Pervaporation Of Ethanol/Water mixtures using PDMS mixed matrix membranes

by

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ABSTRACT

Among the major applications of pervaporation membrane processes, organic separation from organic/water mixtures is becoming increasingly important. The polydimethylsiloxane (PDMS) is among the most interesting and promising membranes and has been extensively investigated. PDMS is an "organicelastomeric material, often referred to as "silicone rubber", exhibiting excellent film-forming ability, thermal stability, chemical and physiological inertness. In this thesis incorporation of nanosilicalite-1 particles into a PDMS matrix and effect of particle loading and temperature variation on membrane performance was studied. A strong influence of zeolite was found on the pervaporation of alcohol/water mixtures using filled PDMS membranes. The mixed matrix membrane showed high separation factor at higher zeolite loading and high flux at higher temperature.

DEDICATION

To my family

Binodkumar Yadav

Geeta Yadav

Anil Yadav

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LIST OF SYMBOLS

Symbol

α	:	Separation factor
Ci	:	Ethanol concentration
Cj	:	Water concentration
J_i	:	Flux of component i (gm/hr/m^2)
P_i	:	Permeability of the composite membrane (Barrer)
P_z	:	Zeolite permeability (Barrer)
P_r	:	Rubber permeability (Barrer)
ϕ_z	:	Volume fraction zeolite
γ	:	Surface tension
β	:	Temperature gradient
h	:	Film thickness
μ	:	Viscosity
α_i	:	Thermal diffusivity
T_g	:	Glass transition temperature
a_i	:	Activity of a component i
Bi	:	Mobility of component i
Di	:	Diffusion coefficient of component i
$D_{o,i}$	:	Diffusion coefficient at zero concentration
γi	:	Plasticizing constant
Lij	:	Interaction parameter for component i and j
μ_i	:	Chemical potential for component i

ϕi	:	Volume fraction of component i (i=1,2,3,p,s)
ε	:	Sorption value
ΔG_m	:	Free enthalpy of mixing
χ	:	Interaction parameter
ΔG_{el}	:	Elastic free energy
M_c	:	Average molecular weight
E	:	Cohesive energy
V	:	Molar volume
δ_i	:	Hansen solubility parameter (i=d,p,h)
ΔE_d	:	Energy to overcome dispersion forces
ΔE_p	:	Energy to overcome polar interactions
ΔE_h	:	Energy to break hydrogen bonds
ΔH_m	:	Partial molar enthalpy of mixing

Chapter 1

INTRODUCTION

1.1 MEMBRANE SEPARATION PROCESSES

To think of membranes is generally to think of separations. The majority of membranes today are applied as semipermeable barrier layers which permit certain components of solutions or suspensions to permeate more rapidly than others. The absolute rate at which a permeant traverse a membrane is known as *flux*, and the rate at which two different species permeate relative to one another is *selectivity*. Flux and selectivity are the primary, but by no means the only, determinants of the practicality of any membrane separation.

Various criteria are used to classify membranes including the morphology of the membrane and the separation process to which it is applied. The membranes discussed in this thesis are free-standing dense polymeric films and supported nanocomposite membranes with nanosized zeolite particles homogeneously distributed in a continuous polymeric film. Transport across the membrane occurs because of a chemical potential gradient. According to solution-diffusion mechanism, the components of the feed mixture traverse through the membrane by dissolving in the membrane at the feed side, diffusing through the film and desorbing at the permeate side (Mulder & Smolders, 1984; Mulder, Franken, & Smolders, 1985; Wijmans & Baker, 1995).(Mulder & Smolders, 1984)(Mulder & Smolders, 1984)

Solution-diffusion membranes are used in various membrane processes including gas separation, vapour permeation, reverse osmosis, and

pervaporation. For pervaporation the feed consists of a liquid mixture and at the permeate side the vapour pressure of the components is kept low by vacuum or a sweep gas. As the separation is based on differences in solubility and diffusivity of the components in the membrane, it is possible to separate azeotropic mixtures by means of pervaporation without using additives (R. Y. M. Huang, 1991).

To be useful in industrial separation processes, a membrane must exhibit at least the following characteristics (Pinnau & Freeman, 2000):

- High flux and selectivity
- Mechanical stability
- Tolerance to feed components (fouling resistance)
- Tolerance to temperature variations
- Manufacturing reproducibility
- Low manufacturing cost
- Ability to be packaged into high surface area modules

Higher flux at a given driving force requires low cross-sectional membrane area; this also canreduce the capital cost of a membrane system. The selectivity determines the separation capability. Membranes with higher selectivity are desired because higher product purity can be achieved in a single-stage of the separation process. For solution-diffusion membranes this is difficult to achieve because a highly permeable polymer generally has low selectivity and polymer with high selectivity has low permeability. Extensive effort is spent on the synthesis and investigation of new polymers and polymer blends as membrane material (S. Chen, Yu, Lin, Chang, & Liou, 2001; Ohya, Matsumoto, Negishi,

Hino, & Choi, 1992; Shieh & Huang, 1998; D. Wang, Lin, Wu, & Lai, 1997) for pervaporation of ethanol/water mixtures.

In this thesis we study the effect of incorporation of nano-sized silicalite molecular sieves into dense polymeric. From literature it is known that this can lead to increase in both flux and selectivity of polymeric membranes (Bowen, Noble, & Falconer, 2004; X. Chen, Ping, & Long, 1998; Jia, Pleinemann, & Behling, 1992).

1.1.1 Membrane materials for alcohol recovery

Various membrane materials have been studied for recovery of organic compounds from water by pervaporation. Membranes used for pervaporation of ethanol/water mixtures can be categorized as hydrophilic and hydrophobic. In case of dehydration, where low concentration of water needs to be separated from solvent, hydrophilic membranes are used because they preferentially allow water to permeate through. Conversely, when a small amount of solvent is required to be removed from a stream of water, hydrophobic membranes are used.

For dehydration of alcohols, different membrane materials like poly-vinyl alcohol (PVA), chitosan, psf, polyimide, polyamide, polyaniline, cellulose acetate have been tested. Table 1 gives a brief summary of some of the hydrophilic materials tested by many researchers. A detailed review on membranes for dehydration of solvents was done by Peter D. Chapman et al. (Chapman, Oliveira, Livingston, & Li, 2008).

Table 1: Dehydration of alcohols using different membrane materials.

Mixture (mass ratio)	**Support**	**Separation Layer**	**β**	**Flux ($kgm^{-2}h^{-1}$)**	**Temp (C)**	**Ref.**
EtOH/H_2O (50:50)	PVA	PVA	100	0.25	45	(R. Y. M. Huang, 1991)
EtOH/H_2O (95:5)	PVA, PAAM	PVA, PAAM	45-4100	0.1-0.06	75	(Ruckenstein & Liang, 1996)
EtOH/H_2O (90:10)	Chitosan	Chitosan	1791	0.472	60	(Ge, Cui, Yan, & Jiang, 2000)
EtOH/H_2O (90:10)	Chitosan	Chitosan	127	0.201	50	(Zhang, Li, Fang, & Wang, 2007)
EtOH/H_2O (90:10)	PSF/PEG	PSF/PEG	325	0.6	25	(Hsu et al., 2003)
EtOH/H_2O (90:10)	PSF	PSF	600	0.7-0.9	25	(S. Chen et al., 2001)
EtOH/H_2O (95:5)	PI-2080 polyimide	PI-2080 polyimide	900	1	60	(Yanagishita, Maejima, Kitamoto, & Nakane, 1994)
EtOH/H_2O (90:10)	BAPP	BAPP	22	0.27	25	(Y. C. Wang, Tsai, Lee, & Lai, 2005)
EtOH/H_2O (90:10)	Nylon-4	Nylon-4	4.5	0.35	25	(K. Lee, Chen, & Lai, 1992)
EtOH/H_2O (90:10)	Nylon-4	Nylon-4/PVA	13.5	0.42	25	(Y. M. Lee & Shin, 1991)(K. Lee et al., 1992)(K. Lee et al., 1992)

β = separation factor = water/ethanol

In hydrophobic membranes PDMS remains to be best material for pervaporation membranes due to inert nature, thermal stability and good film forming tendency.

Table 2. gives a brief summary of some of the hydrophobic materials tested. A detailed review on pervaporation from fermentation broths has been done by Leland M. Vane (Vane, 2005).

Table 2: Pervaporation of alcohols through hydrophobic membrane materials

Polymer	**Temp (C)**	**α**	**Notes**	**Ref**
PTMSP	30	15.1 - 19.9	6wt% EtOH, 14-43 μm thick	(Volkov et al., 2004)
Poly(methyl Phenyl siloxane)	50	11.7	4.1 wt% EtOH	(X. Chen et al., 1998)
PTMSP/PDMS graft copolymer	30	28.3	Max α at 12 mol% PDMS, 7 wt% EtOH	(Nagase, Ishihara, & Matsui, 1990)
Plasma polymerized silane	25	18	4 wt% EtOH, polymer of hexamethyltrisiloxane	(Kashiwagi, Okabe, & Okita, 1988)
Polysiloxaneimide ODMS/PMDA/MDMS	40	10.6	10 wt% EtOH, 1.5:2:0.5 equivalents of ODMS:PMDA:MDMS	(Krea, Roizard, Moulai-Mostefa, & Sacco, 2004)

α = separation factor = EtOH/water
PTMSP = poly(1-(trimethylsilyl)-1-propyne).
ODMS = α,ω-(bisaminopropyl) dimethylsiloxane oligomer.
PMDA = 1,2,4,5-benzenetetracarboxylic dianhydride.
MDMS = 1,3-bis(3-aminopropyl) tetramethyldisiloxane.

1.1.2 Membrane performance: Flux and Selectivity

Performance of a membrane is determined by flux and selectivity. The flux is greatly influenced by driving force and is inversely proportional to the membrane thickness. To compare membrane properties the following definitions and units will be used.

- Separation factor β_{ij} for a pervaporation process is defined as

$$\beta ij = \frac{\left(\frac{ci}{cj}\right)permeate}{\left(\frac{ci}{cj}\right)feed} \qquad 1.1$$

- Flux for a pervaporation membrane is expressed in gm $hr^{-1}m^{-2}$. To correct for the membrane thickness the flux will be normalized to a fixed membrane thickness.

J = (weight of permeate)/(membrane surface area * no. of hours of operation)

- Membrane selectivity (α_{ij}), defined as the ratio of the permeabilities of components i and j through the membrane:

$\alpha_{ij} = P_i/P_j$

where, P is the permeability of the component in kmol m^{-1} s^{-1} kPa^{-1}

1.2 ZOELITES

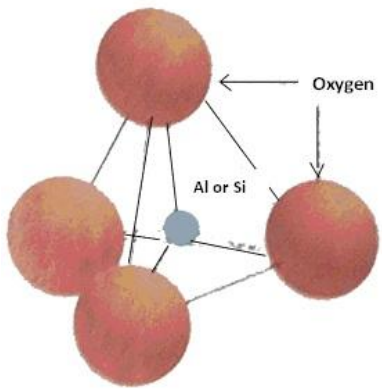
1.2.1 Definition, Structure and Applications

Zeolites are inorganic crystalline solids with small pores running throughout the solid. They are aluminosilicate framework structures made from sharing corners of a SiO_4 and AlO_4 tetrahedron and can be represented by the empirical formula $M_{2/n}O.Al_2O_3.xSiO_2.yH_2O$. In this formula n is the cation valence. As Al has a valence 3 and Si has a valence 4, incorporation of alumina in a silica lattice will lead to a negative framework charge which is compensated by a non-framework cation. The factor x is > = 2 because every alumina tetrahedral has to be surrounded by a silica tetrathedra. The factor y depends on the Si/Al ratio, the pore volume etc. The factor y depends on the Si/Al ratio, the pore

volume etc. As the Si/Al ratio increases, the cation content decreases, the thermal stability increases and the surface selectivity changes from hydrophilic to hydrophobic (Breck, 1975).

Structurally, zeolites are built of primary and secondary building units. Primary unit is SiO_4 or AlO_4 tetrahedron. Si or Al atom sits at the center of the tetrahedron with 4 oxygen atoms covalently bonded to the centered Si or Al atom also called the T-atom. From this primary unit, a number of secondary building units can be built by a linkage through the oxygen atom covalent bonding, which is called an oxygen bridge. The secondary building units are featured by simple geometric shapes as shown in Figure 1.

