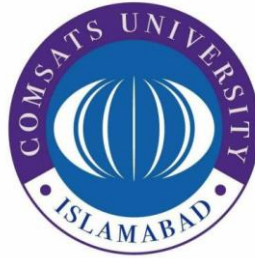


**Mixed Matrix Membranes Comprising of
PDMS an Deep Eutectic Solvents Infused ZIF-8
for Ethanol Dehydration**



By

Muhammad Ahmad

CIIT/FA20-RNE-007/LHR

MS thesis

In

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**Mixed Matrix Membranes Comprising of PDMS and
Deep Eutectic Solvents Infused ZIF-8 for Ethanol
Dehydration**

A Thesis Presented to
COMSATS University Islamabad

In partial fulfillment
Of the requirement for the degree of
MS (Energy and Environmental Engineering)

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A Post Graduate Thesis submitted to the name of Chemical Engineering department as partial fulfillment of the requirement for the award of Degree of M.S (Chemical Engineering)

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DEDICATION

To all who have participated and supported throughout the completion of my thesis including my supervisor Dr. Asim Laeeq Khan, Dr. Muhammad

Yasin, my friends and

Especially

To my parents, for their utmost passion, concern & support; to my sisters, brother and nephews till

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ABSTRACT

Mixed Matrix Membranes Comprising of PDMS an Deep Eutectic Solvents Infused ZIF-8 for Ethanol Dehydration

Mixed matrix membranes (MMMs) specially based on MOFs have shown remarkable separation performance in the past few years. To improve the performance of selective membranes fillers are being modified using different techniques. Direct incorporation of inorganic fillers in MMMs usually results in a poor polymer-filler interaction and unselective voids. To overcome this problem, deep eutectic solvent (DES) has been extensively used as a wetting agent. In this study an inorganic filler Zeolitic imidazolate framework-8 (ZIF-8) was used due to its appropriate pore size, selective property and shape. The properties of ZIF-8 were further enhanced by making a composite of ZIF-8 with a DL-Menthol and Lauric Acid-based DES. DES infused ZIF-8 was then used as a filler to fabricate MMMs. Polydimethylsiloxane (PDMS) was used as polymer matrix. FTIR results confirm DES impregnation over ZIF-8 particles. The efficiency of MMM for ethanol dehydration was assessed in a pervaporation set up at various temperatures and feed conditions. Hydrophobic properties of DES along with the nanoporous structure of ZIF-8 and large surface area provided by ZIF-8, has improved the membrane performance for alcohol dehydration. With the increase in % loading of filler the flux increases as well. MMMs loaded with 10 wt% of ZIF-8 infused DES demonstrated an increase in flux and a 50% reduction in activation energy as compared to pristine PDMS membrane

TABLE OF CONTENT

1. Introductions	6
1.1. Different Purification Techniques	7
1.1.1. Distillation.....	8
1.1.2. Adsorption.....	8
1.1.3. Liquid-Liquid Extraction	8
1.1.4. Ozonation	9
1.2. Membrane Technology	9
1.3. Pervaporation Technology (PV)	9
1.4. History of Pervaporation.....	11
1.5. Fundamentals of Pervaporation	12
1.5.1. Solution Diffusion Model	12
1.5.2. Parameter for Performance	14
1.6. Process Factors Effect.....	15
1.6.1. Pressure	15
1.6.2. Temperature	15
1.6.3. Feed Composition	16
1.7. Membrane Composition	16
1.7.1. Polymers.....	16
1.8. Membranes For Pervaporation.....	18
1.8.1. Polymeric Membranes	18
1.8.2. Inorganic Membranes	18
1.8.3. Mixed Matrix Membranes	19
1.9. Deep Eutectic Solvents (DES).....	20
1.10. Metal Organic Frameworks	21
1.11. Composite	22
1.12. Membrane Synthesis Methods	23
1.12.1. Solution Casting	23
1.12.2. Solution Coating.....	23
1.12.3. Hollow Fiber Spinning.....	24

1.12.4. Interfacial Polymerization.....	24
1.13. Literature Review	25
2. Materials and Method	30
2.1. Materials	31
2.2. ZIF-8 nanoparticles Synthesis	31
2.3. Synthesis of Composite (ZIF-8@DES)	32
2.4. MMMs Synthesis	34
2.5. Experiment.....	35
3. Results and Discussions.....	38
3.1. Characterization of prepared ZIF-8 particles.....	38
3.1.1. FTIR	38
3.1.2. XRD	39
3.2. FTIR of DES	40
3.3. FTIR of prepared DES infused ZIF-8 (Composite).....	41
3.4. FTIR of MMM.....	42
3.5. FTIR of All MMM `	43
3.6. Swelling Study of MMM	44
3.7. Effect of Composite Loading on Mixed Matrix Membranes (MMMs).....	45
3.8. Effect of feed temperature on ZIF-8 Infused Mixed Matrix Membranes (MMMs).....	46
3.9. Activation Energy	47
3.10. Research Limitations	49
4. Conclusion	51
4.1. Practical Implication of Study	51
4.2. Future Work.....	51
5. References.....	54

LIST OF FIGURES

Figure 1. 1 Solution-Diffusion Model	13
Figure 1. 2 MMM comprising of polymer matrix & Filler.....	19
Figure 1. 3 Synthesis of DES	20
Figure 1. 4 Similarities between DES and ILs.....	21
Figure 2. 1 Synthesis of Zif-8 Nanoparticles Solution	31
Figure 2. 2 Zif-8 Nanoparticles (White powder)	32
Figure 2. 3 Mechanism of Composite synthesis	33
Figure 2. 4 Composite (Zif-8 Nanoparticles + DES) (Yellowish Powder)	33
Figure 2. 5 Process flow of DES infused ZIF-8 synthesis.....	34
Figure 2. 6 Synthesis of MMM with Composite loading	35
Figure 2. 7 MMM with 2.5% Composite loading.....	35
Figure 2. 8 Process flow of Pervaporation System	36
Figure 3. 1 FTIR of ZIF-8.....	38
Figure 3. 2 XRD of ZIF-8.....	39
Figure 3. 3 FTIR of DES and its precursors	40
Figure 3. 4 FTIR of DES infused ZIF-8	42
Figure 3. 5 FTIR of MMM	43
Figure 3. 6 FTIR of MMM with loading %	44
Figure 3. 7 Swelling of membrane with different filler loadings of composite	45
Figure 3. 8 Flux vs MMM with different loadings of composite.....	46
Figure 3. 9 Flux vs MMM with different Temperature °C.....	47
Figure 3. 10 Activation Energy of MMMs	49

LIST OF TABLES

Table 1. 1 Different DES with molar ratios	21
Table 3. 1 Activation Energies of MMM with different %loading of composite.....	48

CHAPTER 1
INTRODUCTION AND LITERATURE REVIEW

1. Introductions

Increasing population has raised energy consumption. Due to the severe effects of global warming and energy scarcity issues, it is crucial to research and create environmentally friendly and energy-saving techniques for the chemical industry. As climate change and energy shortages continue to intensify, it is imperative that chemical process industries design and implement energy-efficient, environmentally friendly processes. The main step in each industry's chemical production process is a separation method. They are used to do jobs like cleaning up raw materials, recovering and refining important goods, and getting rid of pollution in the air and water [1].

