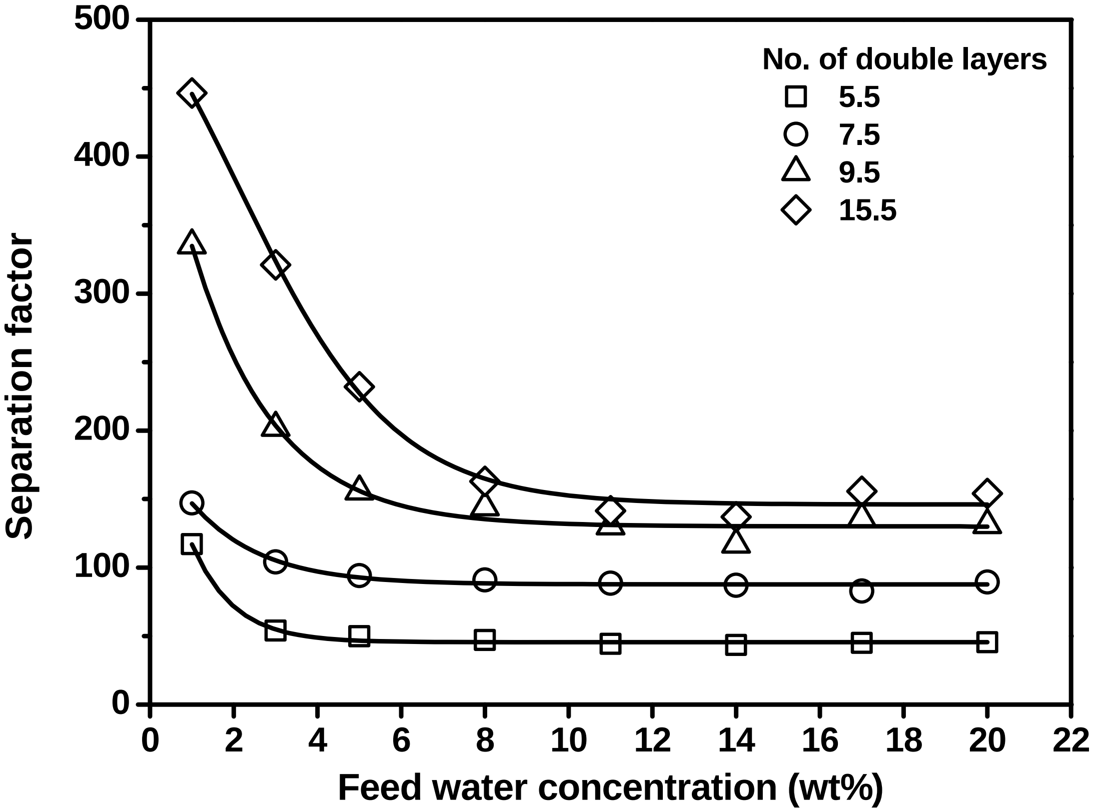

Figure 6. 5 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes. Operating temperature, 25 °C.

The separation factor increased with an increase in the number of polyelectrolyte double layers, as shown in Figure 6.5. For a feed concentration of 1 wt% water, a 4-fold increase in the separation factor was observed when the number of polyelectrolyte double layers increased from 5.5 to 15.5. Figure 6.6 shows the effects of the number of double layers on the partial permeation fluxes of water and isopropanol. Water permeation flux showed a similar trend as the total permeation flux. However, the partial permeation flux of isopropanol decreased when the feed water concentration changed from 1 to 20 wt% compared to the water permeation flux. Variation in isopropanol permeation flux is less, especially for the membranes with good selectivities.

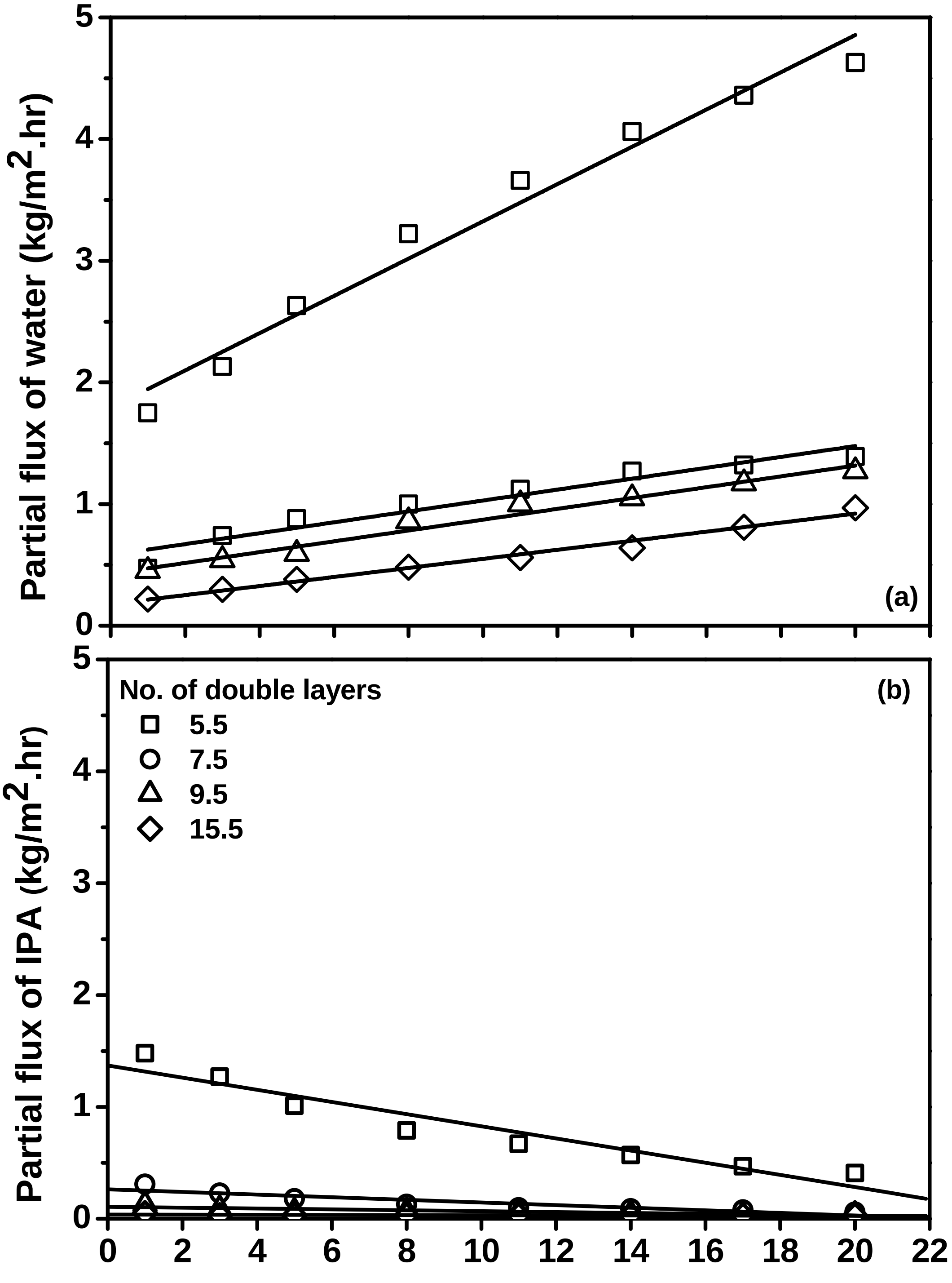

Figure 6. 6 Partial permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membranes. Operating temperature, 25 °C.

6.2.3 Effect of operating temperature in pervaporation

The operating temperature is an important factor for pervaporation because it has direct impact on the solubility and permeability of the permeating species in the membrane. To evaluate the effect of feed temperature on the pervaporation performance, membranes with 7.5 double layers were chosen in the pervaporation experiments with given feed concentrations at various temperatures: 30, 40, 50, 60 and 70 ^{o}C.

In general, an increase in the operating temperature will increase the permeation flux for most polymeric membranes. As the feed temperature increases, the permeating molecules are more energetic, and the polymer chain movement is intensified both in frequency and amplitude, resulting in a higher diffusivity in the membrane. In addition, with an increase in the operating temperature, the vapor pressures of the permeating species increase, which results in an increase in tqhe driving force for the pervaporation process [Huang et al., 2000; Du et al., 2007].

The relationship between the permeation flux and temperature can often be expressed by an Arrhenius type of equation (6.1):

$$\mathrm{J}_i = \mathrm{J}_{i0}\exp(-\frac{\mathrm{E}_{\mathrm{J}i}}{\mathrm{RT}}) \qquad (6.1)$$

where J_i, J_{i0} and E_{Ji}, are the partial permeation flux of component *i*, pre-experimental factor and apparent activation energy for the permeation, respectively. R and T are gas constant and temperature, respectively.

The total permeation fluxes are found to increase with temperature, as shown in Figure 6.7, and exhibit a linear relationship between logarithmic fluxes and reciprocal temperature. That is, the temperature dependence of permeation fluxes follows the Arrhenius-type relationship. The apparent activation energy of crosslinked polyelectrolyte/polyamide membrane was evaluated to be in the range of 21.7-23.9 kJ/mol.

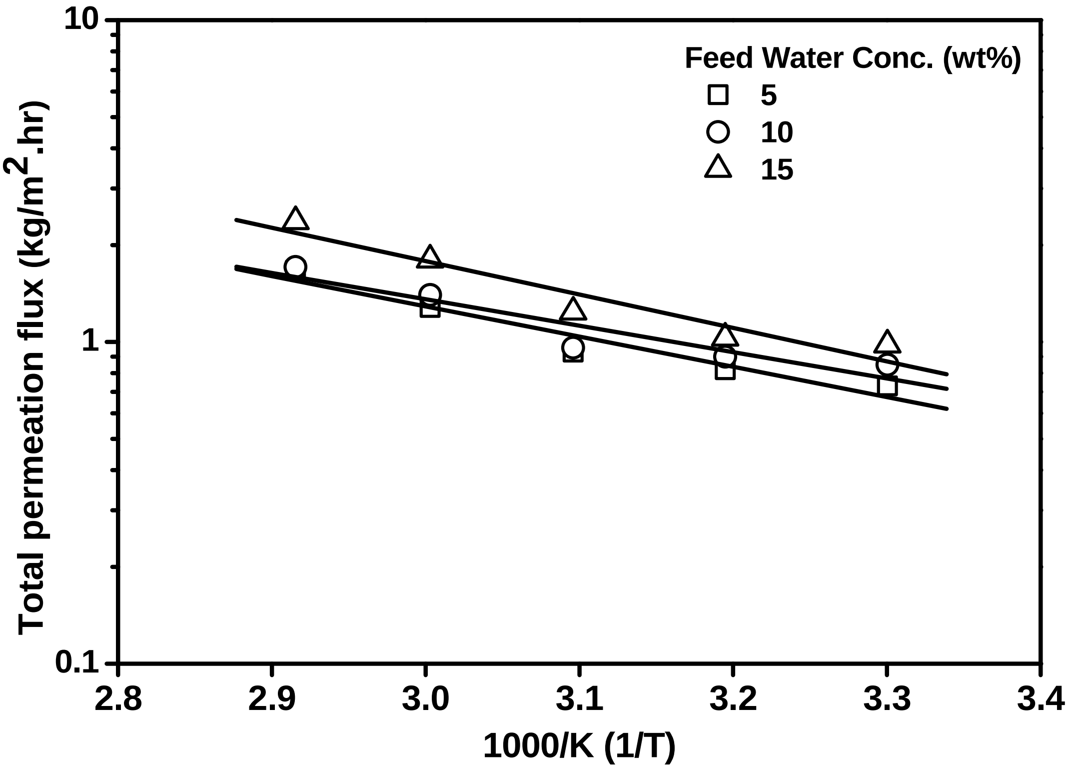

Figure 6. 7 Temperature dependence of total permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membrane $(CS/PAA)_7CSx$.

It is often observed that the separation factor will decrease with an increase in the operating temperature for non-polyelectrolyte based membranes. Interestingly, the separation factor of the crosslinked polyelectrolyte/polyamide composite membrane also increases with an increase in the feed temperature, as shown in Figure 6.8. This may be attributed to the chemical crosslinking which suppresses membrane swelling even at a high operating temperature. When membrane swelling is restricted, the transport of isopropanol molecules through the membrane will not be enhanced by water molecules, and the isopropanol molecules will be retained by the membrane due to its larger molecular size. Therefore, both permeation flux (primarily due to good water permeability) and separation factor were enhanced with an increase in the operating temperature.

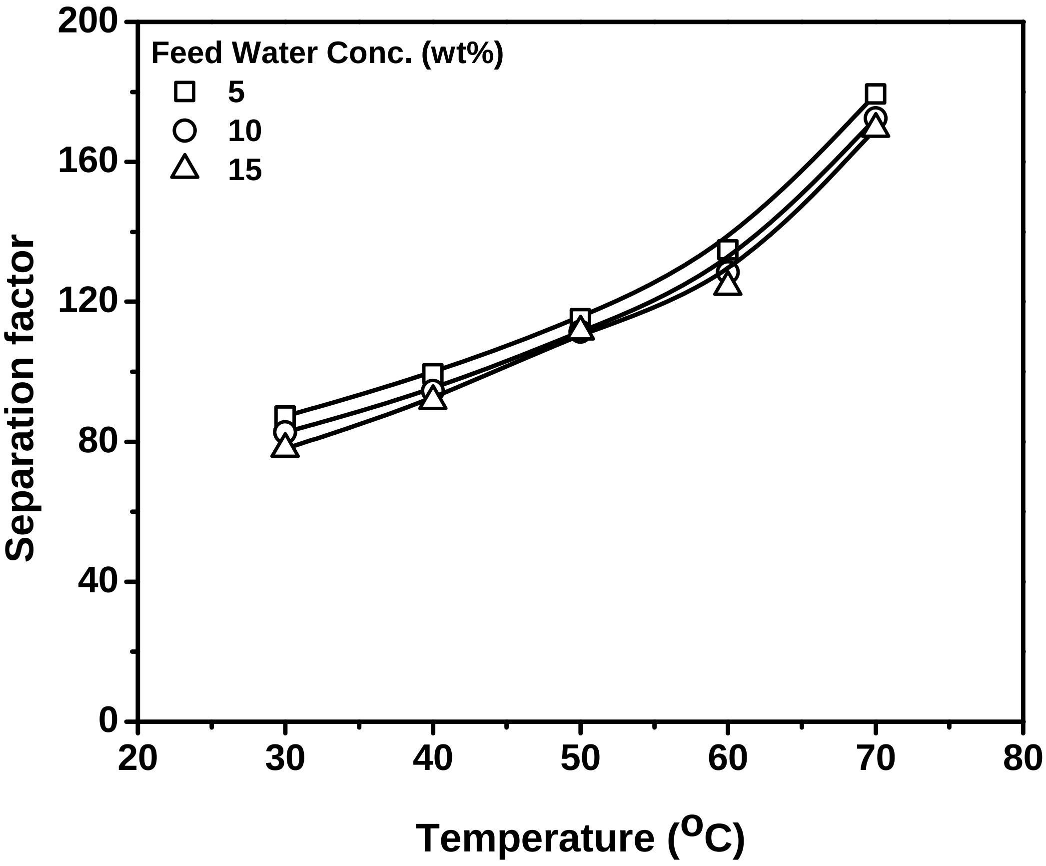

Figure 6. 8 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes (CS/PAA)$_7$CS*x*.