Primary Unit



Secondary Units

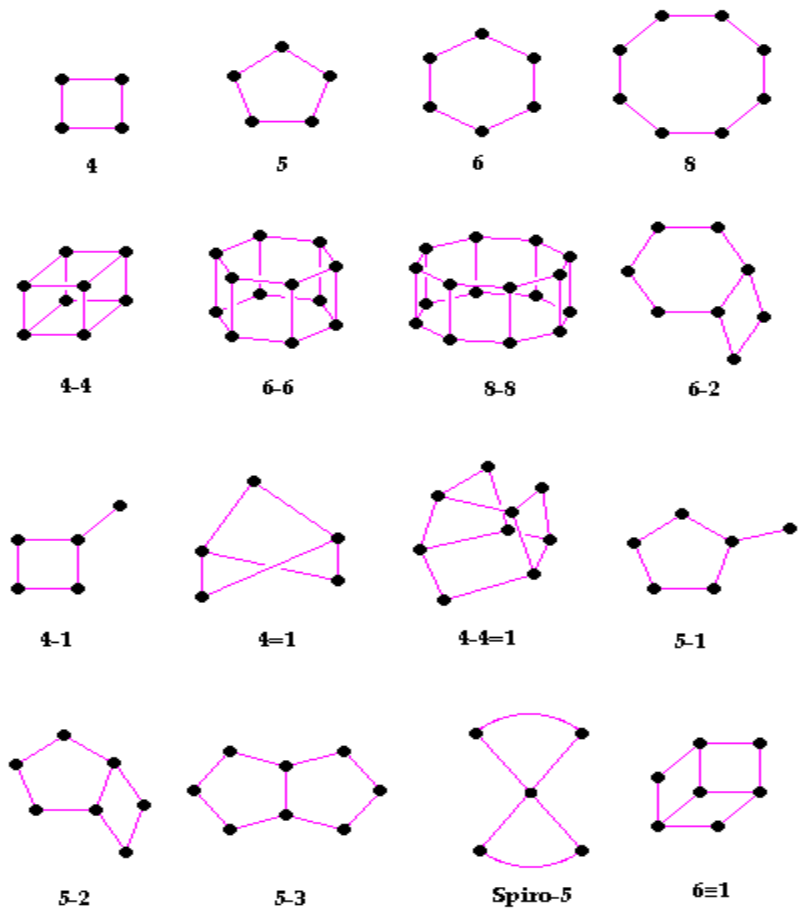


Figure 1: Schematic representation of building units for zeolites (The composition of quartz.).

We will be focusing on nanoparticles of silicalite-1 (the silica version of the MFI zeolite structure) in this thesis. Structure for the MFI zeolite structure is given in *Figure 2*. Silicalite-1 was the first aluminum free zeolite synthesized by Flanigen et al. (Flanigen E.M., Bennett M.J., Grose R.W., Cohen J.P., & Patton R.L., 1978).

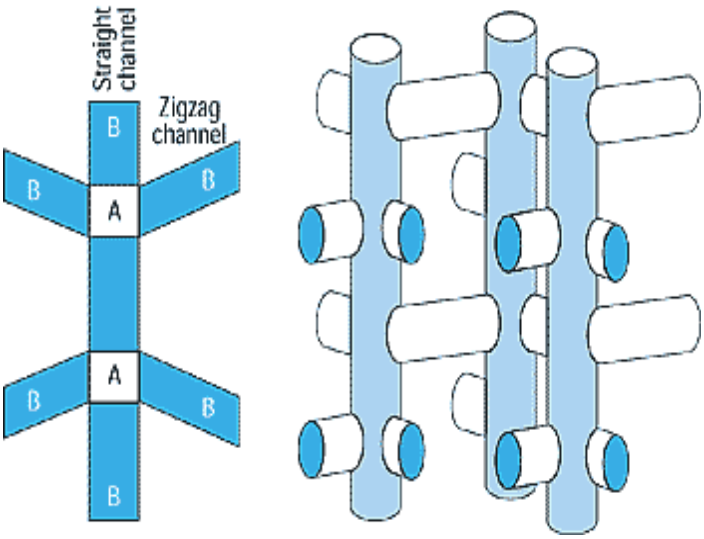


Figure 2: Structure of silicalite-1

In brief, zeolites have the following unique properties.

- Acidity and basicity
- Ion-exchange ability
- Shape selective ability
- High surface are
- Micropores
- Structural stability
- Thermal stability up to 1000 ^{0}C

Because of these unique properties zeolites have found many applications. Their major applications are:

- Ion-exchangers: Making detergent
- Adsorbents: Ethylene recovery, catalytic converters, separating O_2 and N_2 from air, environmental control and protection
- Catalysts: catalytic cracking, catalytic reforming, lube waxing, hydrocracking, isomerization, oligomerization, hydration of olefins etc.

1.2.2 Transport through zeolite filled membranes

Te Hennepe (te Hennepe, Bargeman, Mulder, & Smolders, 1987) derived a model to describe permeation of ethanol/water through zeolite filled membrane. It is easy to describe mass transport in a composite consisting of laminate but for a dispersed phase in continuum, factors like particle size, shape and orientation greatly influence the overall mass transport. In this thesis we discuss two transport models.

Geometrical mean model

This is a very simple approach and is expressed by equation 1.2.

$$\ln(P_i) = \phi_z \ln(P_z) + (1-\phi_z) \ln(P_r) \qquad 1.2$$

where:

P_i permeability of the composite membrane (Barrer)

P_z zeolite permeability (Barrer)

P_r rubber permeability (Barrer)

ϕ_z volume fraction zeolite

Model of te Hennepe

Te Hennepe et al (Hennepe, Smolders, Bargeman, & Mulder, 1991) calculated the overall resistance in a zeolite filled membrane by combining the resistances in the membrane (in parallel and in series) in the same way as is done in electrical circuits. This leads to equation 1.3

$$Pi = 1/ \left((1-\phi_z^{1/3})/ P_r + 3/2\ \phi_{z,i}^{1/3}/ P_r(1-\phi_z) + 3/2\ P_z\ \phi_z \right) \qquad 1.3$$

In the te Hennepe model, it is assumed that the permeabilities of the two phases are independent of each other. Also P_r and P_z are overall parameters and independent of their position in the membrane. This assumption is valid for the permeation of components which have a low interaction with the polymer. However, this model is not correct for three reasons.

First, it can be seen from equation 1.3 that if the zeolite permeability is equal to the polymer permeability, the overall permeability of the membrane is still a function of the volume fraction of filler. This is due to the factor 3/2 which was introduced as tortuosity factor. The physical meaning of this factor is that if a molecule cannot pass through a zeolite cube, the path length is assumed to be 3/2 times larger compared to the path length of a molecule that can pass through the zeolite.

Second, one assumption in derivation of the model is not correct. To calculate the area fraction in a plane in the membrane that is occupied by zeolite, te Hennepe refers to Nielsen (Nielsen L.E., 1967). Nielsen assumed that each zeolite particle is surrounded by an equal amount of polymer. In the model of te Hennepe this condition is not met. Therefore equation 1.4 is more correct.

$$Pi = 1/ ((1-\phi_z^{1/3})/ P_r + \phi_{z,i}^{1/3}/ P_r(1-\phi_z^{2/3}) + P_z \phi_z^{2/3}) \quad 1.4$$

Third, the model is not able to fit all experimental results satisfactorily.

1.3 MIXED MATRIX MEMBRANES

One of the major challenges facing membrane material design is achieving higher selectivity. Zeolites can overcome this challenge, but not in an economical way. Ceramic, glass, carbon and zeoliltic membranes cost around one to three magnitude more per unit area of membrane in comparison to polymeric membranes (Vane, 2005).

Mixed matrix membranes (MMM) are a blend of inorganic (often molecular sieves) within a continuous polymer matrix. The continuous bulk phase (phase A) is typically a polymer; and the dispersed phase (phase B) represents the inorganic particles, which may be zeolite, carbon molecular sieves, or nano-size particles. Mixed matrix membranes (MMMs) combine the processability of the polymer phase with superior transport properties of the molecular sieves.

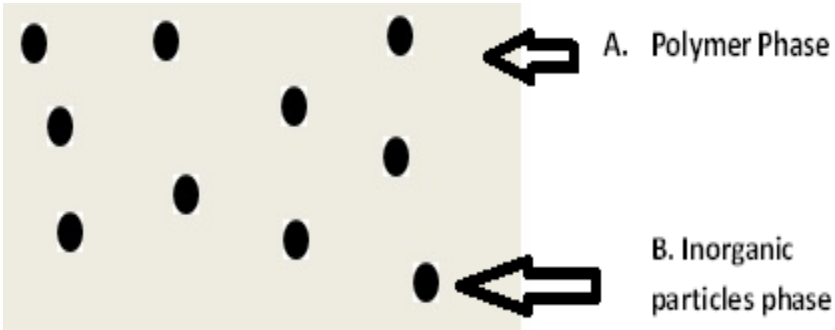


Figure 3: Schematic of a mixed matrix membrane (MMM)

1.3.1 Background

To form a successful mixed matrix membrane one has to choose polymers that can maintain flexibility during membrane formation and have a favorable interaction with the sieve. However this can be a big challenge since flexible polymers lack mechanical stability under high pressure and even moderate temperatures. Also having a large zeolite loading can create pinholes in membranes due to the formation of agglomerates thereby reducing membranes efficiency(Vankelecom, Depre, De Beukelaer, & Uytterhoeven, 1995).

Investigation of MMM's for gas separation was first reported in the 1970s by Paul and Kemp (Paul DR, 1973). In this seminal work it was found that addition of 5A zeolite into rubbery polymer PDMS caused very large increase in the diffusion time lag but had only minor effects on the steady-state diffusion. Researchers at Universal Oil Products (UOP) were the first to report that mixed matrix systems of polymer/adsorbent might yield superior separation performance than pure polymeric system (Kulprathipanja S, Neuzil RW, Li NN, 1988).

1.3.2 Factors affecting MMM's performance

Performance of MMM's is not a simple addition of the intrinsic properties of individual phases. Various variables such as polymer-filler interaction, filler size, filler agglomeration may seriously affect MMM performance thus making it difficult to understand. Currently, the major concerns in MMM research are a suitable combination of polymers and particles, the physical properties of the inorganic fillers and the particle/polymer interface morphology and chemistry.

1.3.2.1 Polymer/Inorganic filler combination

Selection of appropriate inorganic filler was the major concern in the early development of MMM's, however it has been found that the choice of a suitable polymer as the matrix is also important in determining the MMM performance.

In case of non-porous fumed silica filled glassy polymer (PMP, poly 1-trimethylsilyl-1-propyne (PTMSP)) for n-butane/methane separation, a significant increase in n-butane permeability and selectivity was observed with fumed silica addition for PMP. In contrast, the hydrocarbon selective PTMSP becomes less selective for hydrocarbons with increasing fumed silica loading (Chung, Jiang, Li, & Kulprathipanja, 2007). This can be attributed to extremely microporous nature, which, when augmented by fumed silica addition, led to an increasing influence of Knudsen flow.

1.3.2.2 Particle Size

To date, most of the studies reported on polymer/inorganic filler MMMs use large particles, with particle diameters on the order of 10-100s of microns. Smaller particles would increase the polymer/particle interface area and possibly increasing the membrane separation performance. Also, smaller particles would enable formation of thinner MMMs.

No particular studies have been done to study the effect of particle size on ethanol/water separations but comparison of studies done by Moermans (Moermans et al., 2000)(Moermans B, De Beuckelaer W, Vankelecom IFJ, Ravishankar R, Martens JA, 2000)(Moermans B, De Beuckelaer W, Vankelecom

IFJ, Ravishankar R, Martens JA, 2000), Jia Meng-Dong (Jia et al., 1992) and Leland M (Vane, Namboodiri, & Bowen, 2008). Vane shows that smaller zeolite particle offers a better performance with lower zeolite loadings.

S Birgul et. al.(Tantekin-Ersolmaz et al., 2000) reported the effect of different particle sizes of silicalite in PDMS for CO_2/N_2, CO_2/O_2 and O_2/N_2 separation. It was shown that the permeability of MMMs decrease with decreasing particle size of silicalite. This may be due to the enhanced polymer/zeolite contact. Thus it can be concluded that smaller particles offer more polymer/particle interfacial area.

1.3.2.3 Particle agglomeration and sedimentation

Due to differing physical properties and densities of zeolite and polymers, precipitation of zeolite from the casting solution may occur during the MMM preparation, resulting in formation of inhomogeneous zeolite and polymer phases in the filled membrane. The agglomeration of zeolites can cause pinholes between different zeolite particles which possibly cannot be filled by polymer segments; resulting in the formation of non-selective defects in the MMM. Zeolite agglomeration and possible pinhole formation escalates with increasing zeolite loading in the initial membrane casting solution.

Few ways to avoid particle agglomeration are (1) preparation of high concentration polymer solutions to increase the viscosity, (2) slowing particle sedimentation or form membrane rapidly, so that the particles do not have enough time to precipitate or used ultra-fine crystallites (< 0.5 micron) with a consequent reduction in the sedimentation rate (Chung et al., 2007).

In some cases, instead of sedimentation, particles may move to the membrane surface and agglomerate. It is believed that agglomeration at the surface is the result of convection cells that form during casting of films and often occurs with membranes formed at high temperatures. The formation of convection cells in liquids that are heated or cooled can be due to instabilities driven by buoyancy or surface tension (Pearson, 1958).