The need for the development of alternative sources of energy, especially renewable energy, is expanding as a result of the depletion of fossil fuels, the increase in oil prices, and the enforcement of environmental regulations. As a typical biofuel, bioethanol, in particular, is considered a potential replacement for gasoline and even a promising gasoline additive. From the standpoint of large-scale use, ethanol offers clear benefits over the more established fuels, including a larger energy content, lower vapor pressure, and greater compatibility with the existing gasoline supply lines owing to its reduced corrosivity. The excess use of fossil fuels has resulted in severe environmental issues. Biofuels that are clean and renewable are presented as viable fossil fuel alternatives [2].

One of the main global concerns is the scarcity of energy due to the depletion of fossil fuel resources. In recent years, biofuel has garnered a growing amount of interest as an alternative sustainable energy source. Ethanol, one of the most important biofuels, is primarily generated from biomass which is type of renewable source by acetone–butanol–ethanol (ABE) fermentation process. However, yield and productivity are poor during the ABE fermentation process [3].

It is well acknowledged that bioethanol is a valuable liquid biofuel, producing ethanol from biomass requires a significant amount of energy. Depending on the type of biomass used, the hydrolysis technique, and the yeast used, the amount of ethanol in the fermentation broth may range from 1% by weight to 15% by weight. The water content of the ethanol must range from 1% to 3% by weight in order to produce fuel-grade ethanol. Among the various purification techniques, including liquid-liquid extraction, membrane distillation, distillation, and adsorption, pervaporation is an economical and energy-efficient way to

separate ethanol and water. The ability to save up to 50% of the energy needed for standard distillation via the use of pervaporation has made it an attractive process. Due to a variety of disadvantages, such as limited flux, subpar separation performance, and unstable membrane materials, pervaporation has trouble being used in commercial separations [4]. Bioethanol, often known as fuel ethanol, is one of the most essential biofuels generated from biomass resources. It is considered a clean, renewable, and environmentally-friendly alternative to gasoline because of its high-octane number, high vaporization temperature, and low vapor pressure. Additionally, ethanol is readily miscible and is utilized as an oxygenated component in gasoline to reduce emissions. Bioethanol is superior than biodiesel because to the higher environmental sustainability of its raw materials, reduced greenhouse gas (GHG) emissions, cheaper production costs, and other factors [5].

Membrane processes are physical phenomena that take place at room temperature; therefore, the observed components are not subject to heat stress or chemical alteration. This is crucial in several biological and chemical applications requiring the separation of delicate components. Membrane processes need less energy and are more straightforward compared to any other continuously operated process. Scaling up or down is straightforward, and process costs are seldom affected by plant size [6].

The standard unit techniques of distillation, liquid-liquid extraction, adsorption, and ozonation are often employed to separate and purify alcohols from water- alcohol mixtures. These processes use a lot of energy. However, because water and alcohol form azeotropes, the traditional distillation process is also very expensive when used to remove water from alcohols in a single setup. Researchers have suggested pervaporation as a very effective and low-energy way to solve this problem. Because of its simplicity in the integration of systems, process outline, adaptability, and low energy requirements in the process integration, it is an environmentally friendly and cost effective separation process that has been taken into consideration as a potential alternative to traditional processes of separation in alcohol dehydration [7].

1.1. Different Purification Techniques

Several purification techniques are being used for ethanol purification. Widely used techniques are following

- Distillation
- Adsorption
- Liquid-Liquid Extraction
- Ozonation

1.1.1. Distillation

Distillation is the most well-known and widely used purification method in industry. The feed is separated, and components with low boiling points in the mixture are condensed in the vapor phase during distillation by heating the mixture. By bringing the vapors back to condensation, they may be retrieved in the liquid phase. Although distillation is one of the most effective separation methods, it has a number of operational issues. One is aqueous-organic mixture separation. The distillation column is designed to separate alcohols and water mixtures while purifying ethanol. Ethanol is produced at the top, and water is produced at the bottom. It is anticipated that it would still contain contaminants after distillation. The second problem is that it is very expensive. This is because distillation involves repeated evaporation and condensation, which uses a lot of energy and is very expensive [8].

1.1.2. Adsorption

Adsorption is a technique in which a large surface area of the adsorbent is used in the separation process. Different chemicals are easily absorbed by the adsorbent based on their physical and chemical characteristics. Because it is hard to spread out particles with large diameters, they often absorb more than compounds with the same polarity. Because ethanol is polar and may contain contaminants of various sizes, the dispersion of polar and nonpolar surfaces makes them ideal for ethanol purification. The most likely adsorbents from water treatment are activated carbon and activated alumina [9].

1.1.3. Liquid-Liquid Extraction

Certain compounds are exchanged between two solvents that are immiscible or only partly miscible during liquid-liquid extraction. Typically, pure water or an aqueous solution is used as one of the aqueous phases in liquid-liquid extraction, along with one organic phase. It's vital to remember that any phase may contain the desired chemical. It relies on the

characteristics of the substance as well as the aqueous phase. A liquid-bilayer structure is used for liquid-liquid extractions. By combining an organic and an aqueous solvent, this bilayer is created. The sample matrix is typically applied initially as aspect of the aqueous layer. When this produced bilayer is mixed, the analyte will go into the organic layer while the extraneous salts and contaminants will stay in the aqueous layer. More organic layer contributions will cause the aqueous layer to lose more and more analyte. It is possible to carry out further washing processes in which the organic solution enriched with analytes is combined with other aqueous solutions of various compositions to remove contaminants [10].

1.1.4. Ozonation

Three oxygen atoms make up the ozone molecule, which may be broken down into a number of other molecules. Compound decomposition causes a change in the chemical and physical characteristics of a compound, such as an increase in volatility, biodegradability and decreased toxicity. Although ethanol may undergo oxidation, the air conditions are not conducive for this process. By-products of ozonolysis and non-oxidizable chemicals are only two issues that might arise while removing impurities from ethanol using ozonation. It is assumed that certain chemicals will persist even after ozonation since ozone cannot completely oxidize all substances. Since ozonation is an oxidation process, it cannot physically remove the chemicals but may produce new compounds as by-products. Therefore, their removal requires post-ozonation [11].