6.2.4 Effect of concentration of crosslinking agent

The use of a crosslinking is important to the pervaporation performance of the polyelectrolyte/polyamide membranes. Membrane crosslinking will not only increase the membrane selectivity but also improve the membrane stability. This is because crosslinking decreases the mobility of polymeric chains, which results in a decrease in the absolute free volume of the membrane [Huang et al., 2000; Dogan et al., 2010]. It has been reported that glutaraldehyde is one of the most effective crosslinking agents for membranes, especially for chitosan because of its chemical structure which has amine groups [Beppu et al., 2007; Devi et al., 2005]. However, if the glutaraldehyde concentration is too high, the membrane will become rigid and easy to disintegrate, particularly in the washing step of the fabrication process. In order to select a suitable concentration of glutaraldehyde, experiments were carried out by varying glutaraldehyde concentrations (0.5, 0.8, 1.0, 1.2, 1.5, 1.7 and 2.0 wt%) for membrane crosslinking. Pervaporation performance of membranes crosslinked with different concentrations of glutaraldehyde was studied by immersing polyelectrolyte/polyamide membrane into glutaraldehyde solutions for 2 hours for both isopropanol and ethanol dehydration.

Figure 6.9 shows the total permeation fluxes of membranes crosslinked at different glutaraldehyde concentrations for water separation from isopropanol in the feed water concentration range of 1~20 wt%. The total permeation flux decreased with an increase in the crosslinking agent concentration until a glutaraldehyde concentration of 1.2 wt%, beyond which the permeation flux became almost constant with a further increase in the glutaraldehyde concentration. With an increase in the concentration of crosslinking agent, the degree of the crosslinking increases, which results in a decrease of the permeation flux [Hyder et al., 2009]. When the outermost chitosan layer is substantially crosslinked, a further increase in the crosslinking concentration will no longer affect the crosslinking degree significantly, resulting in a constant permeation flux. This is consistent with the separation factor, as shown in Figure 6.10, where the membrane selectivity increased with the glutaraldehyde concentration initially and then maintained a constant value when the crosslinker concentration is high enough. For example, the separation factor for dehydrating isopropanol containing 1 wt% water increased by 63% when glutaraldehyde concentration from 0.5 to 1.2 wt%. In addition, too high a concentration of glutaraldehyde will make the membrane brittle which could be easily broken during membrane fabrication and/or pervaporation process.

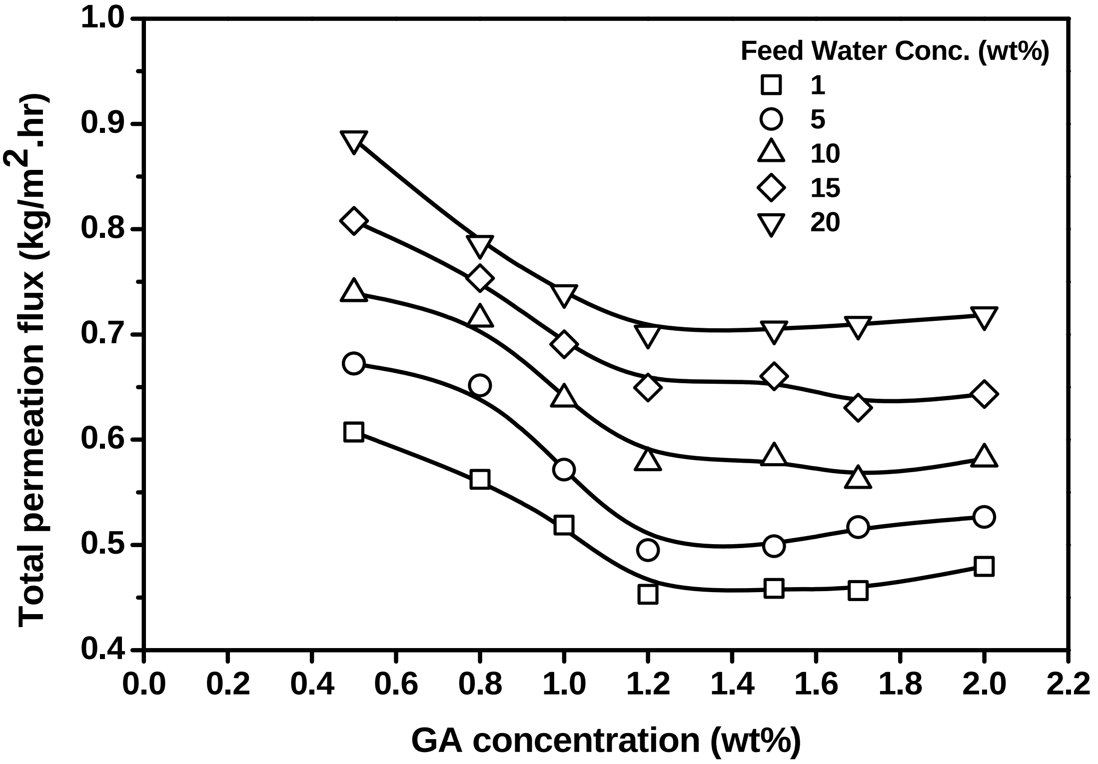

Figure 6. 9 Total permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membranes (CS/PAA)$_7$CS*x* (membrane crosslinking time, 2 h; crosslinking temperature, 25 ^{o}C). Operating temperature, 25 ^{o}C.

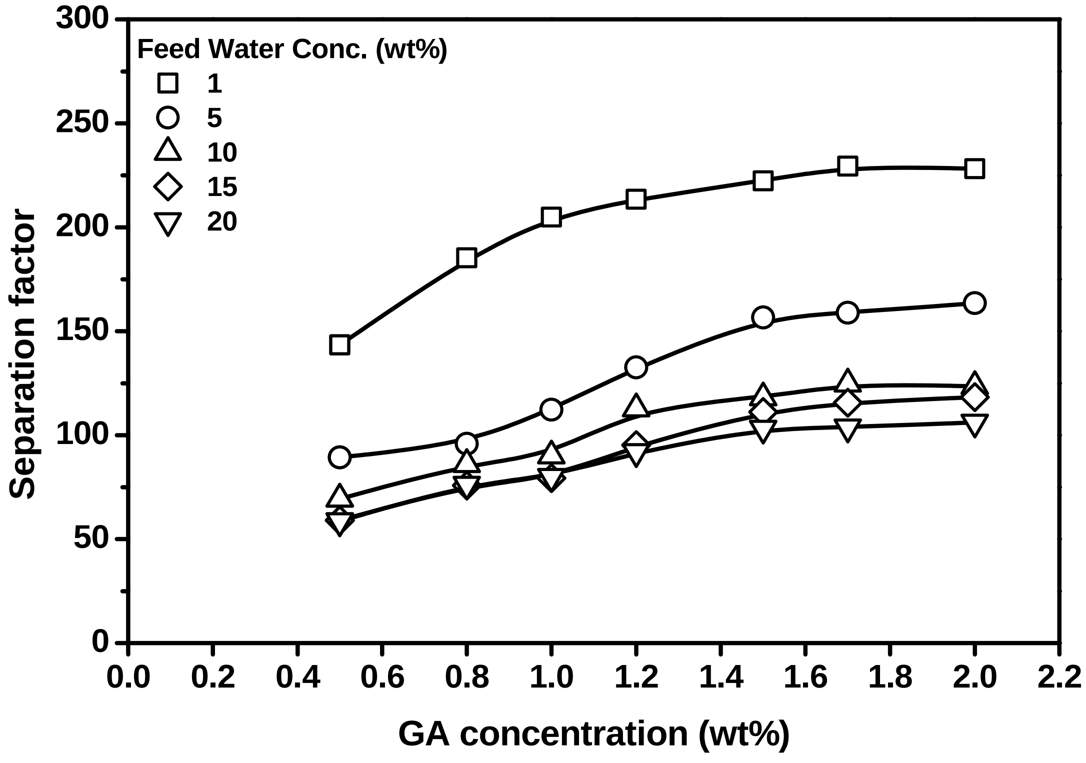

Figure 6. 10 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes (CS/PAA)$_7$CS*x* (membrane crosslinking time, 2 h; crosslinking temperature, 25 ^{o}C). Operating temperature, 25 ^{o}C.

These polyelectrolyte/polyamide composite membranes were also tested for dehydration of ethanol. Figures 6.11 and 6.12 show the total permeation flux and separation factor of membranes for dehydration of ethanol at different feed water concentrations. It is often observed that the pervaporation dehydration of ethanol is more difficult than dehydration of isopropanol [Huang et al., 1999; Huang et al., 2000]. The same trend was observed in Figure 6.11. The membrane permeation flux of the membrane for ethanol dehydration is larger than that of for isopropanol dehydration, which may be due to the smaller size of ethanol molecules and relatively stronger coupling interactions with water molecules and hydrophilic membranes [Huang et al., 2000]. For instance, the permeation fluxes are 0.45 and 0.63 kg/(m^2·h), respectively, for dehydration of iopropanol and ethanol for a feed water concentration of 1 wt% if the membrane was crosslinked with 1.2 wt% glutaraldehyde for 2 hours.

In principle, the separation factor increases with a reduction in permeation flux after crosslinking [Huang et al., 1999]. The polyelectrolyte/polyamide membrane also showed an increase in the membrane selectivity for dehydration ethanol after crosslinking. Compared with pervaporation dehydration of isopropanol, the separation factor for ethanol dehydration is lower. Similar results were reported by Huang et al. [1999] who used crosslinked sodium alginate membrane for dehydration of isopropanol and ethanol.

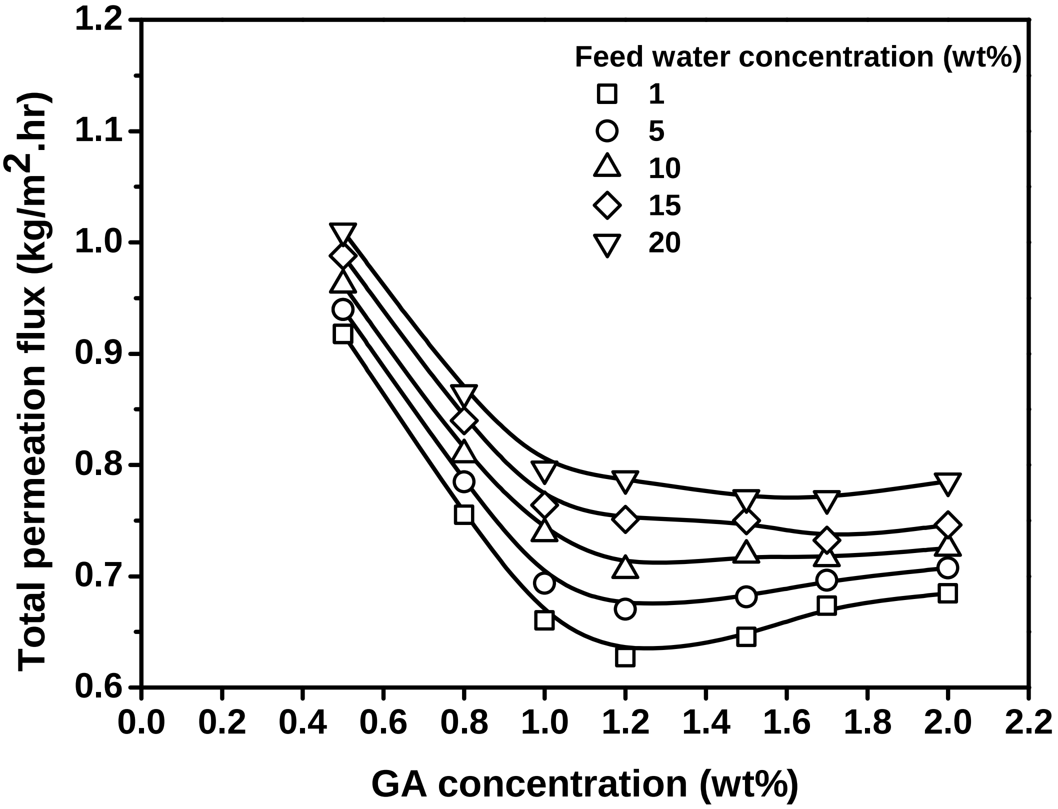

Figure 6. 11 Total permeation flux for separation of water from EtOH using polyelectrolyte/polyamide composite membranes (CS/PAA)7CS*x* (membrane crosslinking time, 2 h; crosslinking temperature, 25 °C). Operating temperature, 25 °C.