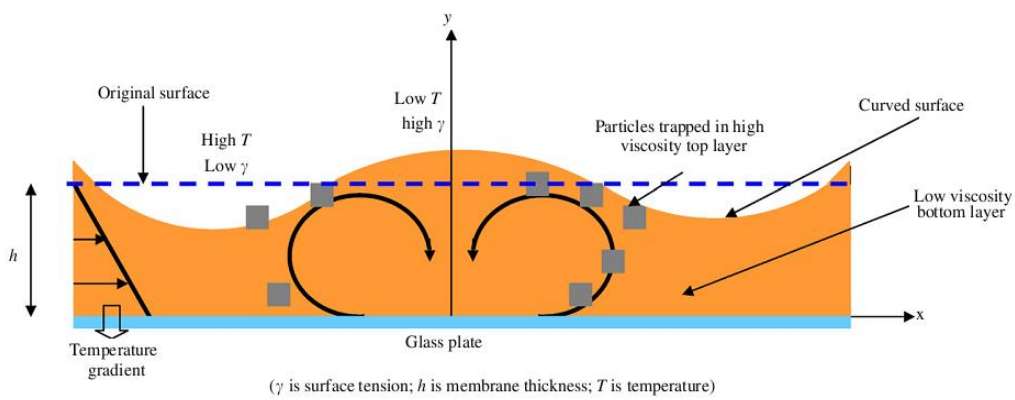


Figure 4: Development of the instability in films cast at elevated temperature (image reproduced from (Mahajan, Burns, Schaeffer, & Koros, 2002)*)*

The schematic for the formation of instability at the surface is shown in Figure 4. The film is at uniform thickness initially, and the instability sets in when a small disturbance causes a point of localized heating on the surface. The result is a decreased surface tension at this point that causes a surface tension gradient to form which causes a horizontal fluid motion away from the point of local heating. Conservation of mass induces bulk fluid flow toward the surface at point of local heating. Due to temperature gradient, the fluid from below is warmer than the fluid it is replacing which further increases the temperature at the point of local heating causing the formation of a self-propagating instability. This

instability can continue if convective motion can overcome viscous forces. Molecular sieves can then become trapped at the top surface, which maintains a higher viscosity than the lower bulk fluid.

Scaling analysis of the above problem was done by Pearson (Pearson, 1958). He described a dimensionless quantity, Marangoni number which is the ratio of surface tension forces to viscous forces. Marangoni number is defined by the following formula:

$Ma = (\delta\gamma/ \delta T)\ \beta^* h^2 / \mu\alpha_i$

where, $\delta\gamma/ \delta T$ is the surface tension gradient with temperature, β is the temperature gradient, h is the thickness of the film, μ is the viscosity, and α_i is the thermal diffusivity. Critical Marangoni number for instability to occur was found to be 79.6 (Pearson, 1958).

Now as the physical meaning of the problem is clear, it is possible to change experimental parameters to eliminate the instability that drives the convective cell formation. The obvious thing is to lower the Marangoni number. Decreasing the film thickness is the best way; but a minimum thickness needs to be maintained to retain mechanical integrity and adequate dispersion of zeolites.

Alternate approach is to examine the onset of the instability. Since heating a film from below causes warmer fluid to flow to the localized heating point, which maintains the instability, if the film was heated from top, the temperature gradients would be reversed. The arising instabilities wouldn't propagate because the colder fluid from the bulk would replace the fluid at the

localized heating point thus reversing the surface tension gradient (Pearson, 1958).

1.3.3 Interface Morphologies

Interface morphology is a critical determinant of the overall performance of MMM. Figure 5 shows a schematic diagram of various nano-scale structures at the polymer/particle interface. Case 1 is an ideal morphology, corresponding to the ideal Maxwell model prediction (Krishna & Wesselingh, 1997). Case 2 shows formation of interface voids due to polymer chains detachment from zeolite surface. Case 3 shows that the polymer chains in direct contact with zeolite can be more rigidified than the bulk polymer chains. Case 4 displays partial pore blockage of the zeolite surface by the rigidified polymer chains.

First attempt to combine zeolites with a variety of organic polymers was done by Barrer and James (Barrer & James, 1960). They demonstrated that adhesion problems occurred at the polymer/zeolite interface when preparing mixtures of a finely powdered polymer and zeolite crystals. This could result in interface voids leading to deteriorated performance as molecules take this non-selective and less resistant by-pass instead of passing through pores in the particle.

The preparation of zeolite-filled membranes from a glassy or rubbery polymer by classic dissolution-casting-evaporation method results in a three-phase membrane: zeolite, polymer, and interface voids. It was hypothesized that

the huge stress occurring during the solvent evaporation step led to the detachment of the polymer from the zeolite external surface. Other possible reasons for interface voids formation include repulsive force between polymer and fillers and different thermal expansion coefficients for polymer and particles (Li, Chung, Cao, & Kulprathipanja, 2005).

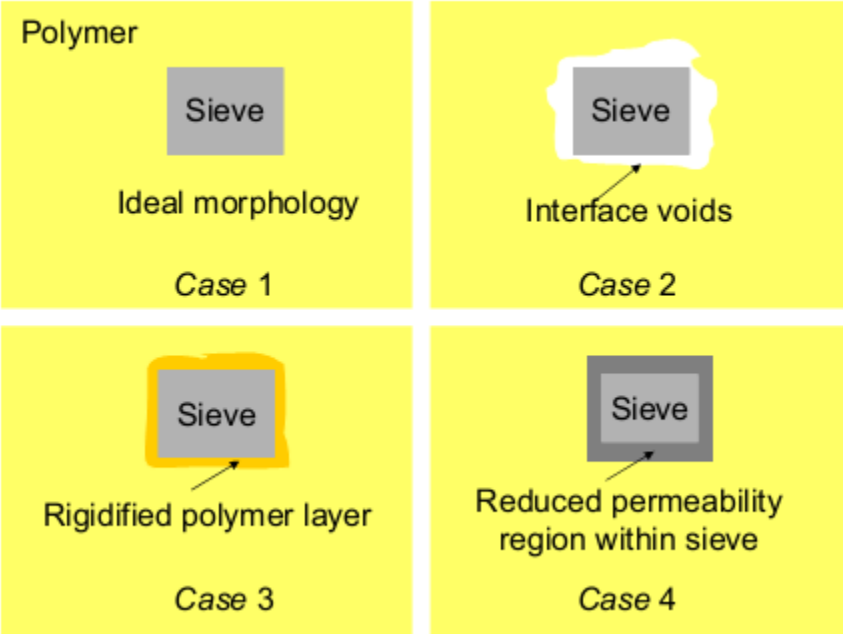


Figure 5: Schematic diagram of various nanoscale morphology of the mixed matrix membrane; image reproduced from (Chung et al., 2007)

In the case of formation of intimate contact between polymer and particles, situations like polymer chain rigidification (case 3) and pore blockage (case 4) might occur (as see in Figure 5). The mobility of polymer chains in the region directly contacting the particles can be inhibited relative to that for the bulk polymer due to an effect called rigidification.

Rigidification enhances the diffusivity selectivity due to lower mobility of polymer chains; that is, the diffusivity difference between larger and

smaller gas molecules is increased. Consequently, higher selectivity in the vicinity of the particles may be obtained due to decreased gas permeability. Glass transition temperature T_g can provide a good estimate of the flexibility of the polymer chains. Higher T_g means higher rigidity and vice (Li et al., 2005; Mahajan et al., 2002).

For MMMs with porous fillers, pore blockage by the polymer chains on the filler surface may occur. Depending on the pore size of fillers, the polymer chain can fill the pores in various degrees. The zeolite could be completely excluded from the transport process due to total pore filling thereby making no difference in performance or on the other hand, the blockage may narrow a part of pores leading to improved separation due to shape/size selectivity.

In effect, in MMMs with porous inorganic fillers, pore blockage is often accompanied by polymer rigidification; and there is no experimental design to distinguish between the influence of these two factors (Mahajan et al., 2002).

1.3.3.1 Optimization of Interface Morphologies

Interface voids

Choosing a polymer with low T_g i.e. flexible backbone at room temperature or membrane formation temperature should significantly reduce dewetting from the zeolite surface. Silicone rubber has a low T_g and is flexible at room temperature. Since silicone rubber is in rubbery state at room temperature it can surround the particles more easily. This is why it is the most popular polymer for preparing MMMs (Vane, 2005).

An attractive force between the particle and the polymer can improve the mophology of MMM. A qualitative characterization of interaction between polymer and zeolite was made by Mahajan et al. (Mahajan et al., 2002). Shouliang Yi (Yi, Su, & Wan, 2010) and Haoli Zhou (Zhou, Su, Chen, Yi, & Wan, 2010) modified the external surface of the zeolites using coupling agents vinyltriethoxysilane (VTES) and vinyltrimethoxysilane (VTMS) respectively. Surface modification of the zeolites showed great improvement in MMM structure but no significant improvement in performance was observed.

Pore Blockage

Since pore blockage by polymer chains can completely eliminate the function of zeolites, investigations are necessary to eliminate this effect. Li et al. used (3-amino)-diethoxymethyl silane (APDEMS) as coupling agent to modify zeolite surface for MMMs. This modification showed improved performance for gas permeability and gas selectivity.

1.4 PERVAPORATION

1.4.1 Introduction

Liquid mixtures can be separated by partial vaporization through a non-porous permselective membrane. This process, which was originally called ‘liquid permeation’ has subsequently been termed ‘pervaporation’ in order to emphasize the fact that the permeate undergoes a phase change, from liquid to vapor, during its transport through the membrane. According to this process (Figure 6), the liquid feed-mixture is circulated in contact with the membrane, and

the permeate is evolved in the vapor state from the opposite side of the membrane, which is kept under low pressure.

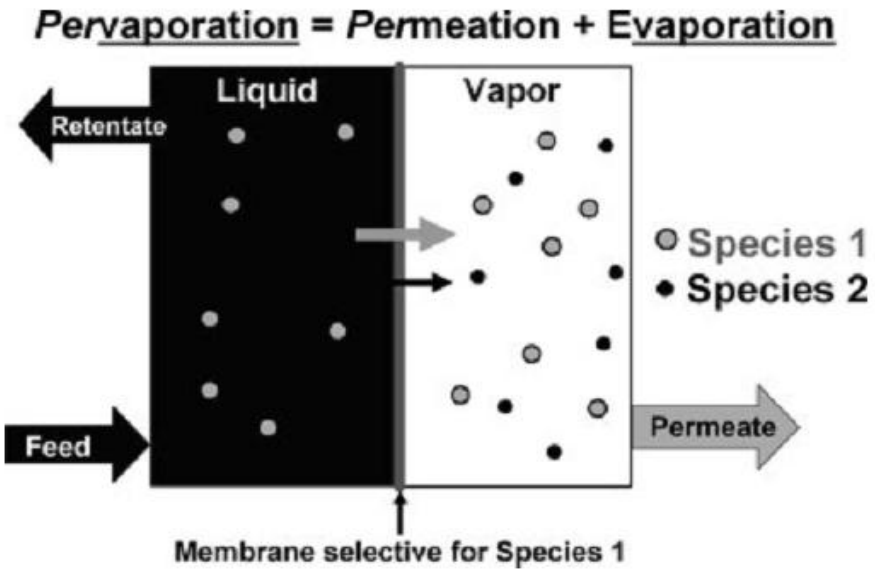


Figure 6: Schematic of a pervaporation process (image reproduced from (Vane, 2005)*)*

The transport of the permeate through the non-porous, selective film involves three successive steps, namely:

1) Selective sorption of the feed components in the upstream layer of the membrane
2) Selective diffusion of the components through the unevenly swollen non-porous membrane
3) Selective desorption in the vapor phase on the permeate side

1.4.2 Thermodynamic Principles Of Pervaporation

1.4.2.1 Single component and binary mixture transport

In pervaporation the vapour pressure at the permeate side is very low, or much lower than the saturation pressure, which means that the activity a''

= (pi / po) is very low or almost zero. For a pure liquid the activity on the upstream side is unity (a' =1) assuming that the interfaces of the membrane are in thermodynamic equilibrium with the upstream and downstream phase. Therefore the activity of a component in the membrane changes from a=1 to a → 0 going from upstream side to the downstream side.

In the case of a pure liquid the activity of liquid just inside the membrane is always one (a=1) and independent of the polymer used. The concentration however is not. The concentration of liquid inside the membrane is strongly dependent on the interaction between the liquid and polymer. In addition the permeation rate through the membrane is strongly dependent on the concentration of the liquid inside the membrane.

For a single component i the flux J_i is equal to the product of concentration and linear velocity, where the velocity is the product of mobility and driving force.

$$Ji = vici = -ciBi\frac{d\mu i}{dx} \qquad 1.5$$

Using ideal conditions (diffusion coefficient independent of concentration) eq 1.5 can be transformed to the Fickian equation.

$$Ji = -Di(c).\frac{dci}{dx} \qquad 1.6$$

In practical situations though the diffusion coefficient of low molecular components in polymers is mostly concentration dependent, and especially in pervaporation the concentration changes much across the membrane. Therefore, often an exponential relation is used to express the concentration dependence of the diffusion coefficient;

$D_i = D_{o,i} \exp(\gamma_i . c_i)$ 1.7

Where $D_{o,i}$ is the coefficient in the membrane at zero concentration and γ_i is the plasticizing constant expressing the influence of the plasticizing action of the liquid on the segmental montions.

Integratiion of eq. 1.7 across the membrane with the boundary conditions

$x = 0 \rightarrow c = c_o^m$

$x = 1 \rightarrow c = 0$

gives the following equation for the flux

$J_i = [D_{o,i} / \gamma_i] [\exp (\gamma_i c_{o,i}) - 1]$ 1.8

Where x is membrane thickness

c_o^m is the concentration of the pure liquid.

From eq 1.8 it can be seen that if the concentration in the membrane increases, the permeation rate increases. In other words, for single liquid transport the permeation rate is solely determined by the interaction between liquid and polymer.

Binary Mixtures

Transport of mixtures through polymeric membrane is complex because the systems are highly interactive. Interaction of the individual permeants with the polymer along with the mutual interaction of the permeants effects the transport through the membrane. Also for binary liquid mixture consisiting of component 1 and 2, the flux can be described in terms of solubility and diffusivity.