1.2. Membrane Technology

Membrane technology is regarded as a crucial component in industries since it has various benefits over other processes of separation, such as cheap cost, high selectivity, and low consumption of energy. As a result, they are regarded as green technology. There are several membrane processes, including pervaporation, gas separation, and nano filtration.

1.3. Pervaporation Technology (PV)

The term permission and evaporation have been combined to form a phrase pervaporation. Because of its simplicity, this technique is used by several industries for a variety of procedures, including purification and analysis. A nonporous perm-selective membrane is

employed in the novel membrane technology of pervaporation to partially vaporize a liquid mixture and separate it. A portion of the feed mixture is produced in the vapor state from the membrane's other side, which is maintained under vacuum by constant pumping, while it flows down one side of the membrane. After condensing on a cooled wall, the permeate is eventually captured in the liquid condition. It is thus more abundant in the feed mixture's faster-permeating component, while the retentate is depleted in it. The part of the feed that cannot go through the membrane is known as the retentate [12].

An energy-efficient coupling of evaporation and permeation is the foundation of the membrane separation technique known as pervaporation. It is used to filter volatile substances from solutions using a selective membrane. By creating a vacuum solely on a single side of the membrane, volatile substances in a liquid flow disperse over it. By using selective membranes, pervaporation may be utilized for dehydration of organic solutions and eliminate organic contaminants from aqueous solutions.

In addition to having a high energy efficiency, pervaporation has no azeotropic restrictions thanks to the utilization of a dense membrane. In pervaporation components must be driven through a membrane with the strong force which is often not dependent on certain vapor liquid equilibrium. At the permeate side, an aqueous and organic stream is obtained. Pervaporation is favored over azeotropic distillation as a solution to these problems since it is less expensive and more manageable [13].

Pervaporation (PV) is considered the greatest replacement to azeotropic distillation since it prevents cross contamination from utilizing entrainers in azeotropic distillation. As a result, it is a method that has great promise for dehydrating aqueous organic mixtures. Over the goal of alcohol dehydration, researchers have been investigating novel high-performance membranes for the last ten years. A pervaporation membrane should be very mechanically and economically viable, have great permeability and selectivity, outstanding stability and durability. Although inorganic membranes work well and have excellent mechanical stability, they are often rejected because of their weakness and costly price [14].

Comparing polymeric membranes to inorganic membranes, they are less expensive and simpler to make, but they have limitations due to the selectivity/permeability trade-off. In order to improve the combined properties of both Inorganic and organic membranes in

separations related to the energy and environment mixed Matrix membranes with inorganic fillers incorporated with different solvents contained in a polymeric matrix may be used. The compatibility of the organic and inorganic phases is crucial for creating mixed matrix membranes (MMMs). Aside from compatibility, eliminating interface flaws is another crucial component of creating MMMs for pervaporation processes [15].

1.4. History of Pervaporation

Despite having its roots in 1917, pervaporation has just recently become a practice in this industry. Binning and his co-workers were the forerunners of the first pervaporation research endeavor. Their efforts helped pervaporation become more significant in applications involving separation. The technique was not commercialized even though this work was explored for a while and multiple patents were published. The energy crisis of the 1970s made people take a second look at their intense interest in purification and separation technologies, which are very energy efficient. Pervaporation was first used in Europe because it could separate aqueous azeotrope combinations. Up until the 1980s, new and innovative membrane materials were also being developed for related separation technologies, including gas separation and reverse osmosis, which increased the likelihood that pervaporation would be a financially viable process. Numerous membrane applications based on innovative symmetric polymer membranes that produced thermally and chemically robust as well as economically advantageous shape of membranes were presented in the middle of the 1980s [16].

Azeotropic mixtures are often separated by pervaporation, a unique separation process. It is a very successful and economical method for dehydrating alcohols or solvent compositions. It works best under various circumstances, such as when separating organic-organic combinations or removing various organic material from aqueous solutions. Bio-solvents may be effectively removed using pervaporation without slowing down the pace at which fermentation broth is produced [17].

Feed that has to be separated flows through the membrane's one side, and under the influence of a vacuum, permeate is collected through the other side. The driving factor behind this kind of separation is the chemical potential gradient. On the side of permeate, the driving force may be produced by using a vacuum pump or an inert purge such that the

permeate vapor pressure is consistently lower than the partial pressure of the feed solution. In essence, pervaporation and vapor permeation are quite similar to one another. Rather than entering as a liquid, feed penetrates by vapor permeation. Since both vapor permeation and pervaporation need the same membranes, the membranes now in use for pervaporation may also be utilized for vapor permeation [18].

1.5. Fundamentals of Pervaporation

Pervaporation is much more complicated than gas and liquid separations when considering the separation features of all technologies. Its complexity is primarily caused by the coexistence of two phases, namely vapor and liquid, which necessitates the involvement of both mass and heat transfer. Phase transformation exists from the feed side to the permeate side. The driving force behind mass transfer is a chemical potential gradient, or fugacity gradient, which may be created by using a vacuum pump or an inert gas on the permeate side to drop pressure there by a lesser amount than on the feed side.

- 1) Physicochemical properties of feed solution and interactions
- 2) The compatibilities between the membrane's constituent elements and its permeate
- 3) The membrane's structural makeup.

There are many various hypotheses for the transport process in pervaporation, however the model of solution diffusion is the most crucial mechanism taken into account [19].

1.5.1. Solution Diffusion Model

The solution-diffusion model is the most often used transport mechanism for porous and non-porous membranes, and it entails the following three steps as mentioned in figure 1.1:

- 1) Selected permeate sorption at the contact between the feed and membrane
- 2) The concentration gradient-induced permeate diffusion in the membrane, and
- 3) The permeate's desorption into the vapor phase on the membrane's downstream side.

