Synthesis Of PDMS Membrane For Recovery Of Aromas From Aqueous Solutions

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Abstract — **Pervaporation is an emerging process in aroma component separation because it is energy efficient and environment friendly process .Aroma components are mainly organics.So for aroma components separation organophilic membranes are used. Mostly cases Polydimethylsiloxane (PDMS) membrane is used. Conventionally PDMS membrane is prepared by cross linking a hydroxyl-terminated Polydimethylsiloxane liquid with a polymethylhydrosiloxanecrosslinker. Here condensation reaction between hydroxyl and hydride groups occur which liberate hydrogen. But here in this study a new cross linked PDMS membrane prepared by cross linking hydroxyl terminated polydimethylsiloxane liquid with long alkyl organochlorosilane in presence of dibutyltindilaurate catalyst and toluene as a solvent under ambient conditions. Long alkyl is trichloro (octadecyl)silane. Here I developed a series of different membranes of different cross linking densities which show good selectivity towards organics. Cross linked structure and properties of membrane characterized by SEM, XRD, FTIR, Contact angle, Swallowing co-efficient and organics separation performance. Membranes prepared with optimal amount of cross linker give better hydrophobic character and separation performance. For pervaporation experiment we use ethanol-water mixture and use different-different composition from 2-10% and see the effect of feed composition on flux and selectivity.**

Keywords — Aromas,Hydrophilic, Hydrophobic,Membrane, Organophilic, PDMS,Pervaporation.

I. INTRODUCTION

Membrane separation processes are most effective demand due to energy efficient and environment friendly nature. Membrane separations are mostly Pressure driven processes. Among the different membrane processes Pervaporation is most effective process for aroma recovery. Aroma compounds are mainly organic compounds that possess a pleasant smell. But it is limited to pilot scale till now. Beside this commercially pervaporation is used mainly in dehydration of alcohol and removal of volatile organic compounds from waste water. In Pervaporation one side of membrane is on contact with feed liquid and other side vacuum is induced to recover permeantliquid. In Pervaporation we use mainly two type of membranes one is hydrophilic and other is hydrophobic (organophilic). Hydrophilic membranes are those which are water loving so they are used in dehydration of alcohols. Hydrophobic membranes are organics loving which are used in organics removal. So hydrophobic membranes are used in separation of aromas as well as in removal of volatile organic compounds from waste water.

Natural aroma compounds occur at very low quantity mainly at ppm level [15].So to recover these compounds an efficient method must be used. Conventionally we use adsorption, flash distillation and solvent extraction[16].But these techniques are unattractive due to certain reasons. Likely in flash distillation we provide extra energy for phase creation so it is energy inefficient process beside this a lot of high volatile compounds are evaporated and must be condensed to save aromas. Many times temperature sensitive aroma compounds are detoriated due to high temperature. In adsorption we use external solvent so we must do utmost care during separation because it may contaminate the aroma compounds.

Pervaporation is a membrane separation process. Membrane separation processes are most effective demand due to energy efficient and environment friendly nature. Membrane separations are mostly Pressure driven processes. Among the different membrane processes Pervaporation is most effective process for aroma recovery. It can overcome to all the above challenges of aroma extraction. So it is a potential alternative in aroma removal. Aroma compounds are mainly organic compounds that possess a pleasant smell. But it is limited to pilot scale till now. Beside this commercially pervaporation is used mainly in dehydration of alcohol and removal of volatile organic compounds from waste water. In pervaporation one side of membrane is on contact with feed liquid and other side vacuum is induced to recover permeant liquid. In pervaporation we use mainly two type of membranes one is hydrophilic and other is hydrophobic (organophilic). Hydrophilic membranes are those which are water loving so they are used in dehydration of alcohols. Hydrophobic membranes are organics loving which are used in organics removal. So hydrophobic membranes are used in aroma removal and removal of volatile organic compounds from waste water. In aroma removal we use organophilic membrane in pervaporation. Elastomers normally show higher chain mobility than glassy polymers and have non polar side groups. So permeate specifically organic substances [1]. PDMS is the most studies membrane in aroma recovery by pervaporation [2-14]. It belongs to a group of polymeric organosilicon compounds and commonly referred as Silicones