The solubility of component 1 in the membrane is not only determined by component 1 but also by component 2. Also the diffusivity of component 1 through the membrane is influenced by the diffusivity of other component because of flow coupling (te Hennepe, Boswerger, Bargeman, Mulder, & Smolders, 1994). Therefore two phenomena have to be distinguished in multi-component transport

1) Flow coupling
2) Thermodynamic interaction leading to preferential sorption

Flow coupling is described through linear non-equlibrium thermodynamics. For a binary mixture the following equations are given;

$$J_1 = L_{11} \frac{d\mu 1}{dx} + L_{12} \frac{d\mu 2}{dx} \qquad 1.9$$

$$J_2 = L_{21} \frac{d\mu 1}{dx} + L_{22} \frac{d\mu 2}{dx} \qquad 1.10$$

First term on the right side of eq. 1.9 described the flux of component 1 due to its own gradient and the second term of this equation describes the flux of component 1due to the gradient of component 2. This second term describes the coupling effect.

Estimation and measurement of coupling effects is very difficult. The flow or selective flow is not only determined by flow coupling but also by thermodynamic interaction. The flux of a component of a binary mixture can be state as;

J = f [(flow coupling),(thermodynamic interaction)] 1.11

In this section the focus is on the thermodynamic interaction. Considering the thermodynamics in relation to pervaporation there is a difference between a ternary system (a binary liquid mixture and polymer) and a binary system (liquid and polymer) because in the former case not only the amount of liquid in the polymer (overall sorption value) is an important parameter but also the composition of that liquid mixture in the polymer. Preferential sorption occurs when the composition of the binary liquid mixture inside the polymer and in the liquid feed mixture are different. If the concentration of a component of a binary liquid mixture in the (ternary) polymeric phase is given by

$$u_i = \frac{\phi i}{\phi 1 + \phi 2} = \frac{\phi i}{1 - \phi 3} \qquad i=1,2 \qquad 1.12$$

and the concentration in the binary liquid feed mixture by vi then the preferential sorption ε is given by

$$\varepsilon = u_1 - v_1 = v_2 - u_2 \qquad 1.13$$

1.4.2.2 Solubility aspects of a single component in a polymer

<u>Flory-Huggins theory</u> (Flory, 1953; Mulder & Smolders, 1984)

This is a statistical lattice model theory developed by Flory and Huggins. According to Flory-Huggins theory the free enthalpy of mixing ΔG_m of a binary mixture consisting of solvent and polymer is given by

$$\Delta G_m = RT\,(n_s \ln \phi_s + n_p \ln \phi_p + \chi\, n_s\, \phi_p) \qquad 1.14$$

The first two terms on the right side give the conformational entropy of mixing whereas the last represents the enthalpy of mixing. The last term contains the binary interaction parameter χ. If the polymer is completely soluble in the solvent

the χ parameter will have a value less than 0.5. With decreasing affinity between polymer and penetrant the value of χ will increase. Differentiation of eq. 1.14 with respect to n_s gives the partial molar free enthalpy or chemical potential μ_s

$$\delta(\Delta G_m)/\delta n_s = \mu_s = RT\ [\ \ln\phi_s + (1-V_s/V_p)\ \phi_p + \chi\ \phi_p^2\ ] \qquad 1.15$$

when the affinity between penetrant and polymer decreases both χ and ϕ_p will increase with the limit as $\phi_p \rightarrow 1$ then $\chi \rightarrow \infty$.

The total change in free enthalpy ΔG is determined by the free enthalpy of mixing ΔG_m and elastic free enthalpy ΔG_{el}. The membrane is a swollen gel or network of polymer chains cross linked due to crystalline regions, chain entanglements or van der waals interactions. Because of the swelling the chain between the crosslink points will be elongated and this causes the networks to exert force to reduce the swelling. The expansion of the network is given by the elastic free energy ΔG_{el}.

$$\Delta G = \Delta G_m + \Delta G_{el} \qquad 1.16$$

At swelling equilibrium $\Delta G = 0$ and eq 1.17 is obtained

$$\ln(1-\phi_p) + \phi_p + \chi\phi_p^2 + (V_s.\ \rho/M_c)\ (\phi_p^{1/3} - 0.5\phi_p) = 0 \qquad 1.17$$

The last term in eq. 1.17 is the contribution of the elastic free energy. M_c is the average molecular weight between two crosslinks. The contribution of the elastic term is mainly determined by two parameters, the amount of liquid in the polymer ϕ_s and the molecular weight between the crosslinks M_c.

The elastic term has significance only when the volume fraction of liquid inside the polymer is high or the M_c is low. For pervaporation the swelling value has to be low otherwise the selectivity will drop. Generally the volume fraction of liquid

inside the polymer is less than 0.25 in which case the elastic term can be neglected. Therefore, neglecting the elastic term the interaction parameter is given by

$$\chi = - [\ln(1-\phi_p) + \phi_p] / \phi_p^2 \qquad 1.18$$

As the affinity between polymer and penetrant increases the amount of liquid inside the polymer increases and χ decreases.

Solubility parameter theory (Dutta, Ji, & Sikdar, 1996-97)

This theory is based on the concept of regular solutions i.e. solutions with ideal entropy of mixing and non-ideal enthalpy of mixing. In liquids there exist strong forces between the molecules and the energy required to break all the bonds associated with one of its constituent molecules is called cohesive energy. The intermolecular forces contributing to the cohesive energy can be divided into 1) nonpolar interactions (dispersion or London forces), 2) polar interactions and 3) chemical bonds like hydrogen bonds. The cohesive energy density (CED) is defined as the ratio between cohesive energy (-E) and molar volume (V).

$$CED = - E / V \qquad 1.19$$

Cohesive energy is assumed to be equal to the total energy of vapourisation. The Hansen solubility parameter (δ) is related to the cohesive energy density.

$$CED = \delta_2 = \Delta E_{vap} / V \qquad 1.20$$

Hansen assumed that the total energy of vapourisation is the sum of the energies required to overcome dispersion forces (ΔE_d), polar interactions (ΔE_p) and to break hydrogen bonds (ΔE_h).

$$\Delta E_{vap} = \Delta E_d + \Delta E_p + \Delta E_h \qquad 1.21$$

Combining eq. 1.20 and eq. 1.21 gives

$$\delta^2 = \delta^2_d + \delta^2_p + \delta^2_h \qquad 1.22$$

A good solvent for the polymer will have a solubility parameter value close to that of the polymer.

From the solubility parameter theory the enthalpy of mixing can be described as

$$\Delta H_m = V\ \phi_1\ \phi_2\ (\delta_1 - \delta_2)^2 \qquad 1.23$$

The partial molar enthalpy of mixing can be obtained by differentiating eq. 1.23 w.r.t n_1.

$$\Delta H_1 = \eth\Delta H_m/\eth n_1 = V_1\ \phi_2\ (\delta_1 - \delta_2)^2 \qquad 1.24$$

and according to Flory-Huggins theory the partial molar enthalpy of mixing can be obtained from

$$\Delta H_1 = \eth\Delta H_m/\eth n_1 = RT\ \chi\ \phi_2^2 \qquad 1.25$$

Combining eq. 1.24 and eq. 1.25 gives

$$\chi = (\delta_1 - \delta_2)^2\ V_1/RT \qquad 1.26$$

Application of solubility parameter theory has some restrictions. ΔG_m, the free enthalpy of mixing, contains two terms, the enthalpy of mixing ΔH_m and the entropy of mixing ΔS_m. In solubility parameter approach only the enthalpy term is considered. Another point is the that the mixing of polymer and solvent is predicted from the properties of the pure components, so specific interactions between polymer and solvent involved upon mixing are not included. And lastly, this theory cannot be used for ternary systems and values for preferential sorption cannot be deduced from this theory. Therefore this theory has minor importance

in predicting or defining separation processes. Only for binary systems consisting of polymer and penetrant this theory is very convenient.

1.4.3 Pervaporation Applications

Pervaporation is effective to dilute solutions containing trace amounts of the target component to be removed. Based on this, hydrophilic membranes are used for dehydration of alcohols containing small amounts of water and hydrophobic membranes are used for recovery of minor quantity of organics from aqueous solutions.

Pervaporation is a very mild process thereby making it very effective for separation of mixtures which cannot survive the high temperature of distillation.

- Solvent Dehydration: dehydrating the alcohol/water azeotropes (Hsu et al., 2003; Mao et al., 2010)
- Continuous ethanol recovery from yeast fermenters (Vane, 2005).
- Water removal from condensation reactions to rate of the reaction (IzÃ¡k, Mateus, Afonso, & Crespo, 2005).
- Removal/recovery of organic solvents from industrial waste waters (Moulin, Allouane, Latapie, Raufast, & Charbit, 2002).
- Combining pervaporation membrane system with distillation
- Hydrophobic flavor compound recovery from aqueous solutions (using hydrophobic membranes)

Organophilic Pervaporation membranes are used for separating organic-organic mixtures, e.g. (Smitha, Suhanya, Sridhar, & Ramakrishna, 2004):

- Aromatics content reduction in refinery streams
- Separation of azeotropes
- Extraction media purification
- Purification of extraction operation product stream
- Organic solvents purification

1.5 RESEARCH OBJECTIVES AND STRUCTURE OF THESIS

More attention is being paid to production of renewable bio fuels after phase-out of methyl t-butyl ether (MTBE) as a fuel oxygenate and the effect of non-renewable fossil fuel combustion on earth's climate. Starting material for the biofuels are agricultural crops, such as sweet sorghum, sugar cane, sugar beet etc. Moreover, a variety of biomass materials are available for production of liquid biofuels, both intentionally grown for this purpose and that which is a side product or waste material from another process. Processing of these materials results in aqueous solutions of biofuels, which requires further purification or concentration. The most commonly used methods for the dehydration of alcohols are distillation, molecular sieve adsorption, extraction and pervaporation. However, for dilute ethanol-water solutions, it is desirable to develop ethanol-selective membranes because it is more effective to remove the minor component from the aqueous solutions (Cooper, 1982; Schultz, 1980).

Membrane separation processes provide several advantages over other separation techniques, including energy efficiency and easiness of use. However, the membrane processes reported in literature to date do not exhibit the high flux, selectivity and stability necessary to make them a viable process. Most of the porous fillers reported up to now have particle sizes in the micron range. As a result, the minimal membrane thickness of the composite membranes was higher than the unfilled membranes and the absolute fluxes remained low.

The improved adsorption of ethanol by nanosilicalite-1 makes MMM promising for aqueous ethanol/water mixtures. This thesis presents a research on incorporation of nanosized silicalites into a polymer matrix. Efforts have been made to prepare a thin, defect-free, filler polymer layer over a porous substrate. The objectives are:

(1) Study the effect of particle loading on the membrane performance

(2) Study the effect of temperature variation on the membrane performance

This thesis consists of two parts. Chapter 2 focuses on the synthesis of free standing PDMS membranes and studying the effect of feed concentration on the membrane performance. Chapter 3 focuses on the preparation of mixed matrix membranes by dip-coating. Characterization and performance of each membrane is discussed. Finally, Chapter 4 presents conclusions and recommendations for future work.

Chapter 2

FREE STANDING PDMS MEMBRANES FOR PERVAPORATION OF ETOH/WATER MIXTURE

2.1 INTRODUCTION

Production of renewable biofuels has been receiving increasing attention due to reliance on sources like fossil fuels, and its effect on earth's climate. Ethanol obtained from corn, accounts for the majority of liquid biofuels in United States. While corn and other agricultural crops, like sugar cane, sugar beet, sorghum, etc, will contribute as the starting material for majority of liquid biofuels, other carbon sources need to be found to increase biofuel production. Various biomass materials, grown intentionally for this purpose or which is a by-product of another process are available. In order to make biofuels economical separation processes need to be optimized since recovery of biofuels is the most energy intensive process. Distillation remains the conventional way for separating biofuels today. New processes like pervaporation and membrane distillation can play an important role if proper membrane material can be developed for biofuels recovery.

Polydimethylsiloxane (PDMS) is the benchmark material for hydrophobic pervaporation membranes for separation of alcohols and VOCs from dilute aqueous solutions because it is an elastomeric material which exhibits excellent film-forming ability, thermal stability, chemical and physiological inertness. The rapid chain segment motion in PDMS leads to a large free volume that favors the

diffusion of the permeating molecules. Table 3 gives the performance of some of the PDMS membranes mentioned in literature.