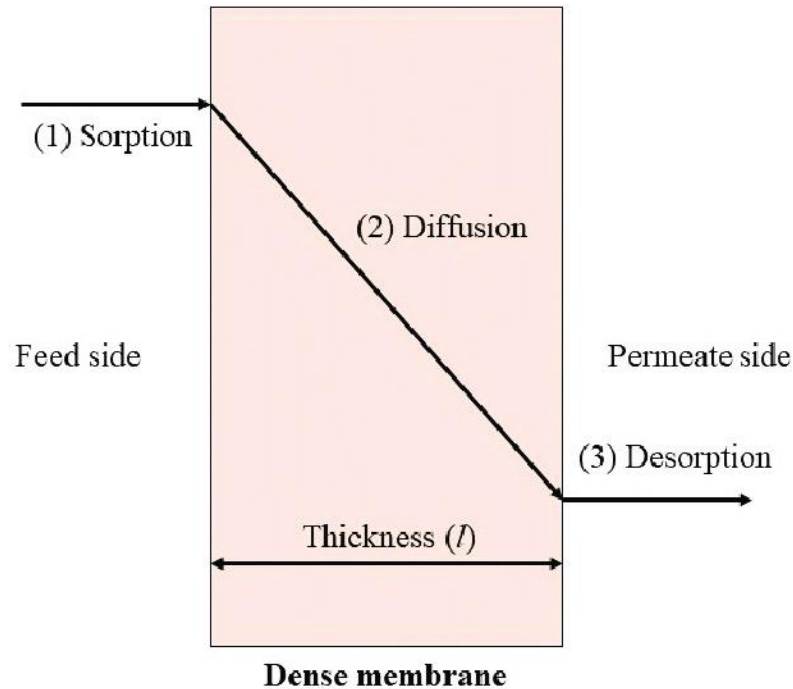


Figure 1. 1 Solution-Diffusion Model

This model describes the mass transfer of a fluid over a thick, non-porous membrane as

$$\text{Permeability (P)} = \text{Solubility (S)} * \text{Diffusivity (D)} \quad (1)$$

The defined feed component solubility in the membrane controls the relationship between the membrane material and the feed being processed. While diffusivity is influenced by chemical and physical factors such as the shape of penetrant molecules, size and interactions between feed component and membrane material [20].

The rate-limiting stage in this process is thought to be the diffusion of the feed element across the membrane. As a consequence, the solution-diffusion model assumes constant pressure within a membrane and solely considers the concentration gradient when describing the fugacity gradient. The diffusion process is often described in terms of Fick's first law. Following equation describes the flux of a component as

$$j_i = -L_i \frac{du_i}{dx} \quad (2)$$

where the term L_i is a proportionality coefficient that connects the flow with the chemical potential driving force, and du_i/dx is the chemical potential gradient. Temperature, pressure, concentration, and electric potential gradients are all examples of chemical potential gradients. The chemical potential gradient, which is applicable to polymeric membranes as

well, may be stated as follows where the driving force is the pressure gradient and concentration.

$$du_i = RT d \ln(\gamma_i C_i) + V_i dp \quad (3)$$

Where c_i denotes the component i 's mole fraction (mol/mol), γ_i denote the activity coefficient (mol/mol) that links activity to mole fraction, p denotes the partial pressure, and v_i denotes the component i 's molar volume. As the permeate is adsorbed rather than diffusing through inorganic membranes, the adsorption-diffusion model may be used instead.

A far more complex adsorption-diffusion model based on Maxwell-Stefan theory is needed to account for the dragging and concentration effects. This model helps explain the transport process for inorganic membranes where surface adsorption happens by switching between one adsorption site and the other.

1.5.2. Parameter for Performance

Two metrics, selectivity/permeability and separation/flux factor, are often employed to assess the separation efficacy of pervaporation. To evaluate the effectiveness of the pervaporation process' separation, flux (J) and separation factor (β) are used. The following equations define these variables:

$$J = \frac{Q}{At} \quad (4)$$

$$\beta = \frac{Y_i/Y_j}{X_i/X_j} \quad (5)$$

In equations above, total mass transported is represented by Q over the time t , the membrane area is A . The mole fractions of one component, x_i , are found in the feed and permeate, while the mole fractions of the second component, x_j , are found in the feed and permeate. The quantity of permeate collected per unit time per unit area of membrane ($\text{kg/m}^2\text{hr}$) is defined as flux after a specific period of time, while the separation factor is defined as the ratio of concentrations of two components.

The invention of the pervaporation separation index (PSI), which may be defined as a product of permeation flux and separation factor, allows for the evaluation of pervaporation

membrane performance due to the tradeoff connection between separation and flux that has been observed.

$$PSI=J_t \beta \quad (6)$$

Where β is the separation factor and J_t is the total permeation flow. The value of PSI, however, may be substantial if β is equal to 1 and the membrane has high flux rates, in accordance with this equation. Because of this, the PSI definition was eventually changed to include J_t as a product. Given that selectivity and flux often behave in opposing ways and that it is challenging to attain high selectivity and flux, the ideal separation performance of membranes may be controlled by this parameter under certain operating circumstances. However, owing to the impact of the given operating circumstances, there are certain constraints on the parameter and it is still not feasible to compare membrane performances under various operating settings in the same separation system [17].

1.6. Process Factors Effect

Parameters that influence the selectivity and permeability of pervaporation are

- 1) Pressure
- 2) Temperature
- 3) Feed composition

1.6.1. Pressure

Permeation requires a driving force at all intervals, and in pervaporation that driving force is either permeate pressure or vacuum. In pervaporation, it might be difficult to produce adequate driving power, which has a direct impact on operating costs owing to the need to maintain vacuum. In addition to affecting component concentration, downstream pressure also has an impact on membrane selectivity. Flux is always exactly proportional to concentration and diffusivity when thick membranes are utilized in pervaporation [21].

1.6.2. Temperature

Another factor that affects the pervaporation membrane's selectivity and flow rate is temperature. Flux increases as temperature rises, although often membrane selectivity decreases as temperature rises. But it is difficult to establish the relationship between

selectivity and temperature because the chemistry involved in how polymers and solvents interact when the temperature changes [22].

1.6.3. Feed Composition

Two key characteristics of the membranes are selectivity and flow in pervaporation, and both of these rely on the feed content. The content of the feed regulates liquid sorption and is crucial for membrane swelling. The two components of a feed mixture. Because the component with the highest interaction with the membrane material controls membrane swelling and flux, if its concentration rises, the flux and swelling of the membrane will both occur. In membrane separation, diffusivity is a phenomenon that heavily relies on membrane swelling but reduces selectivity. The process may be summarized as follows: when the concentration of more interacting components in a mixture containing membrane material grows, the flow also progressively increases while the selectivity gradually decreases [23].

1.7. Membrane Composition

1.7.1. Polymers

High molecular weight compounds called polymers are created from monomers. The degree of polymerization refers to the length of the long chains created by combining different structural elements. The degree of polymerization determines the molecular weight of any polymer. Co-polymers come in three different forms: random, block, and graft. Linear, branching, and cross-linked polymeric chains are all possible. The terms isotactic, atactic, and syndiotactic describe where the vinyl group is located in a polymer chain. The qualities of a polymer are determined by where R is located in the chain. A polymer may become crystalline or amorphous as a result. Chain flexibility, molecular weight, and chain interactions are features of polymer chains that influence the mechanical, chemical, and thermal properties of polymers [24].