[17]. PDMS material are more preferentially selective towards organics than water due to its hydro phobic character. It is also used in applications like sealants and adhesives [18, 19], anti-corrosion [20], micro fluidic device [21], electrical device [22] and as a precursor for template growth of silica nano tubes [23] etc.

A conventional PDMS membrane is prepared by cross linking between a base polymer liquid having $-[Si(CH_3)_2O]-$ repeating units and a liquid polysiloxane having Si-H group, like polymethylhydrosiloxane (PMHS)[24-29]. Cross-linking reaction is affected by multiple factors such as curing temperature, different-different solvent used and curing in presence or absence of vacuum treatment [24]. The sizes of base polymer liquid increased due to cross linking and which further condensed with cross-linker and form a membrane. PDMS membrane show high swelling and great chain mobility which is advantage for it to use as organophilic membrane. Thin PDMS film coated on a porous membrane where porous membrane works as a support exerts a more loose structure. It shows high chain aggregates [30, 31] as compared to structure of unsupported PDMS membrane. A different type of PDMS membrane prepared by cross-linking silystyrene oligomer containing –SiH groups with divinyl-polydimethylsiloxane using Karstedt's catalyst at room temperature[32].Beside this some other alkoxysilane molecules such as tetraethoxysilane(TEOS)[33], phenyltrimethoxysilane (PTMOS)[34] and vinyl-triethoxysilane [35] were also used as cross-linker in formation of silicate cross-linked PDMS membrane where PDMS polymer chains are cross-linked with 3 or 4 functionality of molecular cross-linker[36].These membranes show different characteristics and structure than the above polymeric membranes due to difference between molecule size and functionality of cross-linker.

Here a different type of PDMS membrane is prepare by direct cross linking n-octadecyltrichlorosilane (OTS) with Hydoxyterminated polydimethylsiloxane (HPDMS) precursor polymer in toluene solvent under Dibutyltindilaurate (DBTDL) catalyst. PDMS membrane prepared by this method is a potential alternative in organics separation. The effect of cross-linker on membrane molecular level was studied by varying the ratio of base liquid to cross-linker. The membrane characteristics were studied through various analytical techniques. Membrane's aroma separation performance done through Ethanol-Water model mixture and also studied the effect of feed composition on flux and selectivity.

II. EXPERIMENTAL

a. Materials

LiquidHydroxyterminatedpolydimethylsiloxane (HPDMS) of 18,000-22,000 cSt viscosity, 0.97g/ml density, Trichloro (octadecyl) silane (OTS), Dibutyltindilaurate (DBTDL), were purchased from the Sigma-Aldrich, Solvents like toluene, benzene, Acetone, dioxane, dimethyl ether, CCl_4 etc. were of analytical reagent grade and were purchased from S.D. Fine-Chem. Ltd., India. All the chemicals were used without further purification.

b. Membrane Preparation

PDMS membranes were prepared by cross-linking the base polymer hydroxyl terminated polydimethylsiloxane pre-polymer with trichloro (octadecyl) silane in toluene solvent under Dibutyltindilaurate catalyst.Here cross-linked siloxane (-Si-O-Si-) chains formed by poly condensation reaction between hydroxyl group of HPDMS liquid and chloride of OTS. Here we prepare three membranes of varying cross-linker and pre-polymer amount25:75, 34:66 and 43:57(w/w) and named as SHM-1, SHM-2 and SHM-3 respectively. The amounts (g) of components in composition mixture are shown in Table 1.