Table 3 Ethanol/water separation factors for PDMS membranes

Temp (^{0}C)	EtOH/H_2O (β)	Thick (μm)	Notes	Ref
66	14	5’	1.5 wt% EtOH, porous PTFE impregnated with PDMS in pores	(Mori & Inaba, 1990)
66	10.4	120	1.5 wt% EtOH	(Mori & Inaba, 1990)
30	10.8	100	8 wt% EtOH	(Ishihara & Matsui, 1987)
25	8.8-12.6	25’	Supported liquid membrane, 4 wt% EtOH	(Kashiwagi et al., 1988)
35	9	200-400	6 wt% EtOH,<2 torr	(Moermans et al., 2000)
40	8	160	16.5 wt% EtOH	(Takegami, Yamada, & Tsujii, 1992)
22.5	7.6	NA	5 wt% EtOH	(te Hennepe et al., 1987)
22	7.3	105	7 wt% EtOH	(Jia et al., 1992)
22	4.4	3’	7 wt% EtOH	(Jia et al., 1992)
50	5.3	~120	4.4 wt% EtOH	(X. Chen et al., 1998)
35	~5	NA	6 wt% EtOH	(Vankelecom et al., 1995)
40	5	~225	0.01 wt% EtOH in presence of aroma compounds	(Vankelecom, De Beukelaer, & Uytterhoeven, 1997)
30	8	120	9 wt% EtOH, 6-7 torr	(Nakao, Saitoh, Asakura, Toda, & Kimura, 1987)79
30	6	2.2’	5 wt% EtOH, 5 torr vacuum	(Blume, Wijmans, & Baker, 1990)
25	**8.3**	**100**	**10 wt% EtOH, 1.5 torr vacuum**	**This Work**

’ = supported on a porous support
NA = data not available

2.2 PERVAPORATION SETUP

Pervaporation experiments were conducted with 4 wt% ethanol/water mixtures at temperatures from 25 ^{0}C to 65 ^{0}C. The membrane was sealed in the vertical stainless steel cell (top layer upwards). The liquid feed was maintained at atmospheric pressure and contained in the steel reservoir above while vacuum was applied to the downstream side. Permeate vapors were caught in a liquid nitrogen cold trap and measurements were taken by weighing the trap before and after each run. The pervaporation cell was heated using a heating jacket ordered from HTS Amptek.

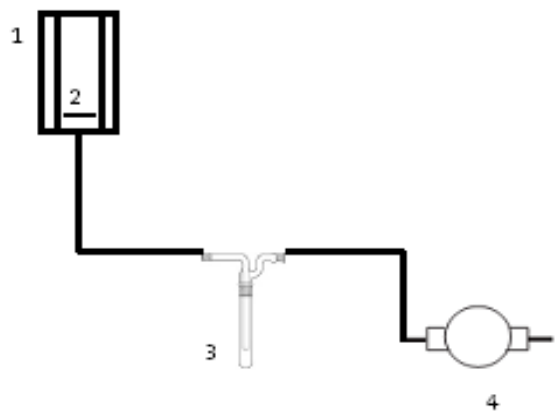


Figure 7: Schematic of a pervaporation setup. Legend: 1-pervaporation cell; 2-membrane; 3-cold trap; 4-vacuum pump

2.3 EXPERIMENTAL

2.3.1 Equipments

Gas Chromatograph (GC):

A gas chromatograph is a instrument for chemical analysis of a sample. It uses a flow-through narrow tube known as the *column*, through which different

chemical of a sample pass in a gas stream (carrier gas, *mobile phase*) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified by the detector. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (*retention time*).

The permeate concentration was measured using SRI 8610C gas chromatograph (SRI instruments, CA). The 8610C can control up to 16 heated zones, three gas sampling valves, and seven gas pressures. Up to six detectors, can be mounted simultaneously. The 86100C column oven is temperature programmable from ambient to 400 ^{0}C with unlimited ramps and holds, and fast cools down.

For our measurements we used the capillary FID GC system. The 30 meter capillary column can efficiently separate hydrocarbons up to C_{40+}. The on-colum injector (for 0.53 mm capillary columns) is good for liquid and gas sample with high and low boiling analytes. The Split/Splitless injector allows for the use of 0.32 mm, 0.25 mm and smaller capillary.

Vacuum Pump:

Edwards A65201903 rotary vane pump was used for pervaporation applications. It has an ultimate pressure capacity of $2x10^{-3}$ mbar and operating temperature range of 12-40 ^{0}C. The permeate vacuum for pervaporation experiments was 0.2 kPa.

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is a technique used to obtain an infrared spectrum of absorption, emission of a solid, liquid or gas. FTIR collects data over a wide spectral range. The spectrum can be analyzed to understand the nature of bonds present in the solid, liquid or gas. For our experiments Nicolet 4700 FTIR Spectrometer obtained from Thermoscientific was used.

Scanning Electron Microscope (SEM):

An SEM images a sample by scanning it with beam of electrons in a raster scan pattern. The electrons interact with the atoms of sample producing signals containing information about sample's surface topography, composition, and other properties. Our analysis was done using XL30 ESEM-FEG obtained from Philips. It has a resolution up to 2 nm and magnification of 12 to 500,000.

Furnace:

The furnace used for calcining zeolite particles was NeyTech Vulcan Benchtop Muffle Furnace obtained from Prosource Scientific. It can heat up to 1100 ^{0}C and has single point analog, digital or three-state digital programmable control options.

2.3.2 Free-standing Polydimethylsiloxane Membrane preparation

The membranes were prepared by solution casting. 4 gm of RTV A (monomer) and 0.4 gm of RTV B (cross-linker) was dissolved in 14 gm of hexane. The chemicals were bought from Fischer Scientific. The mixture was stirred continuously at 500 rpm for 1 hour. After the solution becomes viscous it

was used directly for membrane casting. GARDCO casting blade AP-99501001 was used to cast membranes of 100 micron thickness on glass plate. The glass plate was cleaned with the solvent hexane to remove any impurities on the surface

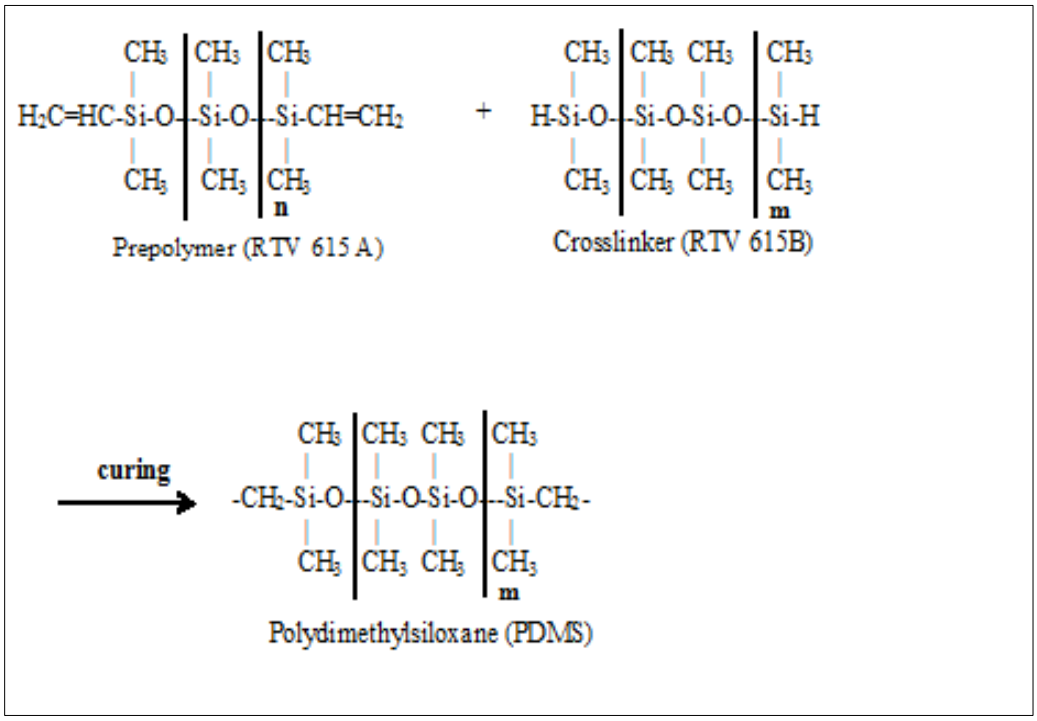


Figure 8: Cross-linking reaction of PDMS

The membranes were cured by drying at 25 ^{0}C for 12 hours followed by heating at 70 ^{0}C for 6 hours and 70 ^{0}C for 3 hours in 5 in Hg vacuum. The whole curing process took place in a vacuum oven. Membrane sheet were peeled off from the glass plate, cut in the required dimensions and used in the pervaporation cell.

2.3.3 Membrane characterization

The chemical structure of the free-standing PDMS membranes was characterized by Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR).

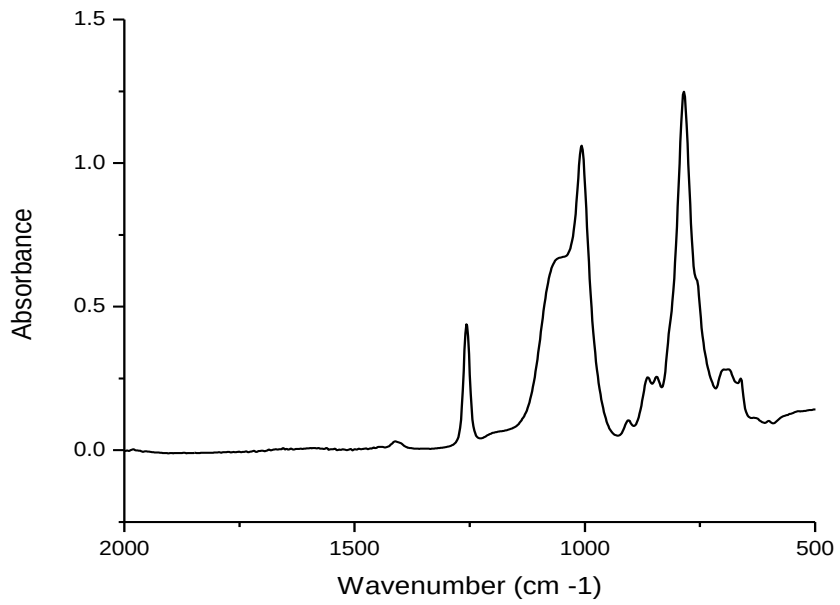


Figure 9: ATR-FTIR spectrum of a free standing pure PDMS membrane

The PDMS sample exhibited strong peaks at 800-880 cm^{-1} and 1260 cm^{-1}. The multiple peaks between 700 and 830 cm^{-1} were due to the methyl (CH_3 group) rocking and the Si-C group (Larkin, 2011; Smith, 1999). The twin peaks at 1000 and 1030 cm^{-1} originated from the asymmetric stretching of the Si-O-Si and the Si-CH_3. The other peaks, at 1255 and 3000 cm^{-1}, were due to CH_3 vibrations (Larkin, 2011)(Smith, 1999)(Smith, 1999).

2.4 RESULTS AND DISCUSSION

2.4.1 Influence of feed concentration

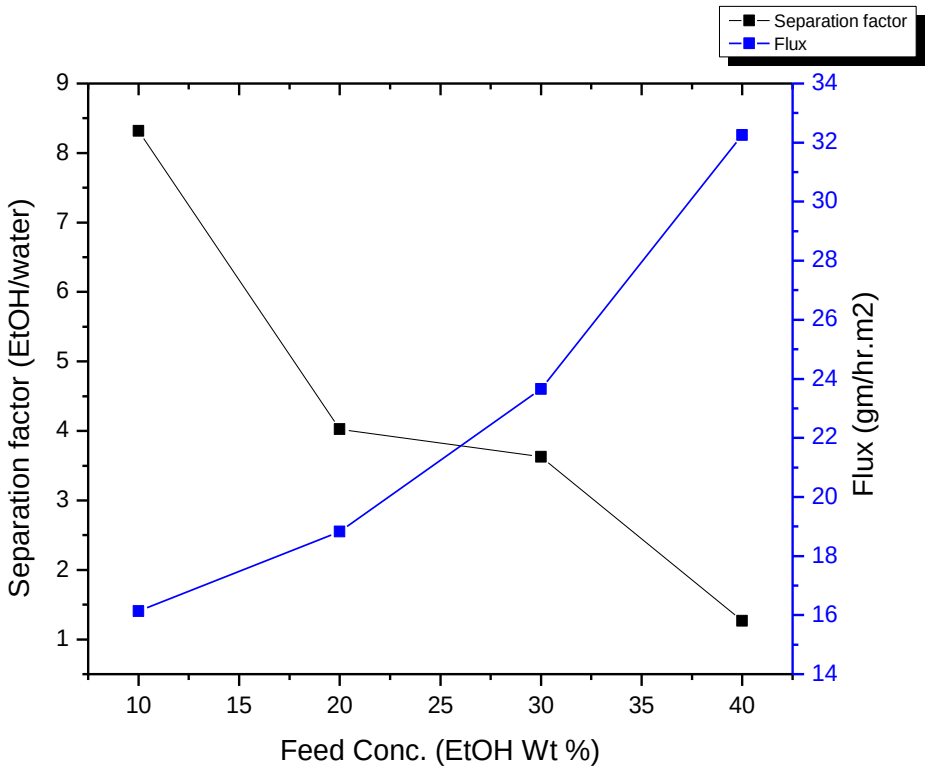


Figure 10: Effect of feed concentration on PDMS membrane (100 micron thickness)

Feed composition is an important variable for the selectivity and the total permeation flux. Figure 10 shows the effect of the feed ethanol concentration on the pervaporation performance of the pure PDMS membranes. With increasing ethanol concentration, the permeation fluxes of both ethanol and water increased, but the selectivity decreased.