Another factor that significantly influences the characteristics of a polymer is its state. The polymer is either in a glassy or rubbery condition depending on the glass transition temperature. Any material's mechanical stability is measured by how it deforms in the presence of a certain force. A stress-strain curve may be used to identify it, and it provides information on the material's hardness, ductility, and brittleness. Elastomers are regarded

as a significant category of materials. They are either thermoset or thermoplastic. The material that may soften when heated above the glass transition temperature is thermoplastic [25].

Due to their chemical and thermal stability as well as surface effects, porous membranes are less sensitive to the condition of a polymer. They are essential for dense membranes because of the differences in their permeability magnitude orders and T_g . The characteristics of a membrane are impacted by the glass transition temperature in the following ways:

- $T < T_g$: main chain bonds not rotated
- $T = T_g$: just enough thermal energy to overcome rotational constraints brought on by large side groups or chain interactions
- $T > T_g$: free rotation of segments and great chain mobility

A polymer's main chain chemical structure and side chains define its state. Another crucial factor that influences a polymer's cross-linking and impermeability is its degree of crystallinity. A polymer's chemical strength, tensile strength, compressive strength, and thermal stability are all impacted by additives. The polymer's glass transition temperature will be lowered by adding a plasticizer [26].

The wide range of industrial uses of membrane technology makes it appealing. For separation, many membrane types are used. A dense, microporous, symmetric polymeric membrane is one option, allowing for high selectivity, flow, and PSI. They feature an asymmetrical or composite structure with a porous support layer and a thin, microporous top layer. The top layer offers efficient separation while yet retaining a high flux. The components could be the same or different. The mechanical strength is provided by the second layer. This may be accomplished by using a single plate, tube, hollow fiber, or honeycomb construction. For the purpose of minimizing vapor transfer and preventing capillary condensation, the sub layer should have an open structure. Applying a thin selective layer directly to the support will be quite challenging if the sub layer pores are particularly large [27].

To prevent all of these issues, a multilayer membrane is often used. The support layer is often cast on a porous support layer formed of a woven or nonwoven fabric and resembles

an ultrafiltration membrane. This structure is covered with the top, thin separating layer, which has a thickness of 0.5 to 5 mm [28].

1.8. Membranes For Pervaporation

Types of membranes used in pervaporation are listed below

- 1) Polymeric Membranes
- 2) Inorganic Membranes
- 3) Mixed Matrix Membranes

1.8.1. Polymeric Membranes

Due to their beneficial qualities, such as their high ease of preparation and excellent separation performance, polymers are often utilized in membranes for pervaporation. Glassy polymers, ionic polymer membranes, and rubbery polymers are the three main categories of polymeric membranes. Due to their water selectivity, glassy polymers are naturally preferable for solvent dehydration, while rubbery polymers are better suited for the selective organic molecule removal from water. The hydrophilicity and hydrophobicity of the polymer materials used in dehydration membranes should be properly balanced [29]. The most popular polymeric material for pervaporating organic-aqueous mixtures is polydimethylsiloxane (PDMS). Along with excellent hydrophobic qualities, it exhibits extremely high chemical, mechanical and thermal stability. Additionally, it is a very affordable and simple to work with material [30, 31].

1.8.2. Inorganic Membranes

These membranes are constructed from inorganic substances like zeolites, alumina, silica, etc. These materials are distinguished by their beneficial characteristics, such as their resilience to swelling, solvent resistance, and thermal and chemical stability. These inorganic membranes have several uses due of their excellent permeability and selectivity. Permeability and selectivity are the main aims in pervaporation, hence inorganic membranes might be quite important in this application [32].

One popular substance that often provides high flux is silica, however it cannot survive in an environment that is hydrophobic. Zeolitic membranes are now the best due to their adjustable chemical and mechanical characteristics [33].

1.8.3. Mixed Matrix Membranes

Mixed Matrix membranes belong to a brand-new category of materials for pervaporation membrane and are essential for the development of membrane-based separation technology today. Mixed matrix membranes (MMMs) combine the high processability of polymers with the high permeability/selectivity of the fillers by enclosing inorganic filler particles in polymer matrix. These membranes offer exceptional selectivity and permeability because to their strong mechanical and chemical stability [34].

One of the materials that provide great flux is silica, although these membranes cannot be employed in hydrophobic settings. Excellent mechanical and chemical qualities are offered by zeolites. Zeolites of various types have been documented in the literature. For investigations on pervaporation, these zeolites may be included into mixed matrix membranes. As fillers for mixed matrix membranes, silica, zeolites, carbon nanotubes, iron, clay, and titanium oxide are all acceptable options. A mixed matrix membrane will be created if certain fillers are added to a polymer matrix. They are made using the phase inversion method and blending. There are two distinct classes among them. Applications involving pervaporation and gas separation employ one class. The performance of the membrane is improved by inorganic nanomaterials (fillers) with a particular shape, size, and interaction. The components of MMM are shown in figure 1.2. Typically, zeolite, carbon nanotubes, and metal-organic frameworks (MOFs) are used as fillers. The MMMs' second class is permeable. It has several uses including adsorption. The fillers mostly consist of ion-exchange particles that interact ionically with other species in the matrix [35].