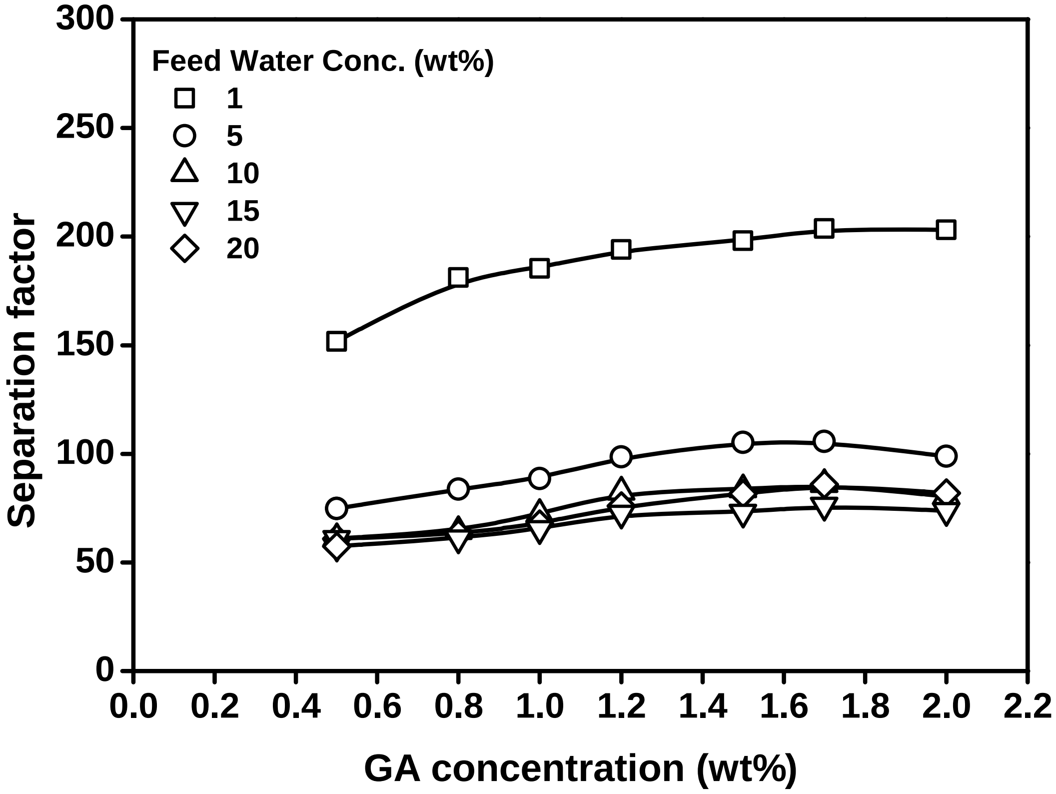

Figure 6. 12 Separation factor for separation of water from EtOH using polyelectrolyte/polyamide composite membranes $(CS/PAA)_7$CS*x* (membrane crosslinking time, 2 h; crosslinking temperature, 25 °C). Operating temperature, 25 °C.

6.2.5 Effect of crosslinking time

Similar to the effects of the concentration of crosslinking agent concentration on membrane performance, the contact time of crosslinking agent with membrane is also important since it affects the degree of crosslinking of the membrane [Kusumocahyo et al., 2000]. A longer crosslinking time allows glutaraldehyde molecules to penetrate deeper into the chitosan capping layer, thereby increasing the degree of crosslinking [Hyder et al., 2009].The influence of crosslinking time on the total permeation flux and separation factor is shown in Figures 6.13 and 6.14, respectively.

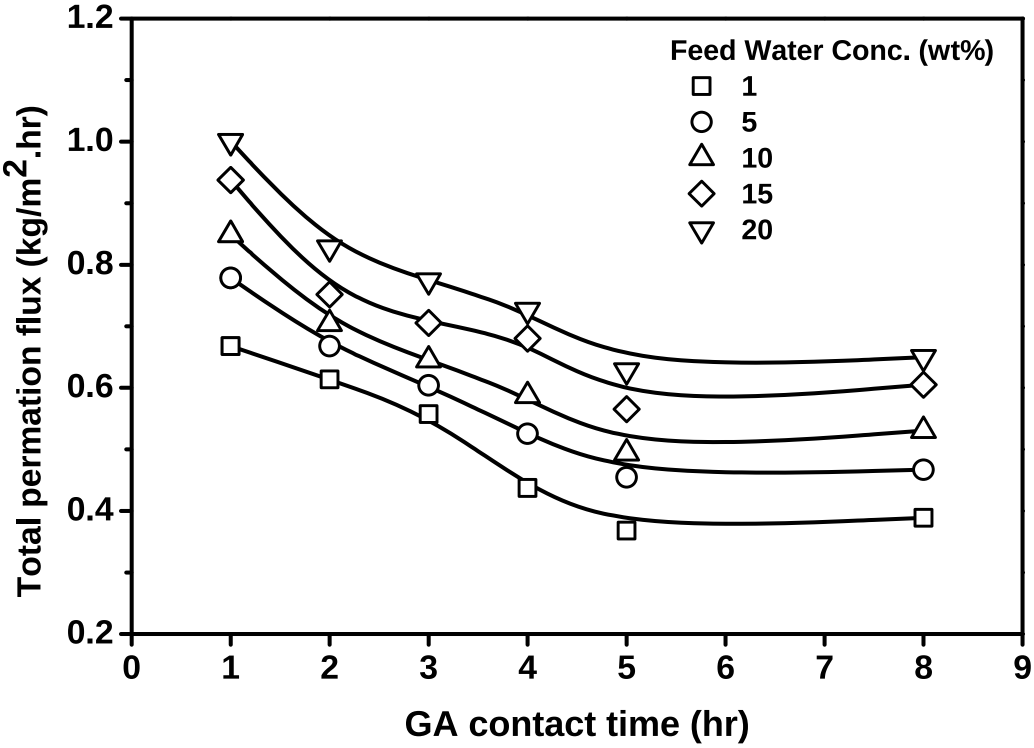

Figure 6. 13 Total permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membranes (CS/PAA)$_7$CS*x* (membrane crosslinking concentration, 1.2 wt%; crosslinking temperature, 25 ^{o}C). Operating temperature, 25 ^{o}C.

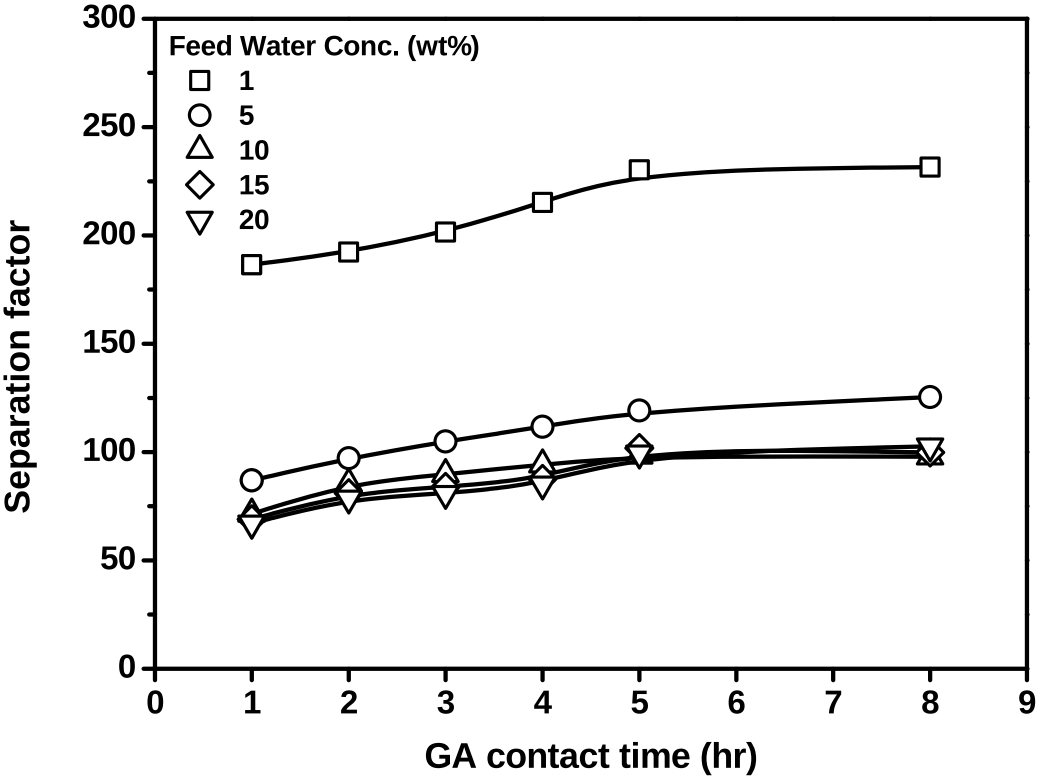

Figure 6. 14 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes $(CS/PAA)_7CSx$ (membrane crosslinking concentration, 1.2 wt%; crosslinking temperature, 25 °C). Operating temperature, 25 °C.

It can be seen in Figure 6.13 that the total permeation fluxes are decreased with the increase of crosslinking time before 5 h and then remain almost constant when the crosslinking time is longer than 5 h, which is maybe because equilibrium of crosslinking reaction is reached [Wu et al., 2004]. Note that the membrane will become brittle if it is subjected to excessive long time contact with crosslinking agent [Lin et al., 2006]. Similar results have been observed by Kusumocahyo et al. [2000]. The effect of crosslinking time on the separation factor of the membrane is shown in Figure 6.14. Increasing crosslinking time will reduce the free volume of the membrane, resulting in a slower transport of the permanent molecules. Thus, the separation factor, which is determinined by relative permeation rates of water and isopropanol, is affected by the crosslinking time less significantly than the permeation rate. Based on the data in Figures 6.13-6.14, a crosslinking time of 5 h appears to be appropriate in order for polyelectrolyte/polyamide membrane to maintain a reasonable permeation flux and separation factor.

6.2.6 Effect of crosslinking reaction temperature

Crosslinking is a chemical reaction, and glutaraldehyde molecules can react with chitosan on the capping layer of the composite membranes. At a higher temperature, glutaraldehyde molecules will be more dynamic and move faster, and consequently the rate of crosslinking reaction will be faster. In order investigate the effect of crosslinking temperature on the membrane performance, membranes crosslinked at different temperatures were prepared, and the membrane performance is shown in Figures 6.15 and 6.16. The total permeation flux decreased with an increase in the crosslinking temperature, while the separation factor increased. This can be attributed to the enhanced reaction rate at higher temperatures. In general, crosslinking at a temperature above ambient temperature did not result in a substantial increase in the membrane selectivity, and the ambient temperature is considered to be appropriate from an application point of view during membrane fabrication.

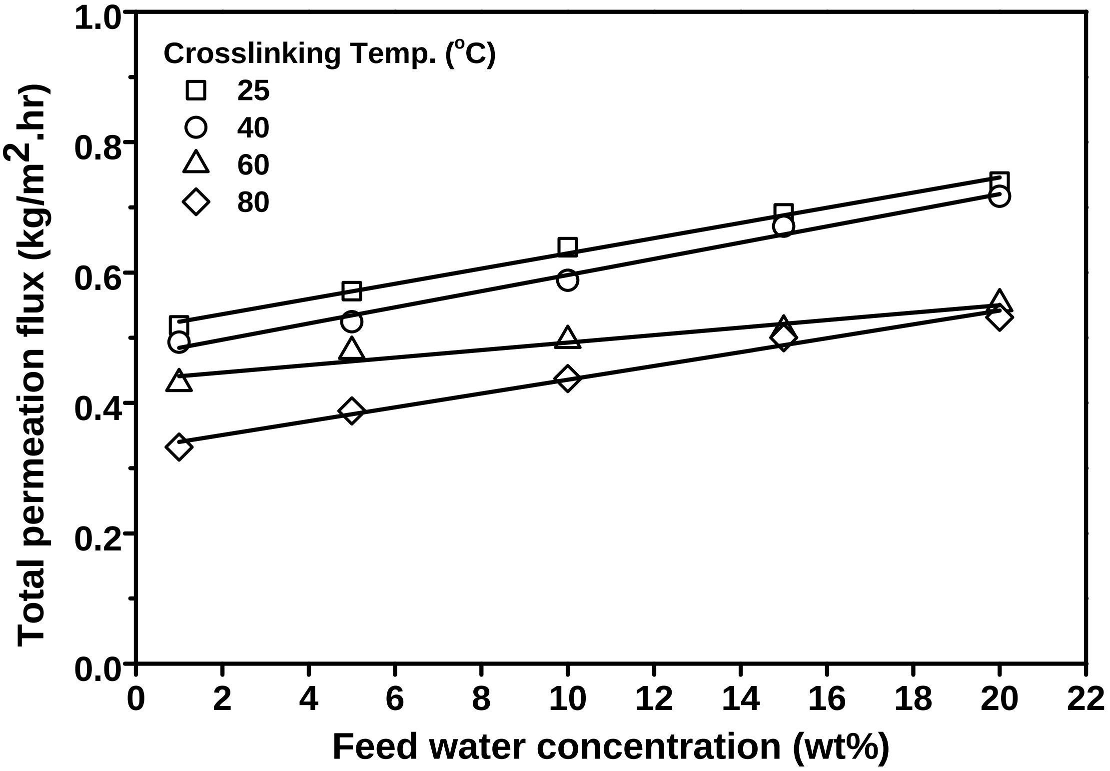

Figure 6. 15 Total permeation flux for separation of water from IPA using polyelectrolyte/polyamide composite membranes $(CS/PAA)_7CSx$ (membrane crosslinking concentration, 1.2 wt%; crosslinking time, 2 h). Operating temperature, 25 °C.

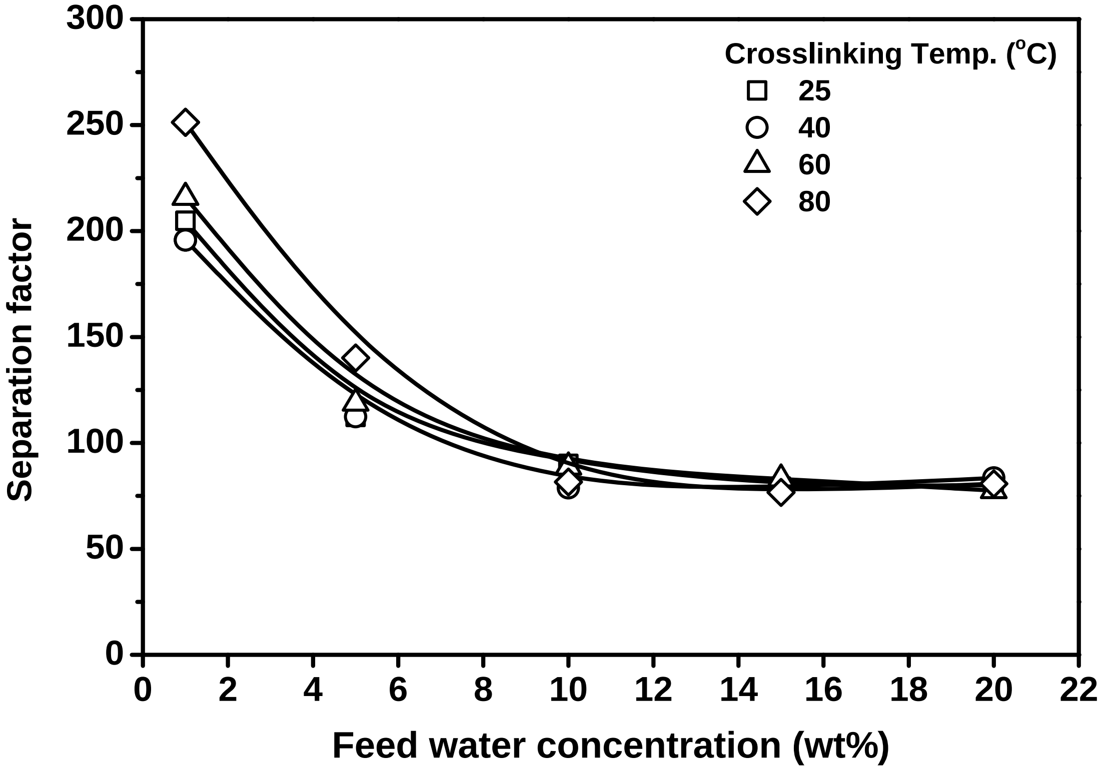

Figure 6. 16 Separation factor for separation of water from IPA using polyelectrolyte/polyamide composite membranes $(CS/PAA)_7CSx$ (membrane crosslinking concentration, 1.2 wt%; crosslinking time, 2 h). Operating temperature, 25 °C.