In all polymer materials, the diffusion rate decreases as the molecular size increases, because large molecules have more interactions with polymer chain than small molecules (Xiangli, Chen, Jin, & Xu, 2007). The sorption is the

process linking the component concentration in the fluid phase with that in the polymer phase. In a binary feed mixture, if the polarity difference between the membrane material and the target component is lower than another component, the membrane will be more swelled by target component and shows preferential selectivity to the target component, to some extent. The less polar the alcohol, the higher the membrane affinity towards the pure alcohol. The polarity of ethanol is similar to that of cross-linked PDMS than water (Bartels-Caspers, Tusel-Langer, & Lichtenthaler, 1992; Jonquières, Roizard, & Lochon, 1994; JonquiÃ¨res & Fane, 1997). By increasing the ethanol concentration, ethanol in the feed phase had more sorption interaction with cross-linking PDMS thereby causing the PDMS to swell. Thus, segments of the rubbery PDMS polymer had more freedom of volume and mobility. By increasing the polymer chain mobility, thermal motion of these segments enhances the diffusion rate of two permeating components. Therefore, the total permeation fluxes of both ethanol and water increases as the ethanol concentration increased. Molecular diameters of water and ethanol are 0.26 and 0.52 nm, respectively (Shah, Kissick, Ghorpade, Hannah, & Bhattacharyya, 2000). As the water molecules are smaller than the ethanol molecules, the diffusion rate of water is larger than that of ethanol through the membranes.

In the pervaporation, the transport process through the membrane mainly is dependent on two processes: the solution of permeating components and the diffusion of permeating components. In the ethanol-water mixtures, Hofmann et al. (Hofmann, Fritz, Ulbrich, & Paul, 1997) found that the sorption process was

the decisive step, compared with the diffusion process. That is to say, the diffusion process was hindered by the sorption process all the time. By increasing the ethanol concentration, the water diffusion effect was greater than that of ethanol sorption through the rubbery PDMS membrane, and as a result selectivity decreased.

2.5 CONCLUSION

Free standing 100 micron thick PDMS membranes were prepared. Effect of feed concentration over the performance of membranes was tested and was found to agree with literature. An increase in flux and decrease in selectivity was observed with increasing feed concentration of ethanol. The flux increased from 16 $gm.hr^{-1}.m^{-2}$ to 32 $gm.hr^{-1}.m^{-2}$ as the feed concentration increased from 10 wt% EtOH to 40 wt% EtOH in feed. The EtOH/water selectivity decreased from 8.3 to 1.2 as the feed concentration increased from 10 wt% to 40 wt%.

Chapter 3

SUPPORTED PDMS MEMBRANES FOR PREPARATION OF ETHANOL/WATER MIXTURE

3.1 INTRODUCTION

In 1987, Te Hennepe et al. (te Hennepe et al., 1987) published a seminal work on ethanol-selective mixed matrix pervaporation membranes made from silicalite-filled silicone rubber; these mixed matrix membranes showed significant increases in pervaporation flux and selectivity compared to the pure polymer. Molecular sieving effects, hydrophobic/hydrophilic properties, and the physical cross-linking functions of the zeolites improved the selectivities and stabilities of the mixed matrix membrane (Vankelecom, Scheppers, Heus, & Uytterhoeven, 1994; Vankelecom et al., 1995). Since then, there have been many publications about micron-sized zeolite/polydimethylsiloxane mixed matrix membranes for pervaporation of alcohol/water solutions (Jia et al., 1992; Vane et al., 2008; Vankelecom et al., 1995). These mixed matrix membranes uniformly have higher alcohol selectivity (α alcohol/water > 20) than the pure polymer membranes (alcohol/water ~ 8). Additionally, all of these membranes had composite films greater than two microns in thickness because of the polymer solution processing technique with which they were cast.

The development of zeolite nano-crystals provides the opportunity to fabricate thinner mixed matrix membranes. Moermans et al. (Moermans et al., 2000) prepared 200 to 400 micron thick free standing mixed matrix membranes incorporating 70 nm silicalite nanoparticles. These membranes had alcohol/water

separation factors ranging from 9 - 16 but limited fluxes (maximum 340 g m^{-2} h^{-1}) as a result of the high membrane thickness. Liu et al. (Liu et al., 2011) used PDMS as filler for their nano-silicalite zeolite membrane for butanol/water separations.

The agglomeration tendency of particles increases with decreasing size, which hampers the fabrication of high quality nanocompostie membrane. However, nanosized particles provide increased surface area for separation at lower loadings. In this thesis, we report for the first time on 25 – 40 micron thick nanosilicalite/PDMS nanocomposite thin films formed through dip coating onto a porous alumina support for ethanol/water separation. The objective is to study the effect of nanozeolite incorporation into a PDMS matrix. With the increased zeolite surface area available, the membrane showed very high ethanol selectivity at lower zeolite loadings.

Table 4 lists ethanol–water separation factors reported in the literature for silicalite-PDMS mixed matrix membranes. Range of ethanol/water separation factors shown in the table (7–59), overlaps the ranges reported for both PDMS and silicalite-1 alone. Performance of these MMM's depends on the silicalite-1 loading, particle size, source of silicalite-1, and membrane casting conditions. Although some performance gains have been observed with a loading as low as 30 wt% silicalite-1 (Matsuda et al., 2002)(Moermans et al., 2000, loadings of 60 wt% may be needed to deliver consistently high separation factors (J. Huang & Meagher, 2001).

Table 4 Ethanol-water separation factors of silicalite-silicone rubber MMM's.

Temp (^{0}C)	Silicalite Loading (wt%)	EtOH/H_2O (β)	Notes	Ref
22	77	59	7 wt% EtOH, 125 μm thick, <1 μm particles	(Jia et al., 1992)
22	77	34	5 wt% EtOH, 20 μm thick, <1 μm particles	(Jia et al., 1992)
22	62	13-16	7 wt% EtOH, 4-12 μm thick, <1 μm particles	(Jia et al., 1992)
50	50	29.3	4.4 wt% EtOH,	(X. Chen et al., 1998)
40	40	28	0.01 wt% EtOH in presence of aroma compounds	(Vankelecom et al., 1997)
35	30	~10	6 wt% EtOH	(Vankelecom et al., 1997)
30	70	17	5 wt% EtOH, 1.8 μm particles, 100μm thick	(AdnadjeviÄ‡, JovanoviÄ‡, & Gajinov, 1997)
22.5	60	16.5	5 wt%, 100 μm thick, 5 μm particles	(te Hennepe et al., 1987)
22.5	40	14.9	5 wt% EtOH, 100 μm thick, 5 μm particles	(te Hennepe et al., 1987)
35	30	15.7	6 wt% EtOH	(Moermans et al., 2000)
60	50	7.5	4.8 wt% EtOH, <40 m particles, supported	(X & S, 1996)
35	50	~7	6 wt% EtOH	(Vankelecom et al., 1995)
25	**30**	**16.2**	**4 wt% EtOH, 200 nm paticles, 27 μm thick**	**This Work**

3.2 DIP-COATING

"Dip coating is precisely controlled immersion and withdrawal of any substrate into a reservoir of liquid in order to deposit a layer of material onto the substrate" (Rahman, 2007).

The dip coating process can be divided into five stages: (Rahman, 2007)

- Immersion: The support is dipped or immersed in the coating solution at a constant speed (preferably jitter-free).
- Start-up: The support has remained in the solution for a while and is starting to be pulled up from the solution.
- Deposition: The thin layer of coating material deposits itself on the substrate while it is being pulled up. The withdrawing is carried out at a constant speed to prevent any deformities. Withdrawal speed determines the thickness of the deposited layer (faster withdrawal gives thicker coated layer).
- Drainage: Excess liquid is drained from the surface by wiping or inclining slightly.
- Evaporation: In this step the solvent evaporates from the liquid, forming the thin layer. Volatile solvents like alcohols, start evaporating during the deposition & drainage steps itself.

In the continuous process, the above steps are carried out one after another.

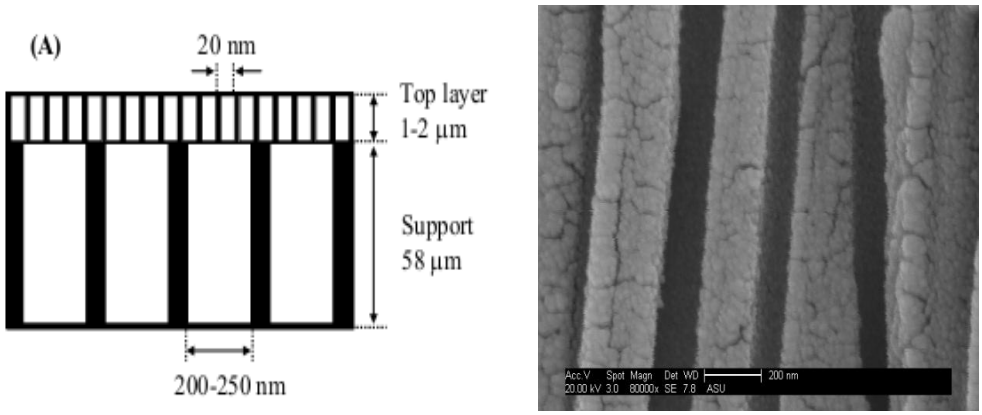
Many factors like the submersion time, withdrawal speed, number of dipping cycles, solution composition, concentration and temperature, determine the final state of a dip coated thin film. By controlling the above mentioned factors, a large

variety of dip coated film structures and thicknesses can be fabricated. Dip coating technique can give uniform, high quality films even on bulky, complex shapes or substrates.

3.3 EXPERIMENTAL

3.3.1 Support structure

Anopore alumina membranes obtained commercially (Whatman Co.) were used as supports. Anopore membranes, also called Anodisc, are alumina films with well-defined cylindrical, straight, and hexagonally packed pores running in the direction normal to the membrane surface (Crawford et al., 1992; Furneaux, Rigby, & Davidson, 1989). They are made by electrochemical anodic oxidation of aluminum and are available in 60 µm thickness. Anopore membranes with smallest pore size available commercially have a pore diameter of 20 nm. The majority of the membrane is comprised of straight, cylindrical, and non-connected pores of 200-250 nm diameter lying over 58 micron of the membrane thickness. The top layer of the membrane consists of 20 nm straight pores and has a thickness of 2 microns. A schematic of the Anopore membrane structure and SEM image of the composite pores, measured in our laboratory are shown in Figure 11. Before conducting pervaportion, the support ring was trimmed out in order to fit the membrane in pervaporation cell.



(a) (b)

Figure 11: Images of straight pore alumina membrane. (a) Schematic of the straight pore structure and dimensions (Seshadri, Alsyouri, & Lin, 2010)*; and (b) SEM cross sectional view showing the support side with 200 nm pore size*

3.3.2 Membrane preparation

Anodiscs were sonicated in deionized water for 10 min to remove impurities that were physically adsorbed on the surface; then the Anodiscs were soaked in deionized water for 1 hour to fill the pores with water. This was done to prevent intrusion of PDMS solution into the pores of anodisc.

Nanosilicalite-1 particles were sonicated in iso-octane for 180 minutes to break the crystal aggregates and improve dispersion into the polymer solution. The suspension is not stable and silicalite particles settle down once sonication is stopped. Therefore it is important to keep stirring the solution till the solution is viscous enough to slow down the zeolite particle sedimentation. After sonication RTV B was added to the zeolite suspension and mixed at 24 ^{0}C for 15 min followed by addition of RTV A and mixing for 15 min at 24 ^{0}C. The final mixture had a composition of 90 wt% solvent, 7 wt% polymer and 3 wt% nanosilicalite-1. The solution was then heated to 65 ^{0}C with continuous mixing

for 180 minutes to partial polymerization of PDMS. As the solution became moderately viscous it was cooled and used directly for dip-coating.

The Anodisc was taken out of the water and taped at the edges to a holder. Excess water on the top was wiped out quickly with filter paper. The Anodisc was dip-coated into the nanosilicalite-PDMS solution for 5 seconds and withdrawn. After drying at 24 ^{0}C for 10 min, the dip-coating process was repeated. Afterwards, the membrane was dried at 24 ^{0}C for 24 hours, 70 ^{0}C for 6 hours and then kept at 70 ^{0}C for another 3 hours under 5 in Hg vacuum to ensure complete cross-linking.

3.3.3 Membrane characterization

The morphologies of the synthesized membranes were studied by Nicolet 4700 ATR-FTIR and Scanning electron microscopy (XL30 ESEM-FEG). The membrane samples were prepared by freeze fraction in liquid nitrogen and sputter coated with gold.