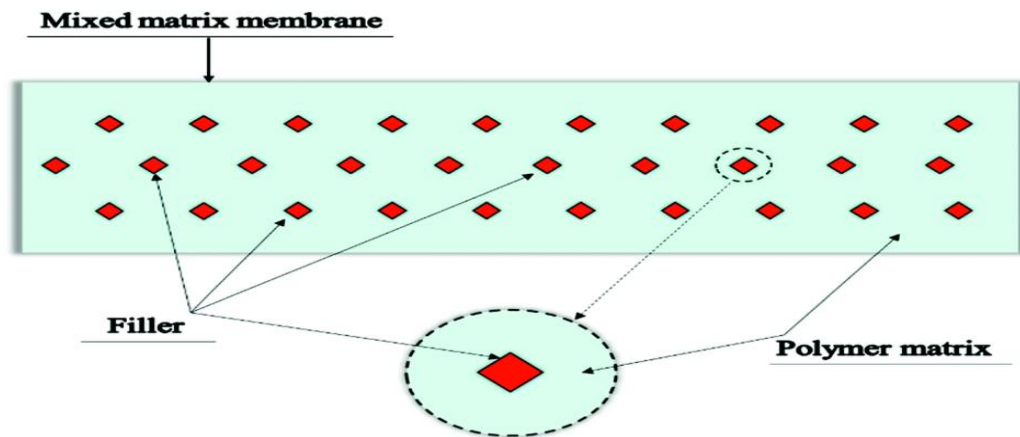


Figure 1. 2 MMM comprising of polymer matrix & Filler

1.9. Deep Eutectic Solvents (DES)

In recognition of the fact that deep eutectic solvents have numerous similarities and differences in accordance to ionic liquids (ILs), deep eutectic solvents (DESs) are all now recognized commonly as a IL equivalents new class. Although the words IL and DES have often been used simultaneously in the literature, it is important to clarify that these acronyms refer to two distinct categories of solvent. In contrast to ILs, which are systems generated from systems comprised predominantly of one kind of discrete anion and cation, DESs are complexes generated from a Lewis or Bronsted bases and acids eutectic mixture that might include a range of cationic and anionic species. Figure 1.4 shows the similarities between DESs and ILs, their chemical characteristics point and diverse potential application fields [36].



Figure 1. 3 Synthesis of DES

While DESs and traditional ILs have distinct chemical characteristics, they share some physical characteristics, particularly the potential to be tailored as tunable solvents for a specific type of chemistry. DES also possess low vapor pressure, broad range of liquid temperatures, and are nonflammable. Number of benefits are provided by DES over conventional ILs, including simplicity in preparation and accessibility from fairly affordable components which can be seen in figure 1.3 which shows the simple synthesis of DES; however, they are typically less chemically inert. The two components are simply mixed together to create DESs, usually with a little heating. By choosing appropriate ratio of precursors required DES can be synthesized. Table 1.1 shows the molar ratio of different hydrophobic DES. In comparison to typical ILs, this retains a relatively cheap manufacturing cost and allows for large-scale applications. However, there is relatively little knowledge regarding the toxicological characteristics of the eutectic solvents directly, and this has to be extensively researched by the scientific community. Individual DES components often have well-defined toxicological profiles [37].

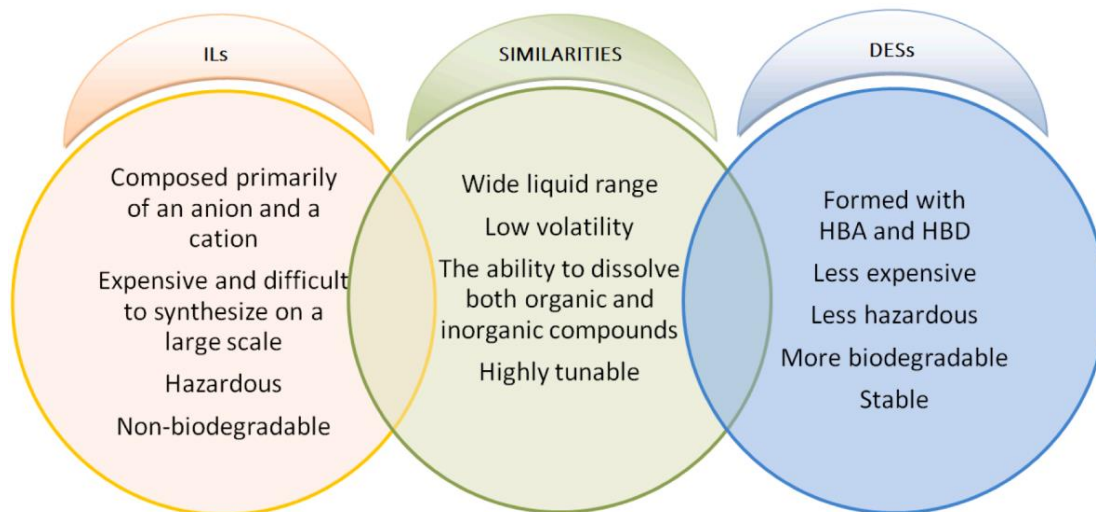


Figure 1. 4 Similarities between DES and ILs

Table 1. 1 Different DES with molar ratios

Different DES (Hydrophobic)	Molar Ratio
C ₈ :C ₁₂	3:1
C ₁₀ :C ₁₂	2:1
DL- Menthol: C ₈	1:1
DL- Menthol: C ₁₀	1:1
DL- Menthol: C ₁₂	2:1
DL- Menthol: Lauric Acid	2:1

1.10. Metal Organic Frameworks

Currently, metal-organic frameworks (MOFs) are the most well-known sophisticated porous materials. MOFs have a number of characteristics that make them more desirable and practical, including novel structures, large surface areas, improved catalytic capabilities, high adsorption rates, and a range of pore diameters. Different synthesis methods are used to create a variety of MOF types, and the characteristics of these materials are improved by combining various functions using the idea of secondary building units (SBUs). The two main components of MOFs are inorganic material and an organic component that serves as a binding linker. Simply altering the arrangement of SBUs allows for the synthesis of MOFs with various morphologies [38].

MOFs are thought to be a brand-new hybrid framework that incorporates zeolitic architecture. ZIFs are receiving a lot of attention because of their adjustable qualities. The subclass of MOFs known as Zeolitic Imidazole Frameworks (ZIFs) includes materials with both organic and inorganic components. It is made up of M-Im-M molecules, which are self-assembled and stand for Zn, Co, and the imidazolate linker, respectively. The structures of ZIFs are relatively similar to those of normal alumino-silicate zeolites; in these materials, silicon is commonly represented by Zn^{2+} ions, while oxygen is represented by imidazolate anions in bridges with a metal-imidazole-metal angle of 145° . As a result, ZIFs often formed topologies that resembled zeolites in terms of structure [39].

ZIFs may build structures that are not possible in zeolites. ZIFs often exhibit all the characteristics, including very large surface areas, unimodal micropores, high crystallinities, a wealth of functionalities, and remarkable thermal and chemical stabilities, since they integrate the features and benefits of both zeolites and MOFs. ZIFs are useful in several applications, including separation, sensing, and catalysis, because to their exceptional characteristics. Using zeolitic-Imidazolate-frameworks (ZIFs), the separation factor of a water/ethanol combination may be improved [40].

1.11. Composite

Organic-inorganic hybrid nano-composites development has advanced significantly in recent years. Natural materials and synthetic substances that have undergone different synthetic processes are included in mineral compounds (host). Numerous organic substances (guests), including solvents, monomers, polymers, etc., may be found within the host molecules' existing holes. Zeolites have received a lot of attention in recent years among the many host-guest hybrid nano-composites [41].