TABLE 1. DETAILS OF AMOUNTS OF POLYMER, CROSS-LINKER AND SOLVENT FOR PREPARATION OF DIFFERENT MEMBRANES

Membrane name	Amounts(g)		
	Base polymer (HPDMS)	Cross-linker (OTS)	Solvent(Toluene)
SHM-1	6	2.0132	32.854
SHM-2	6	3.108	35.55
SHM-3	6.05	4.5797	36.07

In preparation first we mixed measured amount of HPDMS and OTS uniformly in toluene solvent. Then add measured amount of DBTDL catalyst (3% of total mass of polymer liquid and cross-linker). The reaction mixture stirred vigorously at 40^oC for one hour. Cross-linked solution was then left for 15 minutes for degassing. After which this solution poured in a glass plate and uniformed through a glass rod and left for 15 hours for solvent evaporation at room temperature. This lead to formation of cross-linked rubbery film and now cured this in an oven at 85^oC for three hours.

c. Swelling coefficient of the membrane

Swelling experiment[36] were conducted to determine the solubility of solvent in the membrane at equilibrium state as sorption/swelling is one of important control step in solution diffusion model. For this experiment samples were dried in oven at 80^oC for two hours. The dried membrane film sample of $2cm^2$ was initially weighted and denoted as m_0.The sample then put in a petri disk soaked with solvent and air tight with paraffin tape and put it for fixed time. The sample was then removed and wiped off immediately with tissue paper to remove excess of solution on wet membrane. Now the sample weighed and noted as m_t. The mass% uptake M_t was calculated using equation 1.

$$M_t = \frac{m_t - m_o}{m_o} \times 100 \qquad 1$$

Swelling coefficient S of the membranes in various solvents was calculated from the following equation 2.

$$S = \frac{m_t - m_o}{m_o} \times \frac{1}{d} \qquad 2$$

d.   Pervaporation Experiment

Pervaporation separation of Ethanol-Water mixture was carried out with the prepare membranes. The Pervaporation module was equipped with the corresponding membrane and tightened the screws. Feed mixture Ethanol-Water was kept at 60°C by applying a thermostat and was fed in a batch feed. The corresponding membrane area in the module was 122.65 cm². The permeate pressure was kept below 5mm Hg with the help of vacuum pump. Composition of alcohol in the fed was kept 3, 5, 7, and 10% with water. The vapor permeate across the membrane was condensed in a condenser with the help of a chiller and finally collected in the permeate collector. The experiment was repeated two to three times for each membrane to reduce experimental errors and the final results were averaged to be evaluated. The permeate collected in the collector was brought to ambient temperature and then analyzed with Nucon Gas Chromatograph (model 5765) equipped with TCD and FID detector and Porapak Q column of size 60-80 mesh with dimensions 2mx18''x2 mm stainless steel. The injector and detector temperature was maintained at 120°C and sample injector volume was 1μl.To evaluate pervaporation characteristics following parameters used.

e.   Permeation Flux

Permeation flux is given by the equation 3

$$J = \frac{W}{A \cdot t} \qquad 3$$

f.   Separationfactor (α)

Perm selectivity of a specific component can be studied through separation factor and are given inequation 4

$$\alpha = \frac{C'(1-C)}{C(1-C')} \qquad 4$$

Where c′ and c are concentrations of desired permeant component in feed respectively.

III. CHARACTERIZATION

Membrane thickness of membranes was measured by Absolute Digimatic CD-6'' CSX Vernier Calipers. X-ray diffraction spectra of PDMS membranes were obtained at room temperature using RigakuMiniflex 300/600 X-ray diffractometer. The thin polymeric membrane sample was mounted on a sample holder and the pattern was recorded in the reflection mode with a X-ray source radiation at 40 kV, 15mA and at an angle 2θ range of 5-60° at a scanning rate of 2°/min with D/teX Ultra detector. Scanning electron microscopy was used to know the surface morphology of all prepared PDMS membranes. SEM of membranes was performed using a scanning electron microscope Zeiss EVO 18.FT-IR spectra were used to know the functional groups and to know change in hydrophobic character. FT-IR of membranes was performed using Nicolet 5700 spectrometer. Hydrophobic nature of the membranes described through contact angle measurement using KRUSS DSA 25 drop shape analyzer.