6.4 Conclusions

Polyelectrolyte/polyamide composite membranes were fabricated using chitosan and PAA, and they were studied for dehydration of isopropanol, and to a lesser extend, of ethanol. The following conclusions can be drawn:

(1) Chitosan/PAA mutilayers self-assembled on polyamide substrate capped with a chitosan layer were prepared, and the membrane stability and selectivity were increased by surface crosslinking with glutaraldehyde.

(2) The effecs of crosslinking conditions on the membrane performance were studied. Increasing the concentration of crosslinking agent and crosslinking time tended to increase the separation factor, whereas the permeation flux was compromised.

(3) In consideration of the permeation flux and separation factor, the following crosslinking conditions were found to be appropriate for membrane fabrication: crosslinker concentration, 1.2 wt%; crosslinking time, 5 h; crosslinking temperature, room temperature.

Chapter 7

Polyelectrolyte/polyamide composite membranes based on PEI and alginate for ethanol and isopropanol dehydration

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7.1 Introduction

Anhydrous ethanol is widely used in chemical industry as a raw material in chemical synthesis of esters and ethers, and as solvent in production of paints, cosmetics, sprays, perfumes, medicine and food. Furthermore, ethanol is also used as fuel additive that reduces environmental contamination [Gil et al., 2012; Barba et al., 1985; Black et al., 1980; Chianese et al., 1990; Meirelles et al.,1992]. Ethanol and water form an azeotrope at approximately 4 wt% water, and additional chemicals (e.g., benzene, pentane and cyclohexane) are needed in the azeotropic distillation process [Horsley, 1973]. However, the use of entrainers will cause another impurity problem and this is not suitable for such applications as pharmaceutical processes which require a high purity [Chapman et al., 2008]. Pervaporation has been therefore considered to be an alternative method to separate azeotropes and close boiling liquids.

Alginic acid, derived from marine algae, is a natural polysaccharide containing linear chains of 1,4′-linked β-D-mannuronic acid and α-L-guluronic acid [Maureira and Rivas, 2009; Yamada and Honma 2004]. Alginic acid naturally exists in the cellular wall and forms insoluble complexes with such ions as calcium, magnesium and sodium. It is considered to be a promising material for various applications since it is a biodegradable, biocompatible, non-toxic, and a low cost polymer [Kitamura et al., 1997; Iwata et al., 1996]. The presence of carboxylic acid groups makes it hydrophilic and can be soluble in water at specific pH. Maureira and Rivas [2009] used alginic acid to remove metal ions by liquid phase polymer-based retention technique. As a membrane material, it has also shown outstanding performance. Wang [2000] investigated 1,6-hexanediamine crosslinked alginate composite membranes for dehydration of acetic acid by pervaporation, and a separation factor of 161 and a permeation flux of 262 $g/(m^2 \cdot h)$ were obtained to separate a 85 wt% acetic acid aqueous solution at 70 ^{o}C.

In this thesis Chapter 5, crosslinked polyelectrolyte/polyamide membranes have been fabricated based on PEI/PAA and chitosan/PAA. In general, the PEI/PAA based membranes did not perform well for ethanol dehydration. Replacing polycation PEI with chitosan, followed by crosslinking, was shown to improve the membrane performance for ethanol dehydration. The resulting membranes showed acceptable permeation flux, selectivity and mechanical stability for ethanol/water separation [Zhang, et al., 2013]. In order to further improve the membrane performance, an attempt was made to use alginate as a polyanion to fabricate polyelectrolyte/polyamide composite membranes for ethanol dehydration. Therefore, the growth of polyelectrolyte multilayer fabricated with PEI/alginate was studied here to compare with that of PEI/PAA. The effects of feed water concentration and operating temperature on the membrane performance were investigated. The water contact angle on the membrane surface was measured to study how the polyelectrolyte multilayers influenced the surface hydrophilicity of the membrane. It will be shown that these membranes are stable for dehydrating ethanol without requiring chemical crosslinking, which is an advantage for membrane fabrication because of the simplified procedures involved.

7.2 Experimental

Sodium alginate was purchased from Fisher Scientific and used as the anionic polyelectrolyte to fabricate polyelectrolyte/polyamide composite membrane. Other materials and procedures used for membrane fabrication were the same as described in Chapter 3. The LbL growth of the polyelectrolyte multilayers was monitored by measuring absorbance of the multilayers formed on the inner walls of quartz cuvettes. Figure 7.1 shows the chemical structure of alginic acid.

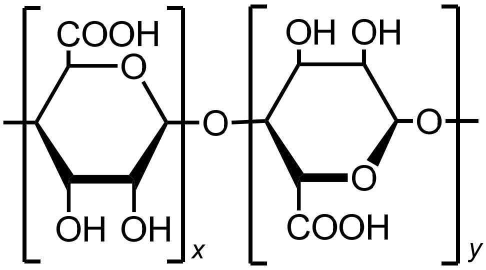

Figure 7. 1 Chemical structure of alginic acid

Sodium alginate (supplied by Sigma-Aldrich, average molecular weight of 500,000) was dissolved in deionized water to form a homogeneous solution, which was filtered to remove any undissolved solids and impurities and was used as polyanion deposition solution.

The LbL growth of the polyelectrolyte multilayers was achieved under the following conditions: polyelectrolyte concentration of PEI and alginate were 0.02 and 0.001 monomol/L (monomol=mole of a monomer unit), respectively; polyelectrolyte concentration of PAA was 0.02 monomol/L; deposition time and temperature are 30 min and 25 ^{o}C, respectively.

7.3 Results and discussion

7.3.1 LbL Growth of self-assembled polyelectrolyte multilayer

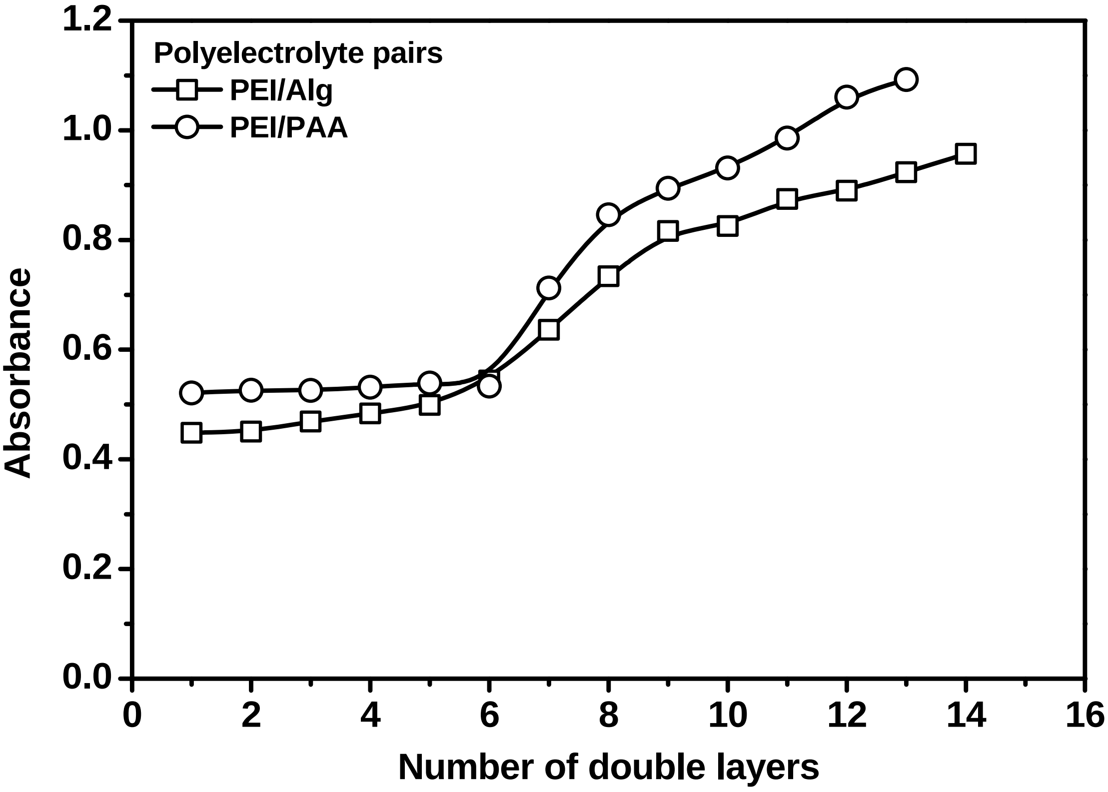

Figure 7. 2 Absorbance of polyelectrolyte multilayer fabricated using PEI/PAA and PEI/Alginate polyelectrolyte pairs.

The LbL growth of self-assembed polyelectrolyte multilayers built on quartz cuvettes using PEI/alginate polyelectrolyte pairs is shown in Figure 7.2. For comparison, the LbL growth of PEI/PAA polyelectrolyte multilayers is also shown in the figure. The absorbances of both the polyelectrolyte multilayers are shown to increase as the polyelectrolyte double layer grows. Again, the absorbance increased slowly in the beginning of the multilayer formation due to the uncharged surface of the inner walls of the cuvettes, and then there is a quick change in absorbance after 6 cycles of polyelectrolyte depositions. Thereafter, the growth of the polyelectrolyte multilayer tends to form uniformly as reflected by the linear change in the absorbance with the number of polyelectrolyte double layers. It is noted that the polyelectrolyte multilayer fabricated with PEI/PAA showed a faster increase in absorbance than that of PEI/alginate, which seems to suggest that the growth of the PEI/PAA polyelectrolyte multilayer is faster. For example, an increase in polyelectrolyte double layers from 6 to 10 increased absorbance from 0.544 to 0.825 for the PEI/alginate pairs, while the absorbance increased from 0.534 to 0.931 for the PEI/PAA pairs. The principal driving force for the formation of polyelectrolyte multilayers is electrostatic attractions between oppositely charged polyelectrolyte components [Toutianoush et al., 2002], and the charge density of the polyelectrolytes is important for the growth of the multilayer films [Decher, 1997]. Polyelectrolytes with a high charge density tend to have more chance to access the overcompensated sites of the polyelectrolyte complex, which favors further deposition of oppositely charged polyelectrolyte [Zhu et al., 2007]. A critical charge density is required for the charge overcompensation to reverse the surface charge and for the stabilization of the polyelectrolyte double layers to withstand desorption in the dipping processes that followed [Sun et al., 2005]. Alginate is a weak anionic polyelectrolyte with low charge density, while PAA is a weak anionic polyelectrolyte but with high charge density. Therefore, the growth of PEI/PAA polyelectrolyte multilayer is faster. Meier-Haack et al. [2000] found that the membranes fabricated from PEI and high charge density PAA are more selective to water permeation for the dehydration of isopropanol than the membranes prepared from PEI and low charge density alginate, but the former membrane was less permeable.

7.3.2 Multilayered polyelectrolyte membranes for dehydration of ethanol

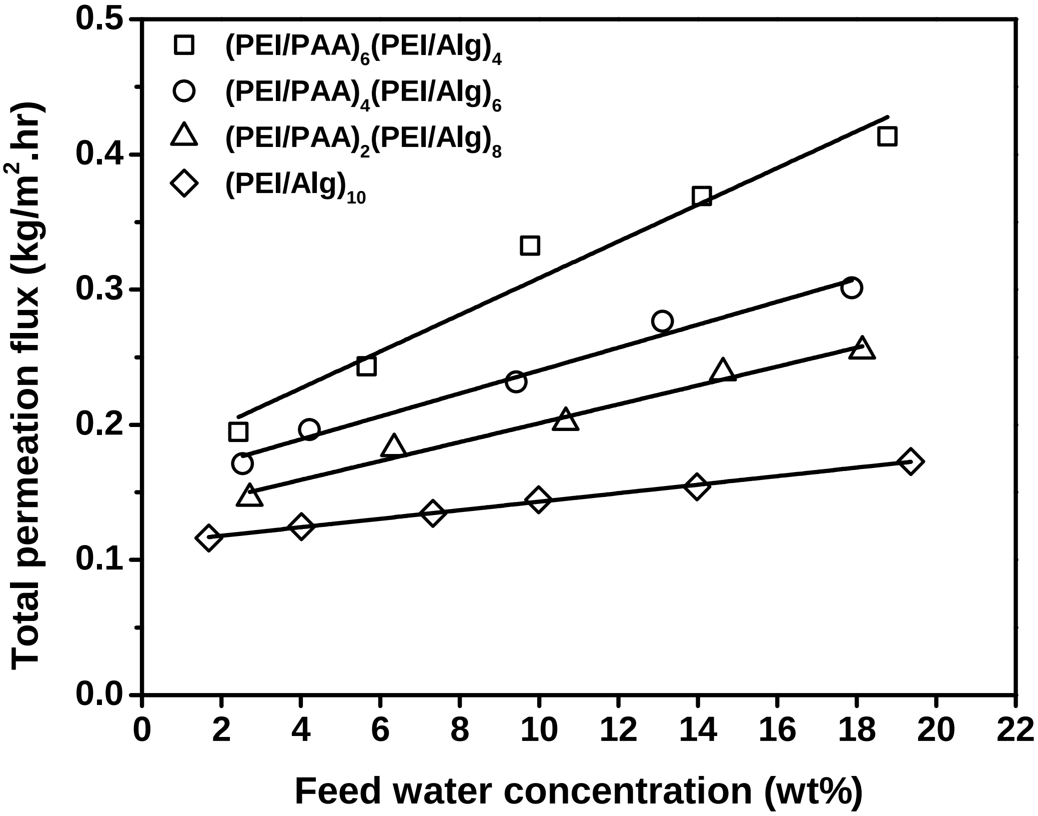

Figure 7. 3 Total permeation flux for separation of water from EtOH using polyelectrolyte/polyamide composite membranes. Operating temperature, 25 °C.