A broad range of intriguing traits are offered by the inherent qualities of zeolites, such as variation in cavity size, geometry, topology, and frame composition. Their generally ionic frameworks may have cages, cavities, or channels. The electro-neutralizing cations of the zeolite may react with the guest cations via an ionic exchange process as well as travel into the interior spaces or cavities of the zeolite from its enclosing aqueous solution. These cavities are a suitable choice for use as a basis for the establishment, consolidation, and entrapment of materials (guests) that spontaneously locate on these bases. Participation of

a guest complex in the zeolite host cavities is one of the most popular and crucial intracrystalline techniques in the fabrication of hybrid nano-composites [42].

1.12. Membrane Synthesis Methods

In the PV process, membranes play a significant role. Synthesis techniques are also introduced in this context. For the fabrication of polymeric membranes, there are several procedures that may be used, some of which include solution casting, solution coating, interface polymerization, and hollow fiber spinning. Commonly used pervaporation membranes are either dense or asymmetric. Since membranes with asymmetric have a rather thick microporous substrate supporting a thin selective layer substrate, they can perform better than dense membrane structures, which are often generated at lab scale and are hindered at industrial scale [43].

1.12.1. Solution Casting

Solution casting is the most used technique for producing flat sheet membranes. The polymer and filler sample are first dissolved in a solvent before being spread out onto a flat surface. After the solvent has evaporated, a flat, thick coating is left behind. In the case of MMM, membranes are created by stirring after fillers have been added to the polymer matrix. To avoid filler agglomeration after stirring, sonication is used [44].

1.12.2. Solution Coating

Typically, this method is used to create composite membranes. Support, which might be a flat sheet of paper or a hollow fiber, is covered with a thin selective layer. In order for the coated selective layer to be able to regulate the separation primarily, the substrate's porosity is crucial. To prevent the coating solution from penetrating, the substrate surface and pore size distribution should be devoid of defects. Before the coating procedure, a pre-wetting approach using a low boiling point solvent may be used to reduce infiltration. The drying procedure helps to eliminate solvent pre-wetting. The coated membrane is produced after drying. Pervaporation typically uses a flat sheet structure. The short fiber sizes make it challenging to create hollow fiber membranes. Because the coated fibers are irregular, separation may be hampered [45].

Solution casting is used for the fabrication of composite membranes, which deposit a thin selective layer of microporous support. This foundation can be tubular, hollow, or flat; however, it must be porous, which reduces structure resistance and leaves a coating layer to primarily regulate membrane resistance. Coating solution intrusion is avoided by the substrate surface, which must have a tight pore size distribution and be devoid of significant flaws. In order to reduce the danger of intrusion, the substrates are treated with a solvent with a low boiling point, which is used as a pre-wetting agent. This method does not work with the solvent for coating prior to coating. In order to accomplish this, the coated layer solvent used as a pre-wetting agent is removed using drying. It is difficult to cast hollow-fibre uniformly because the separation process would have been negatively impacted by hollow-fibre of small diameter with an unequal coating [46].

1.12.3. Hollow Fiber Spinning

Hollow fiber membranes are produced using this method. Comparing these membranes to a flat sheet construction, they are more acceptable. Using this method, several benefits, including high packing density, may be attained. With this method, you may prepare various layers at a lower cost and with customized structures and materials [47].

The hollow fiber membrane offers the benefits of a self-contained vacuum channel, a high filling density, and a self-supporting structure over flat membrane. Phase transition occurs in the period of process of spinning when the main fiber comes into touch with the coagulant. The main fiber quickly hardens on its internal layer as the polymer coating and solution in the inner hole are discharged at the same time. However, a portion of the main fiber freezes on the outer surface when it passes via air gap region because of the humidity in the air. As the single-layer to double-layer co-extrusion spinning process develops, hollow fiber spinning becomes more difficult. This strategy provides more possibilities for the material and structure of the support layer and is more affordable for membrane preparation [48].

1.12.4. Interfacial Polymerization

A well-known method used for reverse osmosis and nanofiltration to create thin composite membranes is interfacial polymerization. Pervaporation membranes have also benefited

from the use of this technology. Since the 1960s, this method has been frequently employed. The membrane flow in this process is significantly influenced by the thin layer on top of the substrate. Compared to alternate production techniques like dip coating, layer-by-layer self-assembly, and photo-grafting, interfacial polymerization (IP) is more customizable because polymerization happens quickly and large molecular weight polymers may be produced even under modest reaction conditions. When making composite films for NF, PV and RO, IP is often used. A unique thin-film composite membrane was created, for instance, by Wu and colleagues using self-polymerization the successive deposition of polydopamine and IP through PA for the ethylene glycol dehydration [49].

1.13. Literature Review

Rezazakemi et al. conducted research on PDMS membranes with different supports. A pre-wetting method was used to create polydimethylsiloxane (PDMS) cross-linked membranes based on polyamide and cellulose acetate microfiltration membranes for the pervaporation and dehydration of ethanol. In the beginning, cellulose acetate (CA) supports were made, described, and compared with commercial polyamide (PA) supports. The effects of the support layer and perm-selective thickness on the separation efficiency of the membrane were specifically examined in the trials at starting ethanol concentrations of 0.3 wt% to 3.0 wt% and temperatures of 30 °C to 50 °C. The findings showed that total permeation flow increased with feed concentration and temperature. Performance-wise, PDMS/PA membrane outperformed PDMS/CA membrane [50].

In order to create innovative mixed matrix membranes, consist of PDMS/DLA-ZIF-90 for recovery of ethanol by pervaporation, zeolitic imidazolate framework-90 particles was modified with dodecylamine which improved surface hydrophobicity. The effective ZIF-90 particles modification is examined in the study by Sheng et al. using a variety of characterisation methods. The PDMS/DLA-ZIF-90 MMMs' shape and physicochemical characteristics are investigated and described. The PDMS/DLA-ZIF-90 MMM exhibits separation performance and morphology homogeneity optimization in comparison to the PDMS MMM with unmodified ZIF-90. This is achieved as the ZIF-90-DLA particles have the inner channel flexibility with improved selectivity, adsorption and the enhanced PDMS

matrix and DLA modified ZIF-90 particles affinity. With an ideal flux of $99.5 \text{ g/m}^2\text{h}^1$ and an associated separation factor of 15.1 at $60 \text{ }^\circ\text{C}$, the MMM with DLA-ZIF-90 loading of 2.5 wt% exhibits the greatest performance. It is also examined how operating temperature affects things. Performance benchmarking reveals that the PDMS/DLA-ZIF-90 MMM performs better in terms of pervaporation than the majority of other PDMS-based membranes, which may provide important information for the creation of high-performance ZIF-based MMMs for organic recovery [51].