FTIR

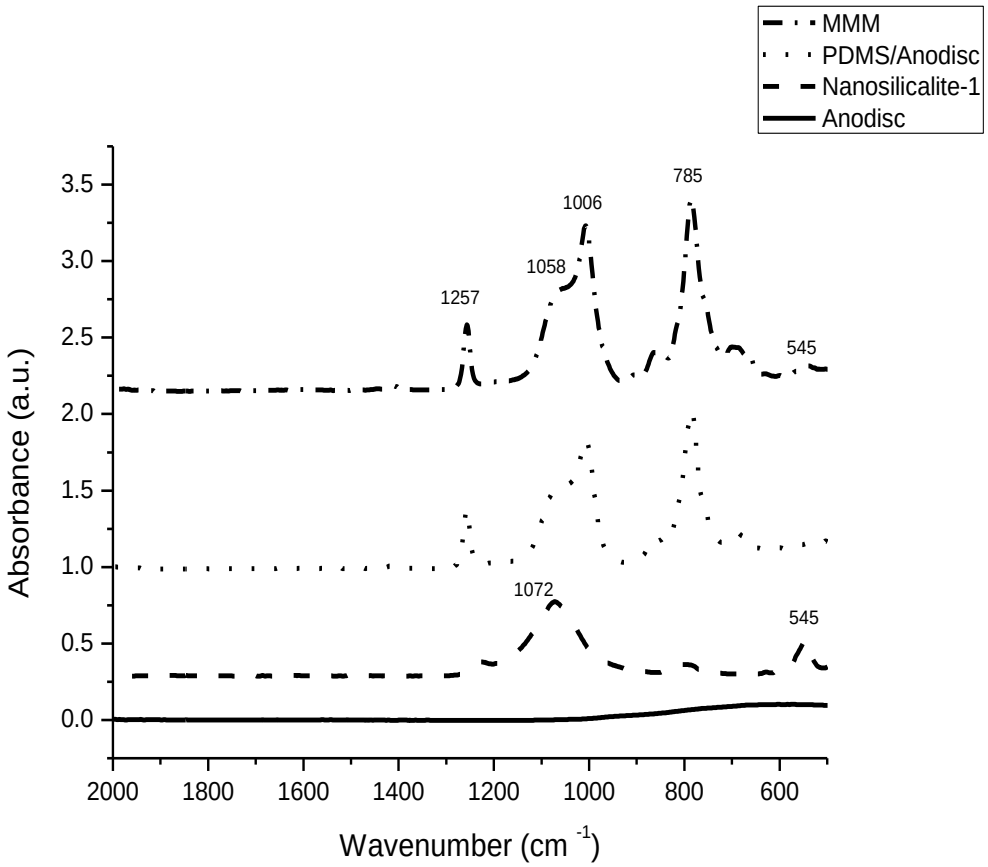


Figure 12: ATR-FTIR spectra of PDMS-zeolite composite membrane (MMM), PDMS coated anodisc, Nanosilicalite-1 zeolite partilcles and anodisc support.

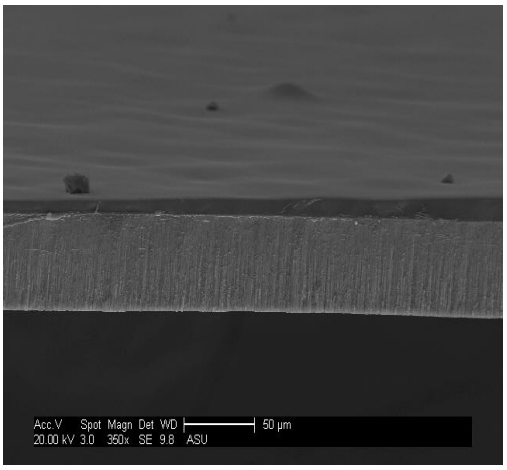
The FTIR spectra of the PDMS films and composite membranes are shown in Figure 12. The PDMS sample exhibited strong peaks at 880-880 cm^{-1} and 1260 cm^{-1}. The multiple peaks between 700 and 830 cm^{-1} were due to the methyl (CH_3 group) rocking and the Si-C stretching vibrations in the Si-CH_3 group. The twin peaks at 1025 and 1080 cm^{-1} originated from the asymmetric stretching of the Si-O-Si and the Si-CH_3 umbrella mode. The other peaks, at 1255 and 3000 cm^{-1} were due to CH_3 vibrations (Larkin, 2011; Smith, 1999).

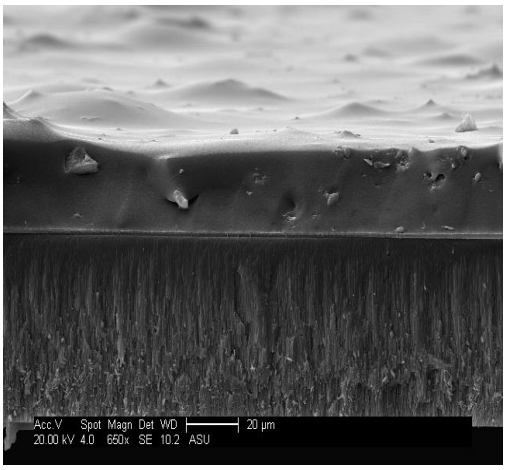
The nanosilicalite-1 exhibited a broad characteristic peak at 900–1100 cm^{-1}, which was due to the Si–O–Si structure. The minor band at 3600–3720 cm−1 was due to the Al–OH, Si–OH (3515 cm−1), and OH bonds (3705 cm−1).

The incorporation of the zeolite into the PDMS matrix did not alter the characteristic peaks of pure PDMS and composite membrane. However, the peak area increased with the increase in silica content. This is due to the filler silica, which includes many Si-O-Si chemical bonds.

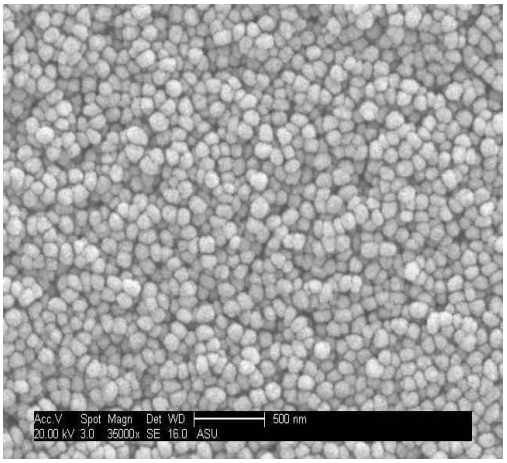
SEM

The difficulties in the preparation of zeolite filled membranes arise from the fact, that zeolites do not disperse well in any organic solvent due to large density difference; have negative affinity towards organic polymers and have higher density than polymers. This makes homogeneous dispersion of zeolite crystals very difficult(Jia et al., 1992). Figure 13(a) and 13(b) show the SEM cross-sections for PDMS coated anodisc and PDMS-nanosilicalite membrane respectively. As can be seen, a defect free membrane as thin as 7 microns could be prepared with pure PDMS solution. However, as the tendency of the particle agglomeration is inversely proportional to the particle size (Vane et al., 2008), preparation of good-quality thin nanocomposite membrane is hampered. Herein the thickness of composite membrane is 28 microns which is several times the size of the nanosilicalite crystallites. This ensures that the membrane is free from possible cracks or pinholes.





(a) (b)



(c)

Figure 13: SEM cross-sections of (a) pure PDMS membrane (b) 20 wt% nanosilicalite-PDMS membrane (c) nanosilicalite-1 particles.

3.4 RESULTS AND DISCUSSIONS

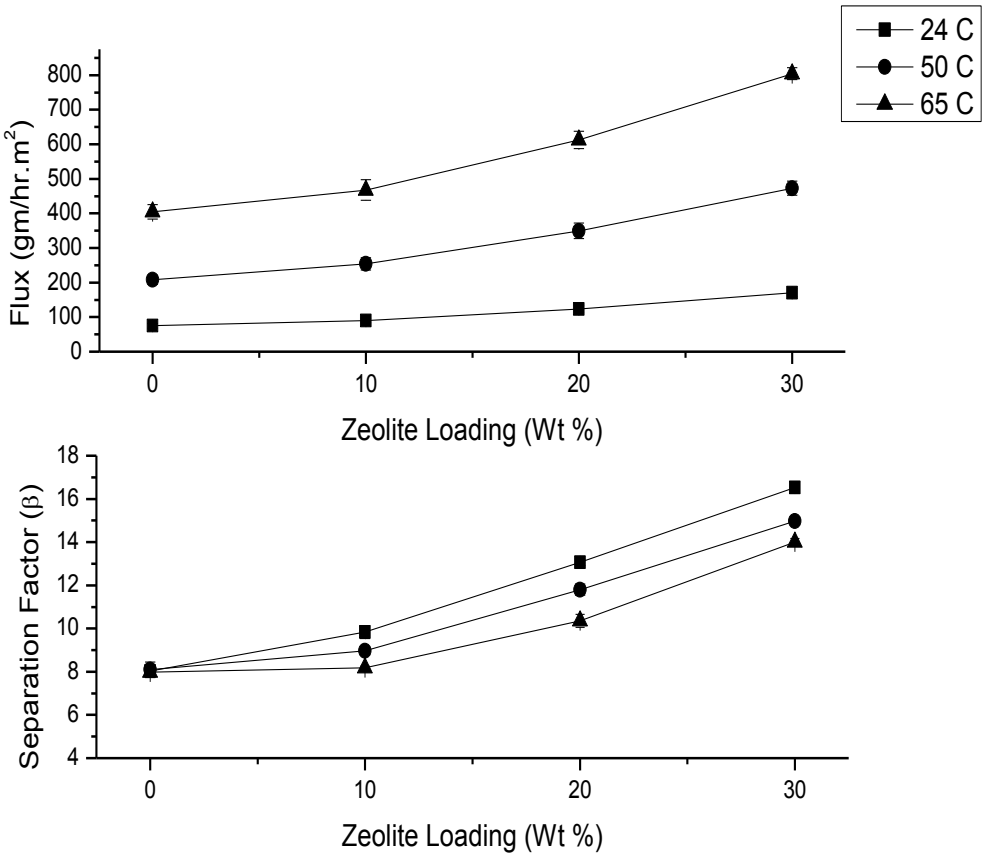


Figure 14: Pervaporation tests of nanocomposite membranes at different temperatures (a) Flux (b) Separation factor (EtOH/Water) for 4wt% ethanol feed solution

3.4.1 Effect of zeolite loading on ethanol and water permeabilities at 25 ^{o}C

Figure 14 (a) shows the normalized fluxes and *Figure 14* (b) shows the separation factor for the pervaporation performance of a 4 wt % ethanol/water solution at different zeolite loadings and temperatures. All samples were fabricated and tested in triplicate, if error bars are not visible; the error is smaller than the symbol. The ethanol-water separation factor increased in the nanocomposite membranes, compared to the pure PDMS membrane, with increasing silicalite loading. At 25 ^{o}C the pure PDMS showed a separation factor

of 8.03 and the 30% silicalite/PDMS membrane had a separation factor of 16.5. In addition to increased ethanol selectivity with increased nano-silicalite loading, the overall flux through the membrane increased with increasing nano-silicalite loading. This is because of the high intrinsic permeability of the silicalite nanoparticles as a result of the increased adsorption and diffusion of ethanol in the silicalite-1 compared to pure PDMS. These results are in agreement with the results presented in literature for other PDMS/silicalite composites with micron-sized silicalite particles (Hennepe et al., 1991; te Hennepe et al., 1987; Vankelecom et al., 1995). Figure 15 shows the pathways taken by ethanol and water in a mixed matrix membrane (MMM).

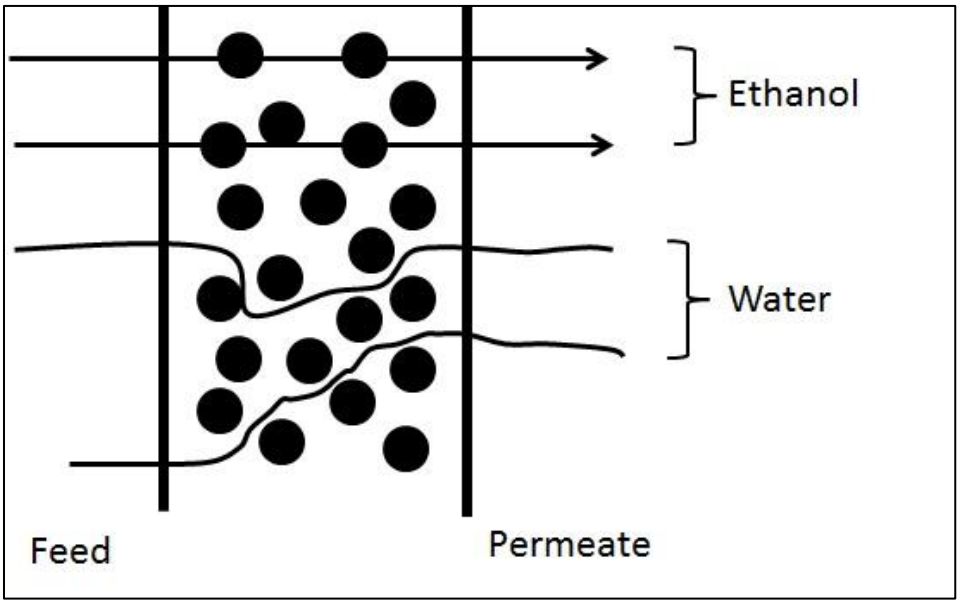


Figure 15 Apparent pathways of ethanol and water transport through a nanosilicalite filled MMM.

Table 5 presents the calculated permeability and selectivity for our nanocomposite membranes at all three temperatures. At 25 ^{0}C the permeability of ethanol in the membranes with 30 wt% nanosilicalite was 3.7 times greater than the pure PDMS

membranes simultaneously, the water permeability of the 30wt% membrane was only 1.8 times that of the pure PDMS membranes Additionally, the ethanol/water selectivity of the 30wt% nanocomposite membranes was 2.1 times greater than that of pure PDMS membranes.