IV. RESULTS AND DISCUSSION

a.   Membrane morphology and swelling coefficient

The thickness of the membrane measured through vernier calipers is given in table 2. The thickness of the membrane increased when we increased the cross-linker amount.

TABLE 2. THICKNESS OF THE MEMBRANES

Sr.No.	Membrane	Thickness(μm)
1	SHM-1	300
2	SHM-2	450
3	SHM-3	500

The surface morphology of different prepared membranes are shown through SEM images in figure 1. We can see as the cross-linker ratio in the membrane is increased, the membranes become more rough due to large cross linking bonding of precursor and cross-linker. But when we further increase the cross-linker ratio then there is some opaqueness appears which may be due to aggregates or clusters. These aggregates or clusters are possible due to some of trichloro(octadecyl)silane molecules are polymerized themselves and converted into poly(octadecyl)silane. Here trichloro(octadecyl)siloane first reacted with atmospheric moisture and release HCl via hydrolysis. Further these molecules were condensed, polymerized and converted into poly(octadecyl)siloxane.
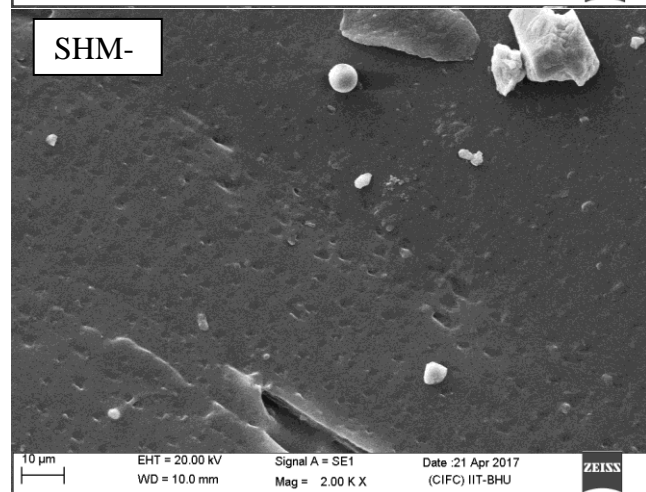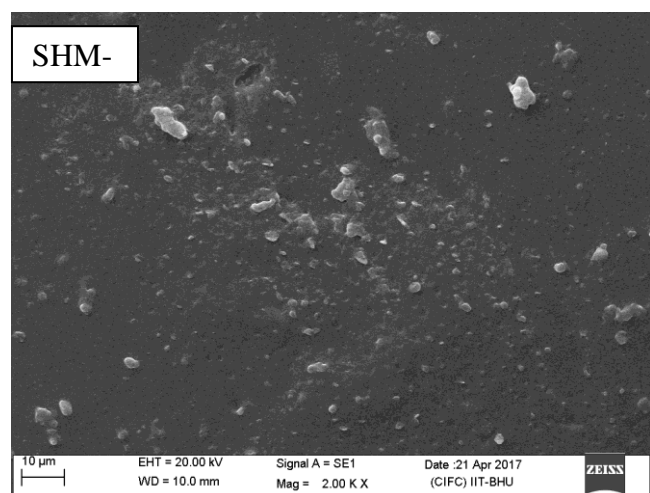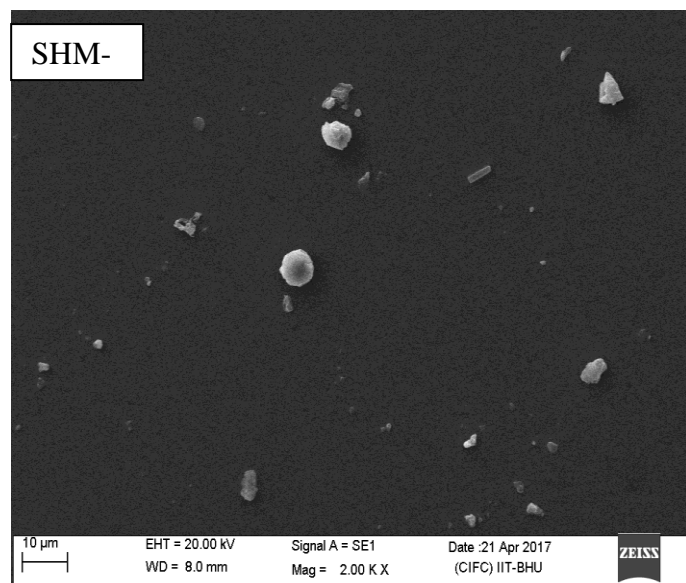
The crystalline and amorphous character of the membrane was studied by X-ray diffraction measurement and shown in Figure 2.
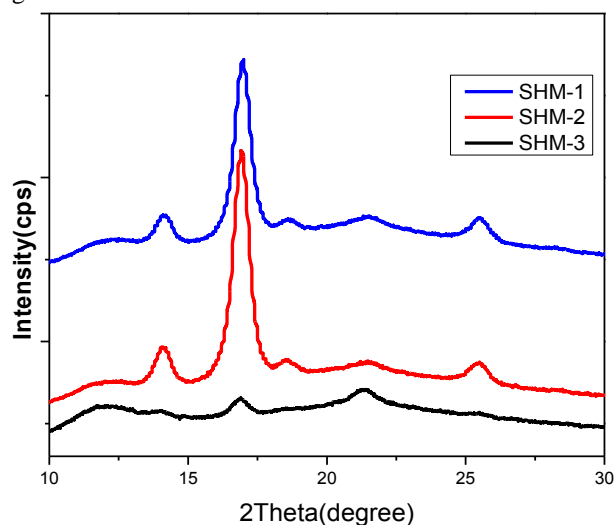