In Chapter 5, it was found that when PEI (polycation) was progressively substituted with chitosan for the last polyelectrolyte double layers in membrane fabrication, the stability and selectivity of the polyelectrolyte/polyamide composite membrane were improved [Zhang et al., 2013]. An attempt was made here to substitute PAA (polyanion) with alginate in the preparation of the polyelectrolyte/polyamide membranes, because alginate is more stable than PAA in aqueous solutions. To demonstrate the viability of this approach, a series of membranes having different number of alginate layers (starting from the outermost layer) but with a fixed total of 10 double layers were prepared and tested.

The permeation flux and separation factor of the membranes are shown in Figures 7.3 and 7.4 for the dehydration of ethanol at an operating temperature of 25 °C. Here, (PEI/PAA)$_m$(PEI/algate)$_n$ means that the polyelectrolyte multilayers were assembled with *m* double layers of PEI/PAA followed by *n* double layers of PEI/alginate (*m*+*n*=10).

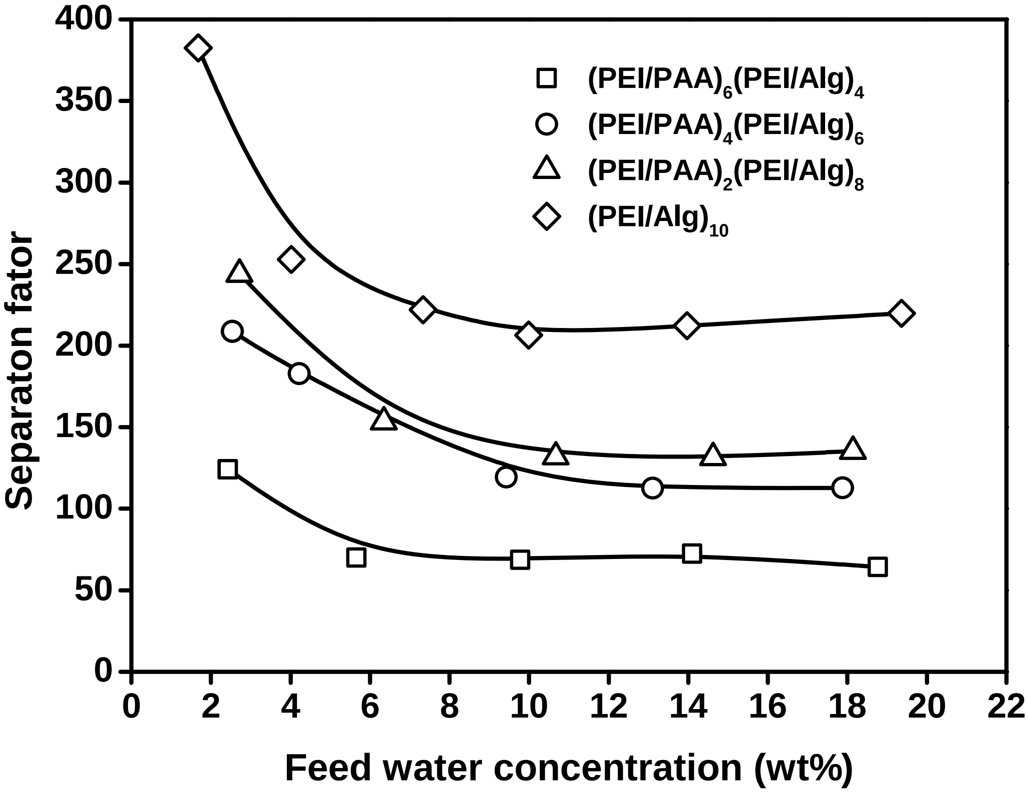

Figure 7. 4 Separation factor for separation of water from EtOH using polyelectrolyte/polyamide composite membranes. Operating temperature, 25 °C.

It can be seen that the membranes become more permselective as the PAA was gradually substituted with alginate, and the separation factor of the membrane increased at the expense of reduced permeation flux. For instance, at 2.5 wt% feed water concentration, the separation factor increased from 124 to 243 while permeation flux decreased from 0.19 to 0.15 kg/(m^2·h) when the composition of the membrane changed from (PEI/PAA)$_6$(PEI/alginate)$_4$ to (PEI/PAA)$_2$(PEI/alginate)$_8$. The improved selectivity of the membrane may be explained as follows. Besides electrostatic attractions, hydrogen bonding is also regarded as a driving force for the formation of polyelectrolyte complexes [Kramer et al., 1997]. Partially protonated alginate is a stronger polyanion than PAA, and the

PEI/alginate complex is expected to be stronger than PEI/PAA not only due to electrostatic attractions but also hydrogen bonding [Zhang et al., 2013, Molyneux, 1984]. On the other hand, the solubility parameters of PAA and alginate are estimated from the van Krevelen group contribution method to be 14 $(MPa)^{0.5}$ and 61 $(MPa)^{0.5}$ [Matsuura, 1994; Addor et al., 2008; van Krevelen, 1965], respectively. Thus there will be greater molecular interactions between PAA and ethanol than those between alginate and ethanol. Therefore, polyelectrolyte membranes based on PEI/alginate pairs are expected to favor selectivity for ethanol dehydration.

It is noted that the PEI/alginate based membranes are more stable than chitosan/PAA based membranes for ethanol dehydration, and no surface crosslinking is needed for ethanol dehydration with PEI/alginate membranes. In the PEI/alginate based membranes, the top anionic polyelectrolyte layer is alginate. The difference in the solubility parameters between alginate and ethanol is greater than that between PAA and ethanol. Therefore, alginate is expected to provide a better protection to the interior double layers than PAA. This is supported by the fact that no crosslinking is necessary for PEI/alginate based membranes for dehydration of ethanol, while still maintaining a considerable selectivity when the membrane has 4 outermost double layers of PEI/alginate. It should be mentioned that a membrane based on $(PEI/PAA)_8(PEI/Alginate)_2$ was also prepared but the membrane selectivity was not acceptable due to inadequate protection offered by 2 double layers of PEI/alginate only.

It has been shown that when PAA was completely replaced with alginate, the resulting membrane was the most stable and selective. Figure 7.5 shows the permeate concentration and total permeation flux for membrane $(PEI/Alginate)_{10}$ at different feed water concentrations. It is clear that the pervaporation is much more selective for water/ethanol separation than distillation (as shown by the vapor-liquid equilibrium data in Figure 7.5)

[Mulder et al., 1983; Kujawski, 2000].

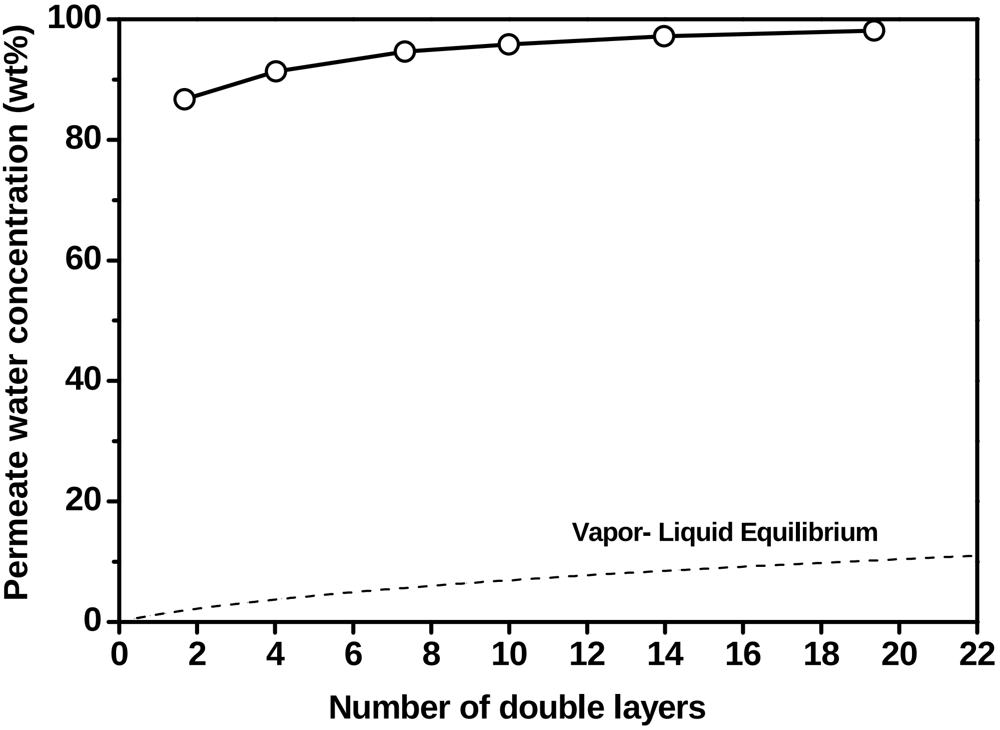

Figure 7. 5 Permeate concentration for separation of water from EtOH using (PEI/Alginate)$_{10}$ polyelectrolyte/polyamide composite membrane. Operating temperature, 25 °C.

For example, the permeate and distillate water concentrations are 95.82 wt% and 7.60 wt%, respectively, at 10 wt% water in the feed. This means pervaporation with membrane is superior to traditional distillation. As water concentration in the feed increases, the total permeation flux also increases, which is shown in Figure 7.3 for the membrane with (PEI/Alginate)$_{10}$ multilayers. The membrane exhibited a permeation flux of 0.125 and 0.144 kg/(m^2·h), respectively, at feed water concentrations equal to 4 and 10 wt%.

The membrane with (PEI/Alginate)$_{10}$ multilayers shows that the separation factor tends to decrease with an increase in water concentration in the feed, as shown in Figure 7.4. The membrane completely based on PEI/alginate multilayers had a larger separation factor, which confirms that a polyelectrolyte membrane with PEI/alginate polyelectrolyte pairs is more stable than the ones with PEI/PAA and CS/PAA polyelectrolyte pairs. For example, the membrane selectivity is 206 for 10 wt% water content in the feed at room temperature, which is 1.5 times larger than that with a crosslinked polyelectrolyte membrane based on CS/PAA described in Chapter 6.

The membrane (PEI/alginate)$_{10}$ was also tested for isopropanol dehydration. Figure 7.6 presents the effect of feed water concentration on the membrane performance. Similar trends for ethanol dehydration were observed for both total permeation flux and seperation factor. That is, the total permeation flux increases but the separation factor decreases with an increase in the feed water concentration. In general, the permeation flux for isopropanol dehydration is slightly lower than the permeation flux for ethanol dehydration. This may be due to the larger size of isopropanol molecules and relatively stronger coupling interactions between water molecules for hydrophilic membranes [Huang et al., 1999]. At 1 wt% feed water concentration, a permeation flux of 0.118 kg/(m^2·h) and a separation factor of 370 were obtained for isopropanol dehydration at 25 $^{\circ}$C, which represents a significant improvement in separation performance as compared with CS/PAA based membranes described in Chapter 6.

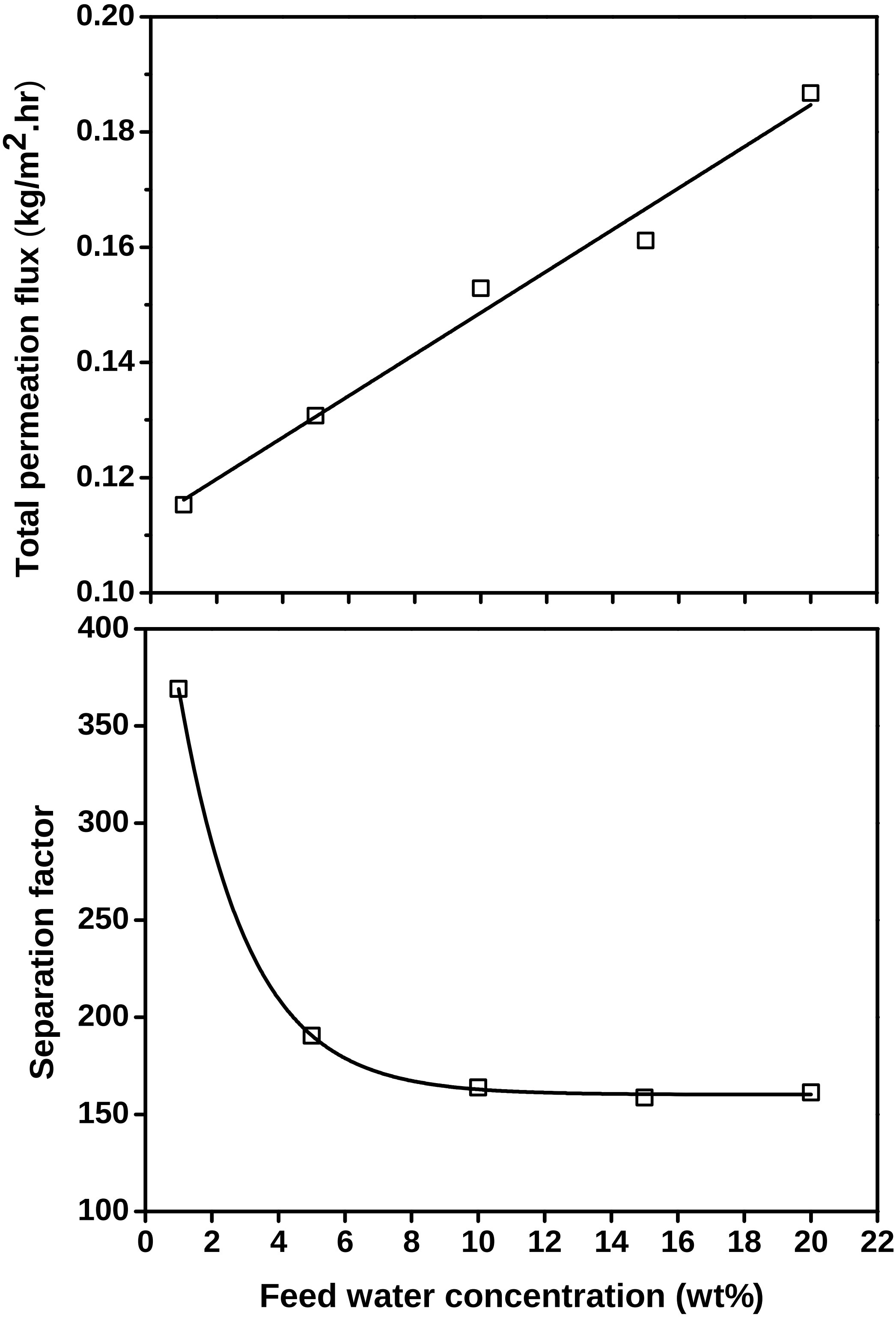

Figure 7. 6 Total permeation flux (a) and separation factor (b) separation of water from IPA using (PEI/alginate)$_{10}$ polyelectrolyte/polyamide composite membrane. Operating temperature, 25 ^{o}C

7.3.3 Effect of number of polyelectrolyte double layers

The contact angle is the angle at which a liquid/vapour interface meets a solid surface and it is commonly used in membrane material science to describe the relative hydrophobicity/hydrophilicity of a membrane surface [Al-Amoudi., et al., 2008; Rosa and de Pinho, 1997]. For example, the contact angle of a very strongly hydrophilic solid will be close to 0°; less hydrophilic solids will have a contact angle up to 90°. On many highly hydrophilic surfaces, water droplets will exhibit contact angles of 0° to 30° [Daffonchio et al., 1995].