Table 5 ***Permeabilities and Selectivities for membranes with different zeolite loadings at varying temperatures***

Temp. ^{0}C	Zeolite Loading	P_{EtOH} x 10^{12} kmol m^{-1} s^{-1} Kpa $^{-1}$	P_{water} x 10^{12} kmol m^{-1} s^{-1} Kpa $^{-1}$	Selectivity α
25.00	Pure PDMS	4.24 ± 0.42	2.93 ± 0.24	1.55 ± 0.09
	10 wt%	6.94 ± 0.37	3.58 ± 0.28	1.94 ± 0.06
	20 wt%	11.52 ± 0.97	4.31 ± 0.35	2.58 ± 0.03
	30 wt%	17.02 ± 1.01	5.22 ± 0.37	3.26 ± 0.04
50.00	Pure PDMS	2.89 ± 0.27	1.97 ± 0.12	1.48 ± 0.07
	10 wt%	4.14 ± 0.26	2.54 ± 0.19	1.63 ± 0.03
	20 wt%	6.92 ± 0.37	3.06 ± 0.22	2.15 ± 0.05
	30 wt%	10.09 ± 0.38	3.70 ± 0.18	2.73 ± 0.03
65.00	Pure PDMS	2.94 ± 0.16	1.89 ± 0.10	1.53 ± 0.03
	10 wt%	3.68 ± 0.27	2.34 ± 0.14	1.57 ± 0.02
	20 wt%	5.71 ± 0.34	2.78 ± 0.10	1.99 ± 0.06
	30 wt%	9.17 ± 0.13	3.41 ± 0.09	2.69 ± 0.03

P_{EtOH} = Permeability of EtOH
P_{water} = Permeability of water
Error in terms of standard deviation

3.4.2 Comparison with previously reported membranes

Table 6 presents a summary of the permeability and selectivities for mixed matrix ethanol selective membranes as reported in the literature. In contrast to our data,Vane et al.(Vane et al., 2008) found ethanol permeability to increase by a

factor of 2.8 for membranes with 50% ZSM compared to pure PDMS for a 5% ethanol solution. However, Vane et al. found that the water permeability did not change significantly between the pure PDMS membrane and the mixed matrix membrane with 50% ZSM. Hennepe et al. (te Hennepe et al., 1987) reported that the ethanol and water fluxes increased as the silicalite content was increased from 0 to 60 wt% for a 5 wt% ethanol solution. In terms of permeabilities, the ethanol and water permeabilites increased 3.3 fold and 1.5 fold, respectively, compared to the pure PDMS membranes.

Table 6 ***Comparison of permeabilities and selectivities for some of the reported PDMS-zeolite membranes***

No.	Normalized thickness μm	Zeolite wt %	Permeability kmol m^{-1} s^{-1} kPa^{-1} Water	Ethanol	α_{ew}	Reference
1	37	50	8.00E-12	1.70E-11	2.13	(Vane et al., 2008)
2	100	60	1.70E-11	2.90E-11	1.71	(te Hennepe et al., 1987)
3	200	30	14.0E-11	18.0E-11	1.29	(Lue, Chien, & Mahesh, 2011)
4	120	40	4.79E-12	1.28E-11	2.67	(X. Chen et al., 1998)
5	100	60	2.38E-12	8.69E-12	3.65	(Yi et al., 2010)
6	100	30	4.04E-12	1.38E-11	3.41	(Moermans et al., 2000)
7	25	30	5.22E-12	1.71E-11	3.26	This work

α_{ew} = Selectivity (EtOH/Water)

As can be seen from the Table 6, Yi et al. and Moermans et al. have better selectivity than our membrane. But Yi et al. have a zeolite loading of 60 wt% which is twice compared to ours. In terms of ethanol permeability, Hennepe et al. and Lue et al. have reported higher values than ours. But Hennepe et al. have a

high zeolite loading of 60 wt% while Lue et al. have poor selectivity. Moermans and ours are the only membranes which show high selectivity along with relatively high ethanol permeability. This surely proves the superior ethanol transport with nanosilicalites.

A comparison of Moermans results and our results was done at higher temperatures and Moermans membranes showed better performance in terms of ethanol permeability and selectivity. But our membranes have much higher flux compared to Moermans membranes due to lower thickness of 25-40 microns.

3.4.3 Effect of temperature on pervaporation performance

Pervaporation performance of the nanocomposite membranes was also measured at 50 and 65 °C. At these higher temperatures higher overall fluxes through the membrane were observed, compared to the fluxes measured at 24 °C. The higher fluxes at higher temperatures are partially because the vapor pressure of the feed solution is increased which in-turn increases the overall driving force (vapor pressure difference) for transport across the membrane (Wijmans & Baker, 1995). Additionally, the PDMS swells due to increased ethanol sorption and chain mobility is increased at higher temperatures which increases the diffusivity of ethanol and water within the membrane (Xiangli et al., 2007). Both of these factors – increased driving force and increased diffusivity – contribute to higher fluxes through the membranes at high temperature.

The variation of the total flux with temperature was determined to follow an Arrhenius relationship:

$J = J_0 \exp(-E_a/RT)$

where J is the total flux, J_0 the exponential factor, E_a the apparent activation energy of permeation for ethanol, R the gas constant, and T the feed temperature. E_a can be calculated from plot of lnJ vs 1/T. For membranes with 0-30 wt% zeolite loading, the E_a values decrease from 34.92 KJ/mol, in the pure PDMS membrane, to 32.48 KJ/mol in the 30 wt% nanocomposite membranes. It can be seen the activation energy for permeation of ethanol decreases with increasing zeolite content of the membranes. A slight reduction in separation factor was observed with increasing temperature (compared to room temperature) for all of the silicalite loadings; this is contrary to results found in the literature for PDMS composites with micro-sized zeolites (X. Chen et al., 1998; Moermans et al., 2000; Vankelecom et al., 1995). We hypothesize that there are two reasons for decreased selectivity of nanocomposite membranes at higher pervaporation temperatures: (1) decreased ethanol sorption capacity in silicalite at higher temperatures and (2) void space at the silicalite/polymer interface. Klein and Abraham found that the ethanol sorption capacity of ethanol decreased with increasing temperature Barrer and James demonstrated adhesion problems occurred at polymer/zeolite interface when preparing mixed matrix membranes (Barrer & James, 1960). At higher temperatures increased polymer chain mobility could result in more void space polymer/inorganic filler. Because we have used nano-sized, and not micron-sized, silicalites there is increased silicalite/polymer interfacial contact area and more opportunity for non-selective voids to appear. Figure 16 shows a schematic of increased free volume and non-selective voids in MMM at higher temperatures.

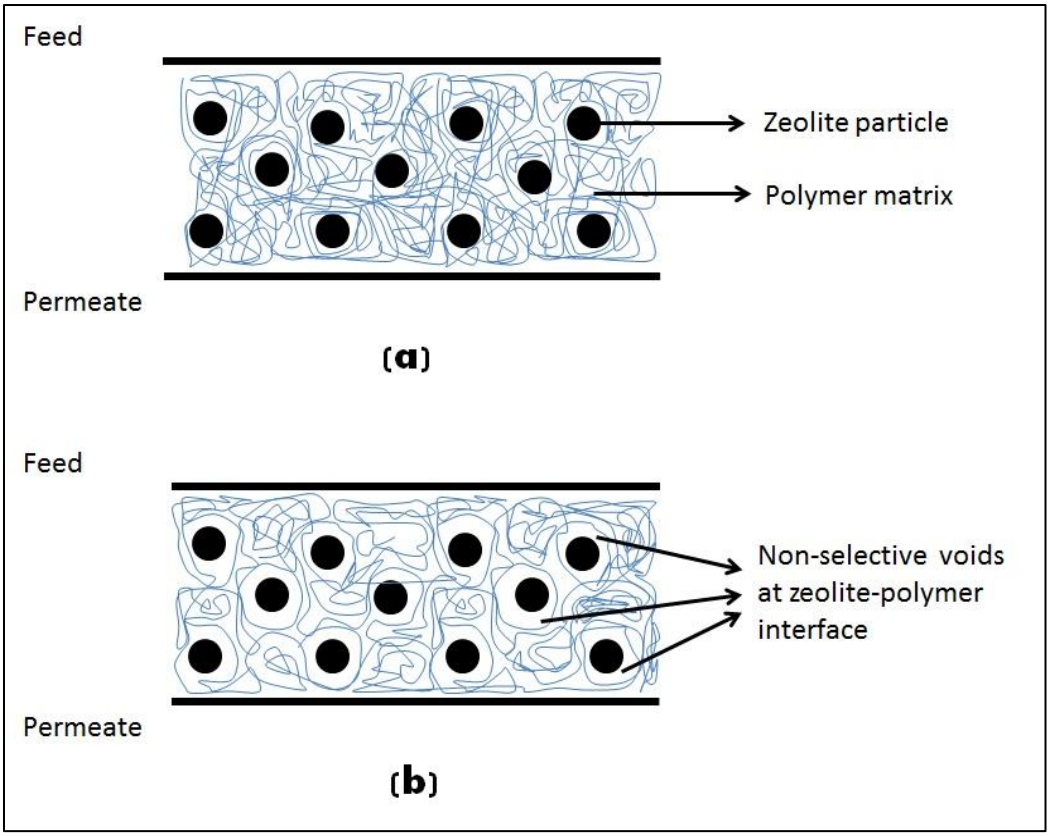


Figure 16 Schematic of (a) densely packed polymer chain matrix at lower temperature (b) increased free volume due to polymer chain mobility and non-selective voids at polymer-zeolite interface occurring at higher temperatures

3.5 CONCLUSION

Mixed matrix membranes with nanosilicalite-1 as filler and PDMS as matrix were prepared. The pervaporation performance of 4 wt% ethanol solution showed that the zeolite incorporation improved the flux and separation factor for ethanol separation. Detailed analyses on the transport phenomena, including sorption and diffusion behaviors of the ethanol-water mixtures in mixed matrix membrane are currently under way. The results would help in elucidation of the mass transfer mechanism of the multi-component solutions through the polymeric and mixed matrix membrane.

Chapter 4

SUMMARY AND RECOMMENDATIONS

4.1 SUMMARY

This thesis presents work on preparing and testing of free standing PDMS and mixed matrix membranes. A brief background about membrane separation processes, zeolites, mixed matrix membrane and pervaporation process is given in chapter 1. Pervaporation is considered to be a potential technology that will facilitate the production of higher bioethanol with lower production costs than the conventional methods.

In Chapter 2, pervaporation of free standing thick PDMS membranes was studied. The feed concentration was varied to study the membrane performance and it was observed that the separation factor decreases with increasing feed concentration. This was due to increased sorption of ethanol moelcules in PDMS matrix causing increased swelling. Swelling increased the ethanol flux along with the water flux and hence the permeation flux increased but separation factor decreased.

Chapter 3 reports the synthesis, characterization and pervaporation test results for supported mixed matrix membranes prepared with PDMS polymer matrix and nanosilicalite-1 zeolite particles as filler. Effect of zeolite loading and temperature variation was studied. It was observed that as that the permeation flux and separation factor increased with increasing zeolite loading. This was due to increased sorption of ethanol molecules by the zeolite particles thereby increasing the ethanol flux more in comparison to water flux. Increasing temperature caused

the permeation flux to increase but a decrease in separation factor was observed. The thermal mobility of polymer chains was enhanced due to increased temperature, reducing the diffusion resistance for the molecules.

4.2 RECOMMENDATIONS

Based on the experimental studies done in this work, the following recommendations are suggested for future study of the PDMS pervaporation:

1. Modifying the external surface of zeolite particles with coupling agents to maximize the achievable zeolite loading and lower film thickness.

2. Experiment with ethanol/butanol mixture separations to study the competing diffusion process. Other aqueous mixtures like acetone/water, butanol/water can be studied.

3. Study the effect of different zeolite particles like ZSM-5 or MOF-5 on ethanol/water separations.

4. Use a continuous flow system to study the effect of flowrate. Also the effect of different vacuum pressures on permeation can be studied.

5. Study pervaporation at higher temperatures.

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APPENDIX A

PREPARATION OF SILICALITE SOL

Version 1, Transcriber: Yang, Date: Unknown, Prof. Jerry YS Lin Lab

Version 2, Transcriber: O'Brien, Jessica, Date: 17 Nov 2005, Prof. Jerry YS Lin Lab

Chemicals: Tetrapropylammonium hydroxide (TPAOH, Aldrich)

Sodium Hydroxide (NaOH)

Silica Powder (SiO_2)

1. Mix 25 mL (1M) TPAOH solution with 0.35g NaOH at room temperature
    a. Stir until a clear solution is obtained
2. Add 0.8 mL de-ionized water to the above solution
3. Heat to 80 C
4. Add 5g silica fine powder to the pre-heated solution with strong stirring until a relatively clear solution is obtained
    a. Usually coats in 10 to 15 minutes
    b. Solution will be very viscous at first; be patient
5. The above synthesis solution is cooled down to room temperature and aged for 3 hours
6. Transfer aged solution to an autoclave
7. Place autoclave in a pre-heated oven at 120 C for 12 hours
    a. To make a smaller particle size, decrease the temperature of the oven and increase the time (e.g. 65 C for 400 hrs)

8. After 12 hours remove the autoclave from oven and allow to cool to room temperature for 1 hour
9. Suspension obtained is centrifuged at 14,000 RPM for 5-6 minutes
    a. DI water is used to wash precipitates
    b. Repeat 3 times
    c. pH of sol should be about 9-10
10. Store obtained sol at room temperature

Safety Precautions:

-Always conduct autoclave reactions (hydrothermal synthesis) in an oven with a maximum temperature below 400C (NEVER PLACE IN FURNACE; EXPLOSION HAZARD!)

-The autoclave will be hot when you remove it from the oven; whether quenching or allowing cooling slowly at room temperature ensure sufficient time has been reached for inner contents to cool as well.

-Resulting sol is corrosive and can burn you; use caution when opening the autoclave