Figure 2. X-RD peaks of cross-linked membranes

Now from figure 4.2 we can see the X-RD patterns of different prepared membrane. Here peaks arise at 2θ value of 14°, 17°, 21° and 25.5^{o}.Broad peaks appeared at 17° and other peaks occur 14°, 21° and 25.5^{o}. Further from figure we can also see that when we increase cross linker amount i.e. OTS amount intensity of peak decreases. Pristine PDMS material exhibits XRD peaks at 2θ value of 12.77^{o}, 21.14^{o} and 24.67^{o} corresponding to tetragonal unit cell present in material[37]. Conventional PDMS membrane prepared from cross linking between Hydroxy terminated polydimethylsiloxane (HPDMS) and Polymethylhydrosilane (PMHS) exhibits peak at 2θ value of12.1^{o} and 23° [38,39].But in the new present membrane different peaks occur than pristine PDMS material and conventional prepared PDMS membrane because this membrane is prepared by crosslinking n-octadecyltrichlorosilane(OTS) with Hyroxy terminated polydimethylsiloxane(HPDMS). Here crosslinking occur between between hydroxyl end group of HPDMS with chloride group in OTSin presence of DBTDL catalyst and release HCl. This membrane consists of dimethylsiloxanenetwok structure of two crosslinks and alkylsiloxane network structure of two or three crosslinks [36]. The dimethylsiloxane group may be assumed as a more structurally regular segment as it comes from PDMS pre-polymer (HPDMS).Apart of it alkyl-siloxane group may be formed due to various types and give hard structure as it is either formed by direct crosslinking reaction with trichloro(octadecyl)Silane.