The contact angles of the polyelectrolyte multilayers fabricated on polyamide substrate are shown in Figure 7.7; the contact angle of the polyamide substrate (i.e., 0 polyelectrolyte layer) is also shown for comparison.

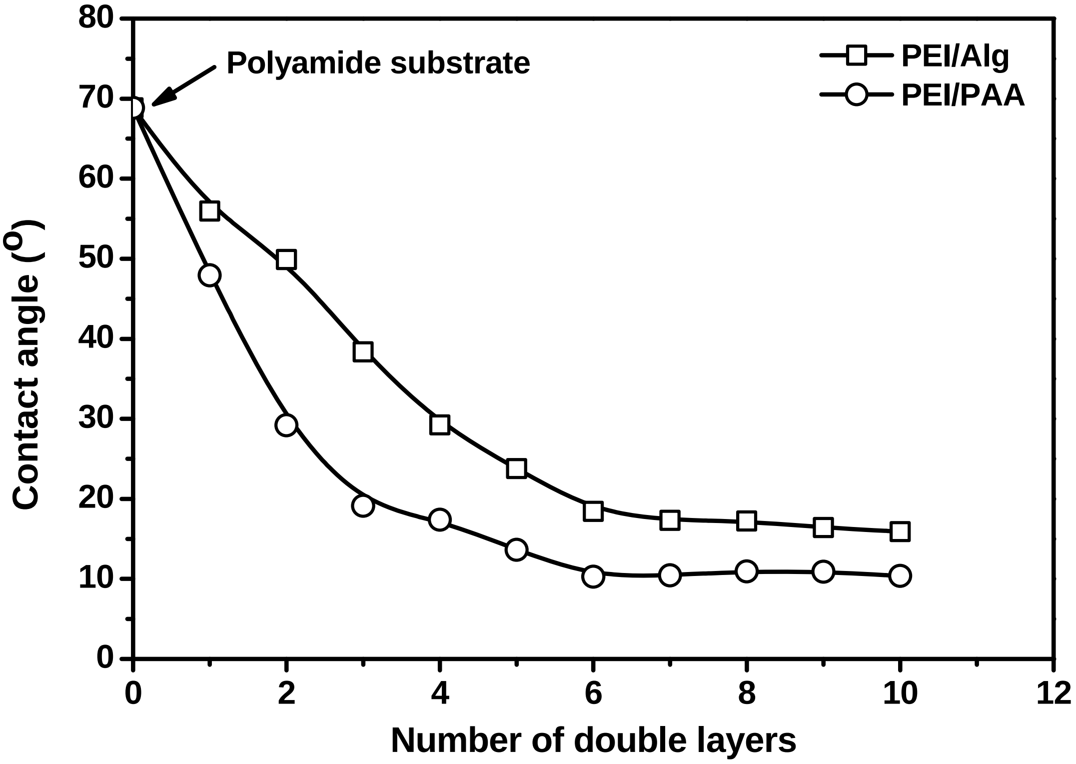

Figure 7. 7 Water contact angle of polyelectrolyte/polyamide membranes based on PEI/PAA and PEI/Alginate pairs.

The water contact angle decreases as the number of polyelectrolyte double layers increases. The polyamide substrate is a hydrophilic material due to the carboxyl groups, having a water contact angle about 69^o, which decreased to $< 20^o$ after polyelectrolyte deposition with PEI/PAA and PEI/alginate polyelectrolyte pairs. This clearly indicates that the hydrophilicity of polyelectrolyte/polyamide membrane is improved by the deposition of these polyelectrolyte layers. Yu et al. [2007] reported that the deposition of polyelectrolyte multilayers (chitosan / dextran sulfate) on a poly(tetramethylene adipate-co-terephthalate) membrane resulted in a sharp decrease in the contact angle from 69.4 to 31.2^o. PEI/PAA polyelectrolyte membranes seem to be more hydrophilic than that of PEI/alginate pairs. For instance, the water contact angle reached 20^o after 3 double layers of PEI/PAA polyelectrolyte were deposited on the substrate, while 6 double layers of PEI/alginate pairs were needed to reach same hydrophilicity. This also agrees with the results from the polyelectrolyte multilayer growth on the cuvette. The higher charge density of PAA than alginate leads to better formation a of polyelectrolyte multilayer resulting in a faster increase in surface hydrophilicity.

Membranes with different numbers of PEI/alginate polyelectrolyte double layers (5, 6, 7, 8, 9, 10) were tested for ethanol pervaporation at 25 ^oC at feed water contents of 5.5 and 10.6 wt%. As shown in Figure 7.8, with an increase in the number of double layers from 5 to 10, the total permeation flux decreases from 0.72 to 0.14 kg/ ($m^2 \cdot h$), while water concentration in permeate increases from 81.4 to 95.8 wt% at a feed water concentration of 10.6 wt%. As the number of double layers increases, the effective thickness of the membrane increases. Thus the resistance for the permeant to pass through the membrane also increases, resulting in a decrease in the permeation flux. In addition, because of hydrophilic PEI/alginate polyelectrolyte multilayers depositied on the polyamide substrate, the water uptake in the membranes will be enhanced and thus the membrane becomes more

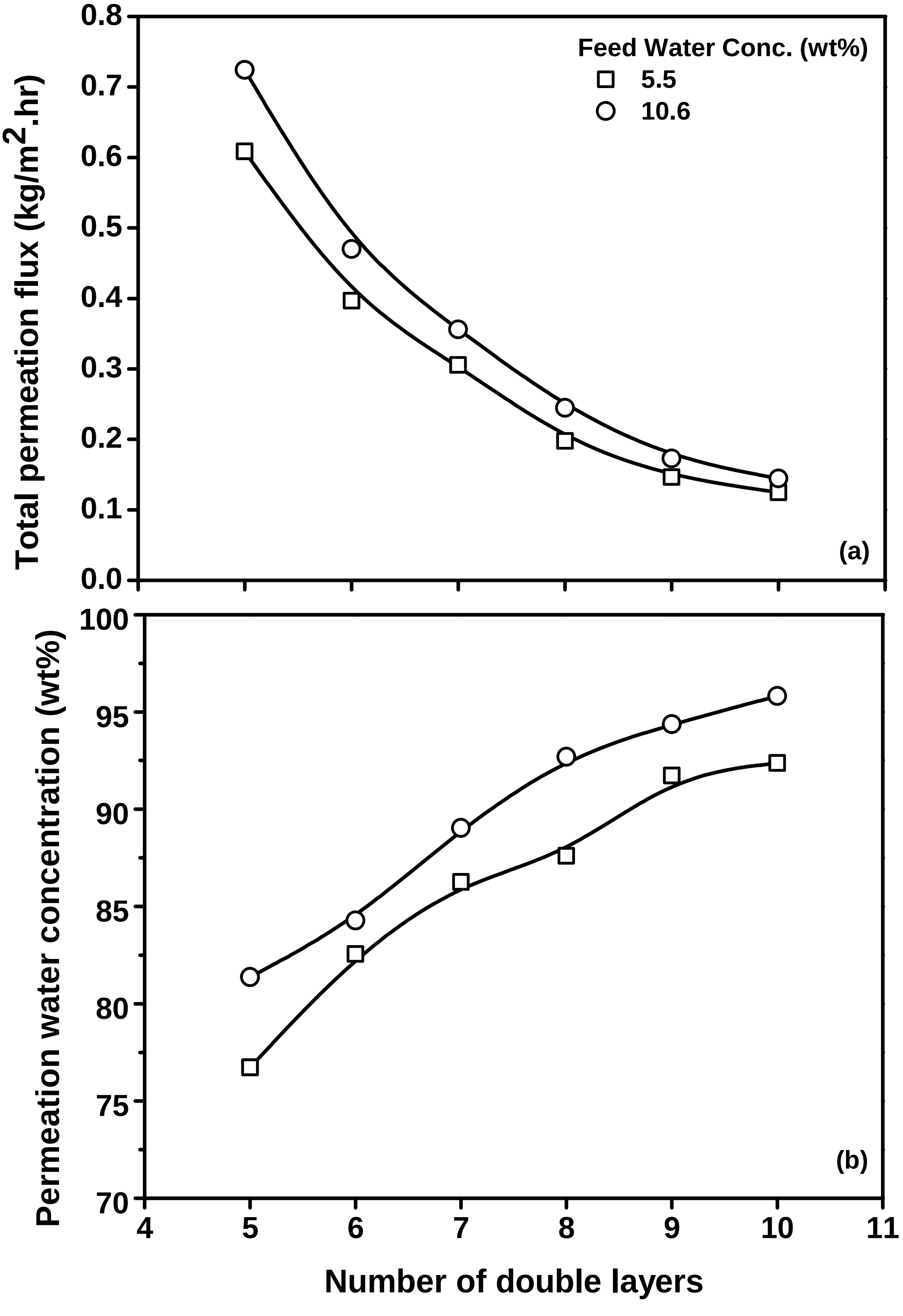

Figure 7. 8 Total permeation flux (a) and permeate water concentration (b) of PEI/Alginate based composite membranes. Operating temperaute, 25 °C.

selective for water during permeation. Similar results were also reported by Wang et al. [2012] for pervaporation using self-assembled graphene oxide polyelectrolyte complex nanohybrid membranes and Zhao et al. [2010] for ethanol pervaporation by PEC nanoparticle complex membrane. Figure 7.9 shows that the separation factor of the membranes increased with an increase in the number of polyelectrolyte double layers.

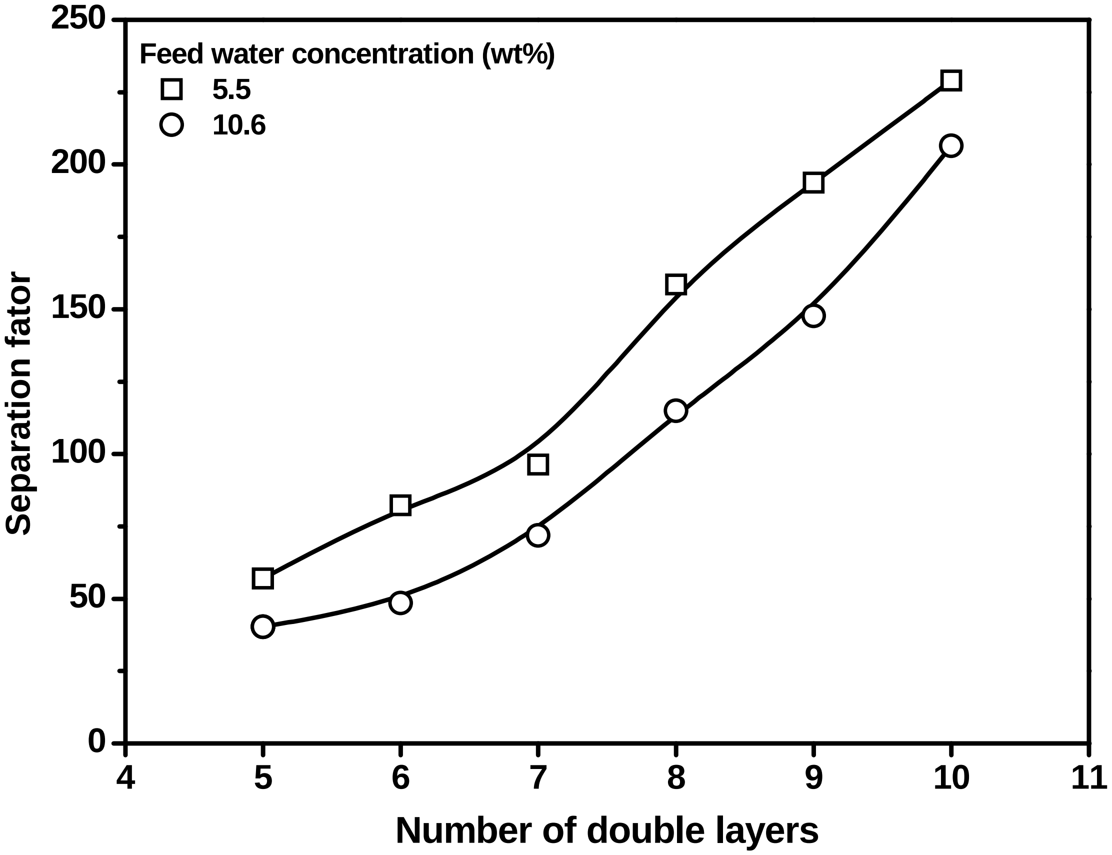

Figure 7. 9 Separation factor of PEI/Alginate based polyelectrolyte membranes. Operating temperature, 25 °C.

7.3.4 Effect of operating temperature

The effect of operating temperature on pervaporation performance was tested with membranes (PEI/Alginate)$_{10}$, which showed good thermal stability. The partial permeation fluxes of water and ethanol at different temperature for given feed concentrations are shown in Figure 7.10.