From the figure we can see that the membrane prepared with large amount of cross-linker (SHM-3) has more irregular structure possess amorphous type structure. The presence of peak at 2θ value of 17° in all the prepared membrane differ

Figure 1. Surface SEM image of membrane SHM-1, SHM-2 and SHM-3

from pristine PDMS material peak at 2θ value of 12.77° suggests semi-crystalline nature of PDMS membrane. The intensity of peak at 2θ value of 17°decreases with increase in cross-linker amount, it show increase in amorphous characteristics of the membrane. The peaks present at 2θ value of 14°,21° and 25.5° are corresponds to poly(octadecyl)siloxane formed upon hydrolysis of trichloro(octadecyl)siloxane with moisture present in environment air, followed by condensation and polymerization reactions of the hydrolyzed species during the preparation process. The swelling coefficient of membranes in various solvents is given in Table 4.2.Membranes are prepared by cross-linking trichloro(octadecyl)silane with hydroxyl terminated polydimethylsioxane. Here HPDMS is a liquid which react with cross-linker and converted into solid form. So as we increased cross-linker ratio the denseness of the membrane increased as swelling coefficient (S) value decreases.

Table 3. Swelling coefficient of membranes in different-different solvents

Membrane	SCCl4	Sdimethyl ether	Sbenzene	Sdioxane	Sacetone	Stolune
SHM-1	9.2	7.3	6.2	0.2	0.35	8.4
SHM-2	6.8	6.4	4.4	0.15	0.25	5.7
SHM-3	5.8	3.2	4.2	0.15	0.15	5.3

b.   *Hydrophobic character of the membranes*

Infrared spectra of membranes are shown in fig. 4.3(a) and (b).Membrane show measure peaks at 1054.9 cm^{-1}, 1603.1cm^{-1}, 1946.4 cm^{-1},2054.3cm^{-1}, 2958.3 cm^{-1} and 3712.1cm^{-1}. The peak at 1054.9 cm^{-1} show asymmetric stretching band of Si-O-Si [40]. Peak at 1603.1 cm^{-1} show Si-O-H-O-Si vibrations i.e. hydrogen bond of Si-O-H group with oxygen of siloxanes and bending mode of absorbed water [41]. The peak at 2958.3 cm^{-1} show asymmetric stretching vibrations of the CH_3 groups of PDMS[42].The peak at 3712.1 cm^{-1} show silanol, symmetric stretching band of –OH for absorbed water [40].

The membranes with low cross-linker ratio i.e. SHM-1 show sharp peak at 3712.1cm^{-1} due to symmetric stretching band of –OH for absorbed water. Which decrease with increase in cross-linker ratio. This show that membrane hydrophobic character increase with increase in cross-linker amount
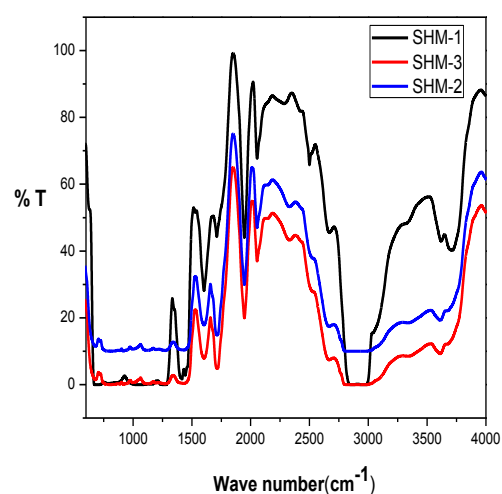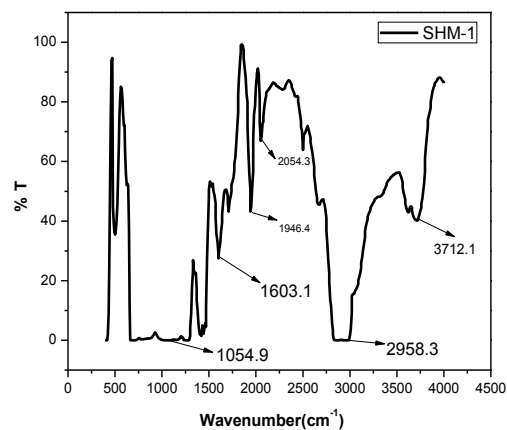
Figure 3(a) and (b) FTIR spectra of various membranes

Water contact angle were measured to check the hydrophobicity of membranes. Contact angle of prepared membranes are given in Table 4.3.From here we can suggest that as the cross-linker amount increases contact angle also increases i.e. hydrophobicity of membranes increases.

TABLE 3. CONTACT ANGLE OF VARIOUS MEMBRANES PREPARED WITH VARIOUS CROSS-LINKER RATIO

Sr.No.	Membrane	Contact Angle
1	SHM-1	117°
2	SHM-2	119°
3	SHM-3	123°

c. *Pervaporationseparation performance for aroma feed*

To check pervaporation separation performance we use Ethanol-Water mixture as aroma feed. We drive out pervaporation process performance with various ethanol water composition mixtures through all three membranes. The flux and selectivity are shown in Figure 4.4 and 4.5
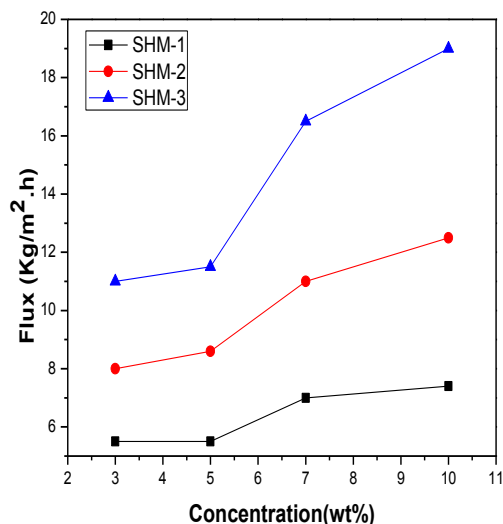

Figure 4. Effect on flux of various membranes and feed concentration

From the figure 4 we can see that when we change the cross-linker ratio for any composition of ethanol water mixture then ethanol flux through membranes was in order of

SHM-3 > SHM-2 > SHM-1

This happen because by increasing the cross-linker ratio, hydrophobicity of membrane increases. Beside ethanol flux, water flux through membrane also increased with increase in cross-linker ratio. Because membrane are prepared through crosslinking reaction between hydroxyl terminated poly dimethylsiloxane and trichloro(octadecyl)silane through condensation reaction between hydroxyl end groups and chloride groups. Here long hydrophobic chain in the cross-linker increase the hydrophobicity of membrane so give high organic flux but trichloro(octadecyl)silane might also do self-polymerization and produce poly(octadecyl)siloxane. When these poly(octadecyl)siloxane particles size are in nanometer scale it give excellent Nano composite morphology and give excellent membrane performance. But when the cross-linker ratio is high it give micro-phase morphology and could not give better separation performance .Here denseness increases but defects arises due to non-proper dispersion of poly(octadecyl)siloxaneparticles. These defects give high water flux together with high organic flux. Water fluxes through these membranes are according to

SHM-1 > SHM-3 > SHM-2

So here separation factor increases with increase in cross-linker ratio but the degree of increment of separation factor decreases.
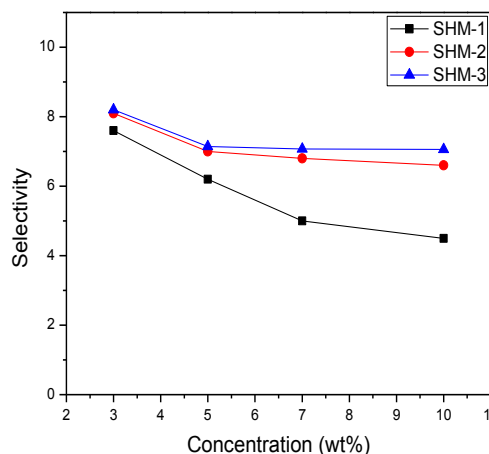