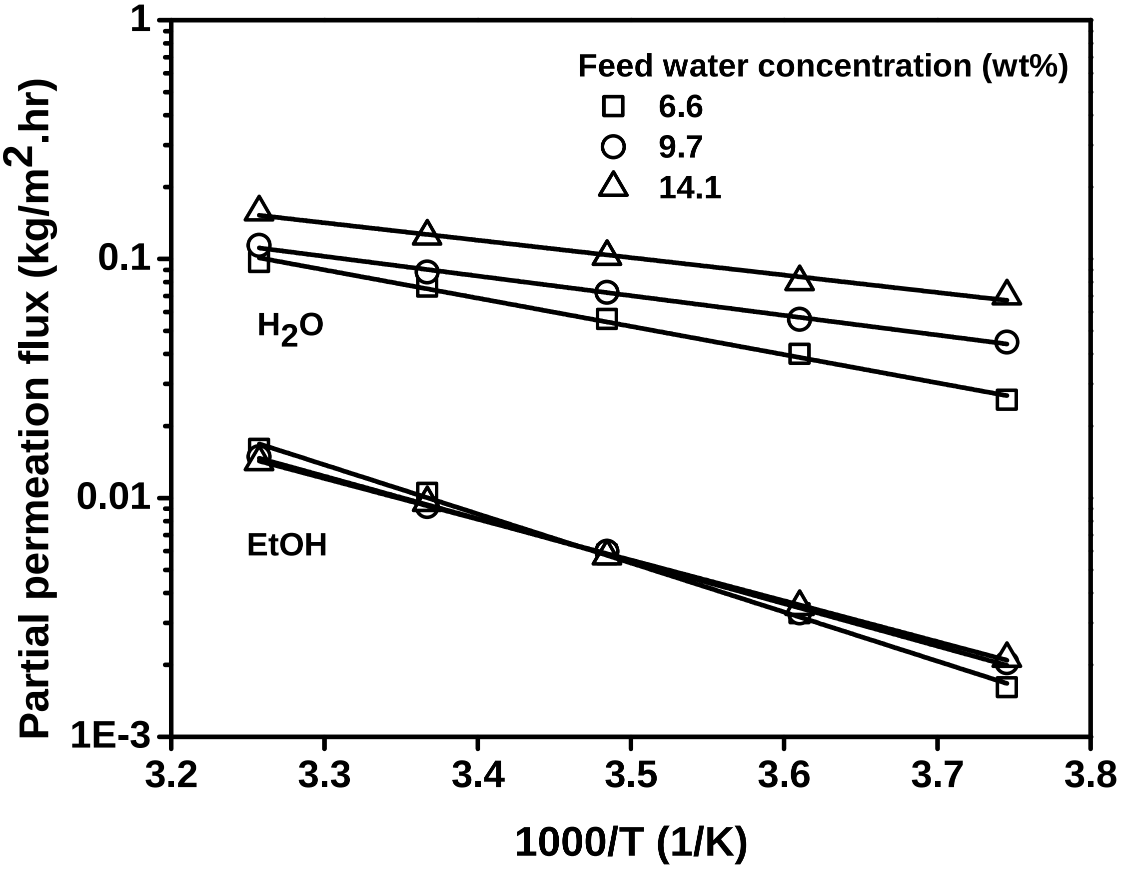

Figure 7. 10 Temperature dependence of partial permeation flux for separation of water from EtOH using $(PEI/Alg)_{10}$ polyelectrolyte/polyamide composite membranes.

The partial permeation fluxes for both water and ethanol increased with an increase in temperature. The relationship between the permeation flux and temperature can be expressed by an Arrhenius type of equation:

$$J_i = J_{i0} \exp(-\frac{E_{Ji}}{RT})$$

where J_i, J_{i0}, E_{Ji}, R and T are the permeation flux, frequency factor, apparent activation energy of the permeation of the component *i*, gas constant and feed temperature, respectively.

In general, an increase in operating temperature results in an increase in the permeation flux for most polymeric membranes. This is easy to understand as an increase in temperature will increase the saturated vapor pressure of the feed, thus increasing the driving force for pervaporation [Hu et al., 2007]. In addition, the diffusivity of permeating molecules is accelerated with an increase in temperature because the polymer chains will be more flexible which favors diffusion of permeant in membrane.

At a feed concentration of 9.7 wt% water, the partial permeation flux of water increased from 0.045 to 0.114 kg/(m^2·h), while the partial ethanol permeation flux decreased from 0.002 to 0.015 kg/(m^2·h) when the temperature was increased from 30 to 70 ^{o}C. Apparently, the operating temperature affects the permeation of ethanol more significantly than that of water, as reflected in the apparent activation energies for permeation of water and ethanol which have been determined to be 14.0~21.1 kJ/mol and 31.5~36.6 kJ/mol, respectively.

The separation factor generally decreases with an increase in the operating temperature, and this is shown in Figure 7.11. Permeating molecules with higher activation energy means a stronger temperature dependence of the permeation flux. The permeation flux of ethanol increases faster than that of water with increasing temperature, which leads to a lower selectivity [Reineke et al., 1987; Hyder et al., 2009]. Similar observations were reported by Xu et al. [2010] for ethylene glycol dehydration using polyelectrolyte self-assembled membranes.

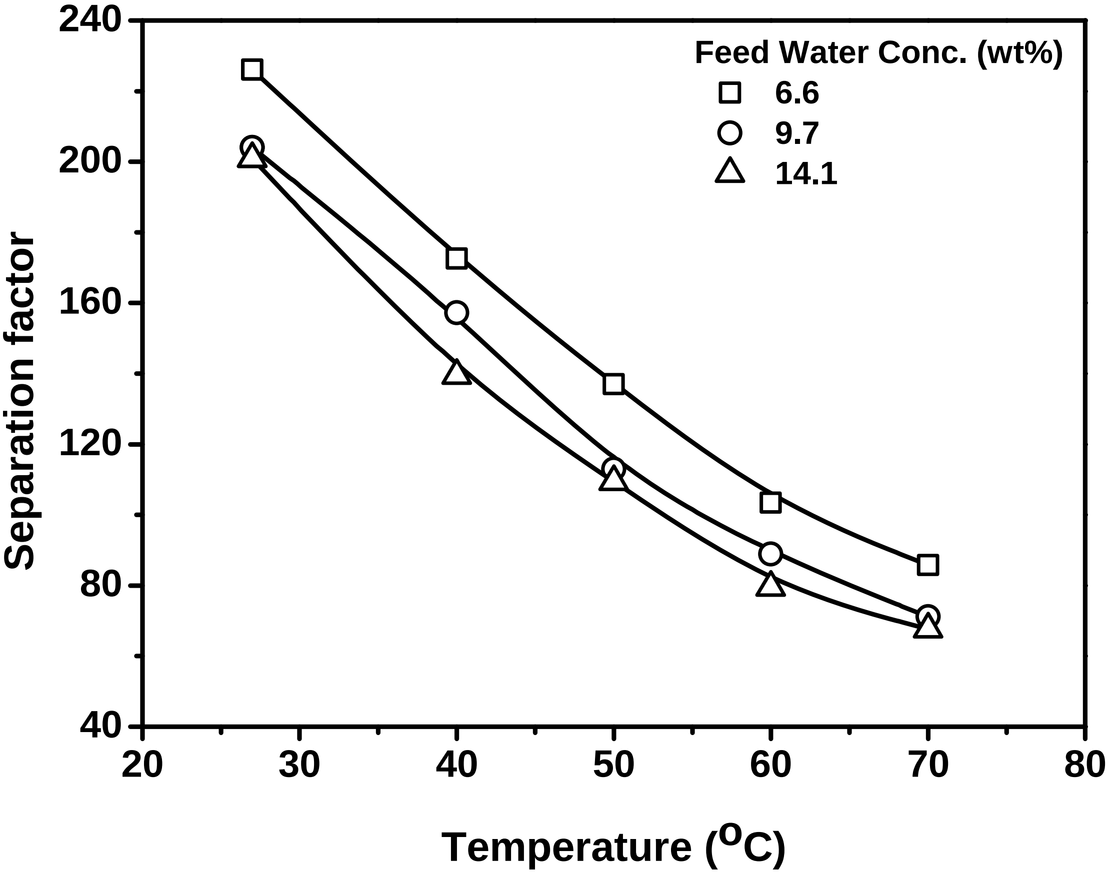

Figure 7. 11 Separation factor for separation of water from EtOH using membrane $(PEI/Alginate)_{10}$.

7.4 Conclusions

LbL self-assembly membranes based on PEI/alginate polyelectrolyte pairs were prepared for dehydration of ethanol (and to a lesser extend, isopropanol) by pervaporation. The following conclusions can be drawn:

(1) Membranes based on PEI/alginate pairs showed good performance for both ethanol and isopropanol dehydration.

(2) An increase in the number of polyelectrolyte double layers increased membrane selectivity, whereas permeability was reduced.

(3) Feed water concentration affected the performance of pervaporation significantly. In the range of the feed water concentrations (0~20 wt%) employed, increasing feed

water concentration increased the permeation flux.

(4) The temperature dependence of permeation flux followed an Arrhenius type of relationship. An increase in operating temperature favored permeation flux while selectivity was decreased.

Chapter 8

General conclusions, contributions to research, and recommendations

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8.1 General conclusions

The following conclusions can be drawn from this thesis work:

(1) A polyelectrolyte/polyamide composite membrane comprising of 3 double layers of polyethylenimine/poly(acrylic acid) showed good selectivity and stability for dehydration of ethylene glycol by pervaporation. With an increase in the number of polyelectrolyte double layers, the permeation flux decreased while the selectivity increased.

(2) The water concentration in the feed affected the pervaporation membrane performance significantly for all the alcohol/water systems. The permeation flux increased while the selectivity decreased with an increase in the water concentration in the range of 0~20 wt% in the feed.

(3) Operating temperature is an important factor for pervaporation. In most cases, an increase in temperature would increase permeation flux, and decrease the separation factor. However, the opposite phenomenon was found for the crosslinked composite membrane based on Chitosan/PAA pairs for isopropanol dehydration.

(4) Both formation of polyelectrolyte multilayers and stability of the polyelectrolyte multilayers after solvent treatment can be evaluated using UV-Vis

spectrophotometry.

(5) The growth of polyelectrolyte multilayers based on PEI/PAA pairs was affected by fabrication factors (i.e., deposition time, polyelectrolyte solution concentration and deposition temperature) in the deposition process.

(6) The selectivity of the composite membranes for dehydration of ethanol and isopropanol was improved by crosslinking of the outermost PEI layer.

(7) The membrane selectivity was also improved by gradual substituting PEI with partially protonated chitosan during membrane fabrication. The membrane showed great selectivity when PEI was completely replaced with chitosan and the crosslinked membranes were capable to separate water from both isopropanol and ethanol.

(8) Higher concentration of crosslinking agent and longer crosslinking time were favored for fabrication of membranes (chitosan/PAA) with high selectivity with sacrifice of the permeation flux.

(9) In order to further improve the membrane selectivity, PAA was gradually replaced by alginate during membrane fabrication without chemical crosslinking. The membranes were selective for both ethanol and isopropanol dehydration when PEI/PAA pairs were completely substituted by PEI/alginate pairs.

8.2 Contributions to original research

8.2.1 LbL growth of polyelectrolyte multilayers and their stability in solvents

In recent work, there are some studies that focused on the growth of LbL self-assembly fabricated on clean quartz slide monitoring by quartal crystal microbalance [Fukao et al., 2011; Lutkenhaus et al., 2008; Shiratori et al., 2000]. This method is used to evaluate the thickness of polyelectrolyte bilayers. In this thesis, the growth of polyelectrolyte multilayers fabricated on the inner walls of quartz cuvettes was studied using UV-Vis spectrophotometry, which is different with the previsous literatures. Although this is not exactly the same as polyelectrolyte multilayers formation on the polyamide substrate, it is an easy, simple and direct method to monitor the growth of polyelectrolyte multilayers. With an increase in the number of polyelectrolyte multilayers deposited on the cuvette, the thickness of the polyelectrolyte multilayers increases, which will be reflected in the absorbance. In addition, the stability of the polyelectrolyte multilayers after solvent treatments also can be studied by monitoring the change in absorbance. It was accomplished by immering the cuvettes (fabricated with polyelectrolyte multilayers) into solvents for a certain period of time. If the polyelectrolyte multilayers are not stable in solvents, there will be a decrease in absorbance with treatment time. On the other hand, if the polyelectrolyte multilayers are stable in solvents, there will be no obvious changes in absorbance with treatment time.

8.2.2 Improved permselectivity and stability of polyelectrolyte/polyamide membranes for alcohol dehydration

Chemical crosslinking is often used to improve the stability and selectivity of pervaporation membranes. Chemical crosslinking will increase the membrane selectivity while decreasing the permeation rate [Huang et al., 1999]. Surface chemical crosslinking was applied to improve the self-assembled polyelectrolyte composite membranes. The outermost polyelectrolyte layer (polyethylenimine or chitosan) crosslinking with glutaraldehyde was shown to significantly increase the membrane selectivity for isopropanol and ethanol dehydration.

8.2.3 Further improved stability of polyelectrolyte/polyamide membranes by alginate

By replacing PAA with alginate (at least for the outermost polyelectrolyte layers), the PEI/alginate bilayers formed were shown to be effective in improving the membrane stability and selectivity without chemical crosslinking. This presents a further improvement in the membrane performance, while eliminating the need for chemical crosslinking.

8.3 Recommendations for the future work

In this thesis, the effets of polyelectrolyte concentration, deposition time and temperature on the membrane pervaporation were evaluated. Other factors (e.g., pH, ionic strength) and mode of deposition (e.g., dynamic vs static deposition) are expected to have an impact as well [Krasemann et al., 2001].

8.3.1 Impact of pH of deposition solution

When weak polyelectrolytes are used as constituents of multilayers, the amount of charges in the multilayers can vary with the acidity of dipping solutions. Therefore, changes in pH might trigger changes in film structure because the degree of ionization of polyelectrolyte maybe change with pH [Kharlampieva and Sukhishvili, 2003, Wang et al., 2010; Shiratori et al., 2000]. To achieve a high crosslinking density, both the cationic and anionic polyelectrolytes need to be adsorbed in a highly charged state. The polar groups of polyelectrolyte will be protonated at low pH, and the opposite situation will happen when the pH value is very high. For example, the amine groups of PEI will be present as positively charged ammonium groups while the carboxyl groups of PAA will be mainly non-ionized at low pH. Therefore, a considerable deal of ionization occurs at an intermediate pH, which was considered to be the optimum pH for membrane [Krasemann et al, 2001]:

$$pH_{opt} = \frac{pK_a(polyanion) + pK_a(polycation)}{2}$$

The cationic and anionic polyelectrolytes will be partially ionized if the pH value stays above or below pH_{opt}, and as a consequence the membrane will have a lower degree of crosslinking. According to literatures, values for pK_a of PAA in the absence of added salt range from about 5.5 to 6.5 [Bromberg, 1998; Philippova et al., 1997] and pK_a of chitosan is around 6.5 [Liu et al., 2004]. Consequently, the optimal pH for chitosan/PAA polyelectrolyte pairs without salt should be around 6~6.5.

8.3.2 Impact of salt in deposition solution

Addition of salt can also influence the formation and function of polyelectrolyte multilayer membranes. The presence of a salt in the polyelectrolyte matrix can reduce the electrostatic repulsion between the polyelectrolyte chains. The chains will be absorbed at the coil state which tend to make the polyelectrolyte layer thicker and eventually decreases the permeation flux. Krasemann et al. [2001] studied the effect of salt addition on the membrane performance and found the resulting membranes with salt addition showed the lower permeation flux and greater separation factor than those of without salt addition. It is mainly due to the increased thickness of polyelectrolyte multilayers.