Figure 5. Effect on selectivity of various membranes and feed concentration

So for better organic separation membrane should be prepared with optimum amount of cross-linker ratio which provides both the hydrophobicity and better structure denseness without large defects.

d. *Effect of feed concentration*

Feed composition has a greater impact on selectivity and total permeation flux. Figure 4 and 5 show the effect of feed composition on permeation flux on selectivity. By increasing the ethanol concentration the permeation flux of both water and ethanol increases but selectivity decreases. Mainly pervaporaton is governed by two main steps i.e. diffusion and sorption. Diffusion is the process which shows the effect of environment on the molecular motion. In polymeric materials diffusion rate increases as the molecular size increases because a large molecule can interact with a large segment of membrane comparatively to small molecule [43]. In any binary mixture if there is one target component and if polarity between targent component and membrane material is low comparatively to other then membrane swelled more by target component and give preferential selectivity to the target component. Same case is here for ethanol water. Here membrane gives preferential selectivity to ethanol. By increasing the ethanol concentration in feed, ethanol interact more with cross-linking phase of PDMS. So here membrane swelled more and it gives high mobility. By enhancing the chain mobility thermal motion of these segments also increases and gives high diffusion rate to permeation flux. So permeation flux of both ethanol and water increases by increase in feed concentration. But the molecular size of water is less than ethanol [44]. So the diffusion rate is higher for water than ethanol.

But according to Hoffman et al. [45] sorption process is the decisive step compared to diffusion step for ethanol water mixture. Means we can assume that sorption step is dominant most probably. So by increasing the ethanol concentration, the flux of both water and ethanol increases but the selectivity decreases.

V. CONCLUSION

A new hydrophobic PDMS membrane series were prepared by varying cross-linker to pre-polymer ratio from 25, 34 and 43 (wt %).The increase in cross-linker to pre-polymer ratio in membrane increases the hydrophobicity of the membranes. Thickness of three membranes was 300,450 and 500 respectively which increases with increase in cross-linker ratio. The roughness of membranes increases with increase in cross linker to pre-polymer ratio but when we increase more cross-linker to pre-polymer ratio it shows opaqueness to the membranes due to molecule clusters or aggregates. Clusters or aggregates and roughness in membranes observed through trends of SEM images. From the XRD curve it was observed that intensity of peaks decrease with increase in cross linker to pre-polymer ratio. It show that structure transform from crystalline to amorphous. Membrane structure denseness increased with increase in cross-linker to pre-polymer ratio. It was also shown through swelling test because swelling coefficient for various solvent decreased with increase in cross-linker to pre-polymer ratio. From the FT-IR image it was shown that sharp peak at 3712 cm^{-1}of symmetric stretching band of –OH for absorbed water decreased with increase in cross-linker ratio, it also suggest about increase in hydrophobicity with increase in cross-linker to pre-polymer ratio. Contact angle for membranes increases from 117° to 123° with increase in cross-linker to pre-polymer ratio, it suggest the increase in hydrophobic character with increase in cross-linker amount. The ethanol flux through membrane increases with increase in cross-linker to pre-polymer ratio but high increase in cross-linker to pre-polymer ratio create defects in membranes so with high ethanol flux it also give high water flux. Separation factor of ethanol to water increases with increase in cross-linker ratio but rate of increment of separation factor decreases. Feed composition also show a great impact on separation process. By increase in ethanol composition of feed mixture, the flux of water and ethanol both increases but due to small size of water molecule diffusion flux of water is more than ethanol. So the selectivity decreases. Thus the membrane prepared with optimum amount of cross-linker give excellent hydrophobicity, denseness to membrane structure and separation performance

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