On the other hand, the addition of a salt in the polyelectrolyte solution can sometimes cause a partial decomposition of the polyelectrolyte films and consequently decrease the stability of polyelectrolyte multilayers. Without addition of salt, the polycation charges are compensated by polyanions. When NaCl is added, the ions can enter the interior of a multilayer to compensate for the polyelectrolyte charges, which makes the polyelectrolyte chains more tortuous, resulting in a rearrangement at the surface of the substrate. The structure of the polyelectrolyte multilayers will become looser and swelling to certain extent, and consequently the selectivity will be reduced [Wang et al., 2010]. For an extremely case, if the swelling is sufficiently enough, the multilayers will partially decompose and go back into the external solutions.

8.3.3 Impact of dynamic deposition

Moreover, the dynamic deposition method is reported to be more effective than static deposition. The deposition of polyelectrolyte is a two-step process. First, the polyelectrolyte particles deposit on the surface of the substrate and then rearrange on the surface to form a dense and high ordered crosslinked structure. For example, using static despotion, membranes with 50-60 number of polyelectrolyte multilayers were required to achieve considerable separation performance in the studies of Tikek and co-workers [Krasemann et al., 2001; Toutianoush and Tieke, 2002; Toutianoush et al., 2002]. It is a very time-consuming procedure to prepare membranes. The dynamic deposition method is used to simplify this procedure as the dynamic deposition may help speed up the deposition of the polyelectrolyte macromolecules [Zhang et al., 2008]. Both electric field and external pressure can be used to improve the polyelectrolyte deposition.

The main driving force for LbL self-assembly is electrostatic attractions. The charged polyelectrolyte chains in dilute solutions will transfer to specific orientation in electric field [Zhang et al., 2006]. Therefore, external electric field should be an effective tool to promote the assembly during the self-assembly process. Under an electric field, the fluidity of the polyelectrolytes increases greatly and the disordered chain shapes will be oriented which will shorten the time for rearrangement during the adsorption process [Zhang et al., 2008].

Similarly, under an external pressure, the polyelectrolytes solutions were prone to aggregate at the places with higher permeate rate, which will help seal the membrane pores and form uniform layers within only a few pairs. In addition, the polyelectrolyte multilayers will become more compact than those without pressure and consequently, increasing the membrane separation performance [Zhang et al., 2006].

8.3.4 Research on membrane modules

In order to make the polyelectrolyte membrane commercially viable, membranes need to be packed into modules. Industrial applications often require hundreds to thousands of square meters of membranes to perform the separation required on a commercial scale. A plate-and-frame module is one of the earliest types of membrane systems, and this configuration is now mainly used in electrodialysis and pervaporation. The disadvantage is that it gives the lowest surface area/unit volume ratio. Spiral-wound modules are used mainly for extraction of organics, with low concentration of organics and lower temperatures. The major problem for this module is the large pressure drop, especially at high flow rate. Hollow fiber modules are comprised of hollow-fiber membranes, which allow very large fiber membrane areas to be contained in a small volume.

For pervaporation applications, little work is reported in the literature about module design. Because of the LbL buildup of polyelectrolyte membranes, it would be of interest to further develop the polyeletrolyte membranes for spiral-would modules and hollow fiber modules, which may require the substrate to be packed in the module before LbL buildup of the active separation layer.

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Appenix A

Solubility parameters

The solubility parameter is an important concept that can be used for the rational selection of solvents. Both total solubility parameter and its constituent partial solubility parameters [Stefanis and Panayiotou, 2008] are widely used for the selection of appropriate solvents for given solutes. The solubility parameter, δ_t, is defined as the square root of the cohesive energy density:

$$\delta_t = \sqrt{\frac{E_{coh}}{V}} \qquad \text{(A-1)}$$

It has been assumed that ΔE is given by the simple sum of the energies from dispersion forces, ΔE_d, polar force ΔE_p, and hydrogen bonding forces, ΔE_h [Hansen, 1967]. That is,

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h \qquad \text{(A-2)}$$

Dividing quation (A-1) by the molecular volume yields,

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad \text{(A-3)}$$

If defined $\delta_d = (\Delta E_d / V_m)^{1/2}$, $\delta_p = (\Delta E_p / V_m)^{1/2}$, $\delta_h = (\Delta E_h / V_m)^{1/2}$;

where δ_t is the total solubility parameter, δ_d , δ_p and δ_h are the dispersion force component, dipole component and hydrogen bonding component of the solubility parameter, respectively.

The three parameters can be treated as the coordinates for a point in three dimensions. If the two species are closer in this three dimensional space, they are more likely to dissolve into each other. For polymeric membrane and solvent system, if the difference between these two parameters is small, the polymeric membrane could not be stable in this solvent.

Table A-1 shows the solubility parameters and the components for the polymers and some commonly used solvents, and Table A-2 presents the values of group contributions to $E_{coh,i}$ and V_i.

Table A- 1 The Hansen solubility parameter of various pervaporation solvents [Shao and Huang, 2007]

Solvent	Dispersion($cal^{1/2}cm^{-3/2}$)	Polar ($cal^{1/2}cm^{-3/2}$)	Hydrogen ($cal^{1/2}cm^{-3/2}$)
1,2-Diethy benzene	17.7	0.1	1
1,4-Dioxane	19	1.8	7.4
1-Butanol	16	5.7	15.8
1-Butene	13.2	1.3	3.9
1-Heptene	15	1.1	2.6
1-Hexene	14.7	1.1	0
1-Pentanol	15.9	4.5	13.9
1-Propanol	16	6.8	17.4
2,3-Dichlorobenzene	19.7	12.6	4.4
2,4-Dichlorobenzene	20.4	8.7	4.2
2-Butanol	15.8	5.7	14.5
2-Pentanol	15.6	6.4	13.3
2-Propanol	15.8	6.1	16.4
Acetic acid	14.5	8	13.5
Acetone	15.5	10.4	7
Acrylic acid	17.7	6.4	14.9
Benzene	18.4	0	2
Butane	14.1	0	0
Carbon tetrachloride	17.8	0	0.6
Chlorobeneze	19	4.3	2
Chloroform	17.8	3.1	5.7
Cyclohexane	16.8	0	0.2
Diethyl carbonate	16.6	3.1	6.1
Diethyl ether	14.5	2.9	5.1
Diethyl ketone	15.8	7.6	4.7
Diethylene glycol	16.6	12	20.7
Dimethyl carbonate	15.5	3.9	9.7
Ethanol	15.8	8.8	19.4
Ethyl acetate	15.8	5.3	7.2
Ethyl benzene	17.8	0.6	1.4
Ethylene dichloride	19	7.4	4.1
Ethylene glycol	17	11	26
Glycerol	17.4	12.1	29.3
Heptane	15.3	0	0
Hexane	14.9	0	0
m-Dichlorobenzene	19.7	5.1	2.7
Methanol	15.1	12.3	22.3
Methylacrylic acid	15.8	2.8	10.2
Methylene dichloride	18.2	6.3	6.1
n-Butyl acetate	15.8	3.7	6.3
Octane	15.5	0	0
Octanol	17	3.3	11.9
o-Dichlorobenzene	19.2	6.3	3.3
o-Xylene	17.8	1	3.1

p-Dichlorobenzene	19.7	5.6	2.7
p-Diethyl benzene	18	0	0.6
Phenol	18	5.9	14.9
Propionic acid	14.7	5.3	12.4
Tetrahydrofuran	16.8	5.7	8
Toluene	18	1.8	2
Trichloroethylene	18	3.1	5.3
Triethylene glycol	16	12.5	18.6
Water	15.5	16	42.3
Xylene	17.6	1	3.1

Table A- 2 Group Contributions to $E_{coh,i}$ and V_i [Matsuura, 1994]

Structural group	Ecoh,i (cal/mol)	V_i (cm^3/mol)
$-CH_3$	1,125	33.5
$-CH_2-$	1,180	16.1
＞CH-	820	-1.0
＞C＜	350	-19.2
$H_2C=$	1,030	28.5
-CH=	1,030	13.5
＞C=	1.030	-5.5
HC≡	920	27.4
-C≡	1,690	6.5
-CONH-	8,000	9.5
$-CONH_2-$	10,000	17.5
-CON＜	7.050	-7.7
-OH	7,120	10.0
-O-	800	3.8
-CO-	4,150	10.8
-COOH	6,600	28.5
$-NH_2$	3,000	19.2
-NH-	2,000	4.5
-N＜	1,000	-9.0
-N=	2,800	5.0
Phenyl	7,630	71.4
-F	1,000	18.0
$-NF_2$	1,830	33.1
-NF-	1,210	24.5
-CN	6,100	24.0
$-NHHO_2-$	9,500	28.7
-SH	3,450	28.0
-S-	3,380	12
$-SO_2-$	9,350	23.6

Appendix B

B-1 Calculations of the permeation flux and separation factor for the membrane

Sample calculations for separation of ethylene glycol/water at 25 ^{o}C, collected 0.284g of permeate over 2 hr with membrane cell of 16.6 cm^2.

Calculate total permeation flux

$$Flux\ (J) = \frac{m}{A*t} = \frac{0.284/1000}{\left(\frac{16.6}{10000}\right)*2} = 0.085\ kg/(m^2 \cdot h)$$

J = permeation flux, kg/(m^2·h);

m = amount of the permeate, kg;

A = area of membrane, m^2;

t = operating time, h

Calculate sparation factor

$$Separation\ factor\ \alpha_{\mathrm{ij}} = \frac{\mathrm{Y_i/Y_j}}{\mathrm{X_i/X_j}} = \frac{94.2/(100-94.2)}{10.6/(100-10.6)} = 145.2$$

α_{ij} = separation factor;

Y_i, Y_j = concentration of component i and j in permeate, respectively;

X_i, X_j = concentration of component i and j in feed, respectively

Caculate partial permeation flux

$$Partial\ permeation\ Flux_{\ p,i} = Flux_{\ t} * X_i$$

$$Flux_{p,H_2o} = 0.085 * 94.2\% = 0.081\ kg/(m^2 \cdot h)$$

$$Flux_{p,EG} = 0.085 * (1 - 94.2\%) = 0.004\ kg/(m^2 \cdot h)$$

Partial permeation flux$_{p,i}$ = Partial permeation flux of component i;

B-2 Calculation of the Apparent Activation Energy from the Arrhenius Equation

The relationship between the permeation flux and temperature can be expressed by Arrehenius equation and the apparent activation energy can be obtained from ln*F* vs. (1/*T*) plot based on the following form of the equation:

$$\ln F = \ln A + \left(-\frac{E}{R}\right)\left(\frac{1}{T}\right) \qquad \text{(B-1)}$$

$$slope\ k = -E/R \qquad \text{(B-2)}$$

E = activation energy of permeation

R = 8.314 J/(mol.K)

1000/T is used to simplify the unit conversion to kJ.

Plot partial permeation flux vs. 1000/T for H_2O and ethylene glycol in Figure B-1, resulting slope (k) and intercept (b) are:

k_1= -1.57, b_1= 1.79;

k_2= -4.49, b_2= 8.39;

$$E_1 = -k_1 * R = -(-1.57) * 8.314\ \frac{kJ}{mol \cdot K} = 13.05\ kJ/mol$$

$$E_2 = -k_2 * R = -(-4.49) * 8.314\ \frac{kJ}{mol \cdot K} = 37.33\ kJ/mol$$

So, the activation energy for water and ethylene glycol are 13.05 and 37.33 kJ/mol.

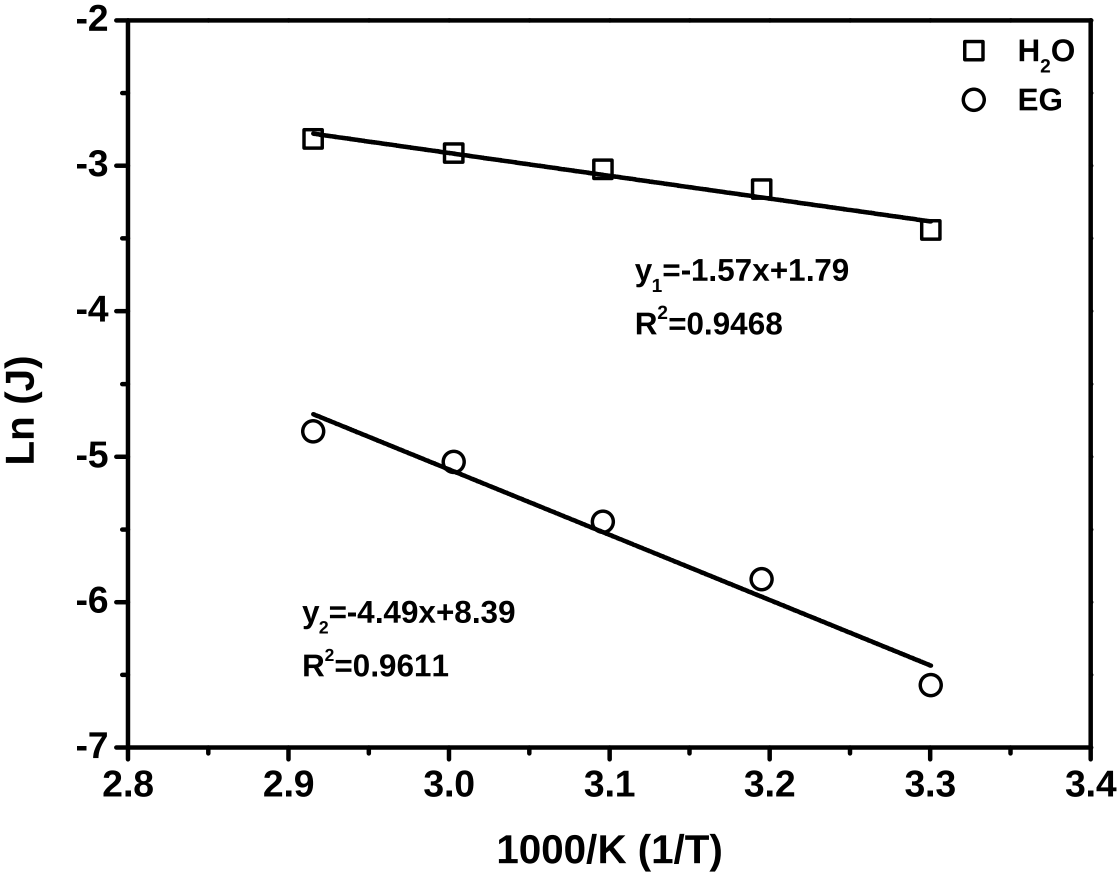

Figure B- 1 Caculation for the activation energy of ethylene glycol and water