Boya et al. constructed a model for mass transfer which consists of the theory of solution-diffusion of ethanol recovery by pervaporation using polydimethylsiloxane (PDMS) membrane taking concentration polarization into consideration. The limiting diffusivity of ethanol, the ethanol plasticization coefficient, the water/polymer interactions parameter, and the ethanol/polymer interaction parameter were all identified. Based on the convective mass transfer occurring upstream of the membrane, the concentration polarization coefficient was determined. On ethanol flow and concentration polarization coefficient, the effects of convective mass transfer coefficient, partition coefficient, and ethanol diffusion mass transfer in membrane were investigated [52].

Using a novel in-situ synthesis method, Guozhen et al. created mixed matrix membranes (MMMs) based on ZIF-8 and polydimethylsiloxane (PDMS) with excellent permeability. ZIF-8's adaptable pore shape and potent hydrophobicity could provide an effective pore structure for selectively recovering organic compounds. During the process of making a membrane, C and D solutions were mixed using spin-coating at the C-D interface. The crystallization of ZIF-8 and the polymerization of PDMS occurred simultaneously. The physical inclusion of porous materials was made easier by making an active layer with a continuous, defect-free layer of PDMS and a layer of ZIF-8/PDMS that can be used to add diffusion channels. The total flow rate was $2046.3 \text{ g/m}^2 \text{ h}$, which is 1.6 times that of a pure PDMS membrane, with no decrease in separation factor below 20 wt%. ZIF-8 loading and defect-free MMMs based on the ISS method have these traits. The ZIF-8/PDMS MMM that the ISS produced showed excellent n-butanol separation performance [53].

By growing nanoparticles of zeolitic imidazolate framework-8 (ZIF-8) in situ on graphene oxide (GO) nanosheet surface, Tengyang et al. were able to create GO modified ZIF-8 composites which has inner channels sustained for molecules of ethanol, which were then

filled into a matrix of PDMS as polymer to create mixed matrix membranes consists of PDMS/ GO modified ZIF-8 for recovery of ethanol. Different methodologies were used to characterize the GO modified ZIF-8 novel composites and MMMs synthesized by PDMS/ GO modified ZIF-8 as they were created. The findings demonstrated that nanoparticles of ZIF-8 were evenly distributed on the GO nanosheet surface, and that GO modified ZIF-8 composites had higher hydrophobicity than GO as a consequence of modifying GO's surface with hydrophobic ZIF-8. Furthermore, as compared to ZIF-8 nanoparticles, GO modified ZIF-8 composites as the filler demonstrated outstanding compatibility with PDMS as well as good dispersion in PDMS matrix. As a result, MMMs based on GO modified ZIF-8 outperformed ZIF-8-based MMMs in terms of separation performance [54].

Zhihao et al. synthesized ZNC, a nanoporous carbon derived from ZIF-8, to substitute ZIF-8 in traditional MMM in order to enhance the diffusion process. ZNC has greater pore sizes and pore volume. In comparison to ZIF-8/PDMS MMM, n-butanol permeation of ZNC/PDMS MMM increased by 68.7% with a 3 wt% particle loading. Because ZNC and PDMS get along well, ZNC was evenly distributed across the grid. As a consequence, n-butanol recovery from 1.5 wt% n-butanol/water solution at 55 °C produced an n-butanol permeability of 109,583 Barrer and an n-butanol/water selectivity of 4.47, which were raised by 145.4% and 17.6%, respectively, compared to the pure PDMS membrane. Overall, real-world applications reveal that the ZNC-filled PDMS membrane can effectively separate n-butanol [55].

In their study, Geng et al. coated a mixed matrix membrane (MMM) made of polyvinyl alcohol (PVA) and ZIF-8 onto hollow fibers made of aluminum oxide (Al₂O₃) for the pervaporation method of dehydrating ethanol. To achieve a uniform distribution MMM, a drying-free, water-based ZIF-8/PVA solution was created. A pure PVA solution was initially dip-coated onto the hollow fiber as a guttering layer to stop phase separation before the MMM was applied. We created several weight ratios of ZIF-8-loaded MMMs. According to the findings, a high permeate flow which is 685 g/m² h and high separation factor of 4821 may be shown with high ZIF-8 loading of 39 wt% [56].

In order to dehydrate n-butanol using the pervaporation method, Abu Bakar et al. study the effectiveness of Deep Eutectic Solvents (DESs) based membranes. They employed three

DES which are DL-menthol: Lauric acid (DES), [TETA] Cl: Thymol (DES) and DL-menthol-Palmitic acid (DES) each of which had a distinct arrangement of hydrogen bond donors and acceptors. The synthesis of the DESs was confirmed by FTIR analysis and the liquid mixture's physicochemical properties. The permeable support was then filled with the DESs to create supported liquid membranes (SLMs). To stop DES from leaking out, polydimethylsiloxane second layer was immediately deposited on the DES-PSf layer. A feed with a 6-weight percent butanol aqueous solution was investigated at various temperatures. When DES was added to membranes, the separation factor increased significantly while maintaining a respectable flux. Separation factor of membrane based on the DL-menthol: Lauric acid (DES) had the greatest which is of 57 and the highest overall flux which is $0.11 \text{ kg/m}^2 \cdot \text{h}$. among all the membranes [57].

The advancement of DES-based MOFs with adjustable functionalities and their use for the adsorption of hazardous gaseous contaminants is highlighted by Onome et al. Various MOF derivatives have been prepared using a variety of synthesis techniques that have been established. DESs however, are one-of-a-kind solvents that have received a lot of attention lately since they may be used as vital precursors for creating advanced composite materials and many applications where environmentally friendly techniques are necessary. These environmentally friendly solvents are attracting significant interest as a template for the simple, direct mixing into MOFs since they are simple to make, cost less to produce, and have good control over the shapes, pore sizes, and particle morphologies, all of which have been shown to significantly affect their adsorptive properties [58].

Chapter 2

Material and Methods

2. Materials and Method

In comparison to conventional distillation procedures, pervaporation has emerged as a viable method for cleaning bio-alcohols and has the ability 50% energy savings. High performance membranes with greater chemical and thermal resilience to a variety of feeds and varied compositions are necessary to accomplish such crucial performance [59].

The production of PV separation materials has a bright future thanks to the porous particle fillers dispersion in polymeric matrix made up of Mixed matrix membranes (MMMs), which has advantageous properties of both polymers and particle fillers. Inorganic particles employed in alcohol separations often include zeolite, silica-lite, carbonaceous particles and silica. However, its performance is limited by the incompatibility of the inorganic and polymeric phases, which causes membrane flaws. As a result, as compared to the original polymer membranes, MMMs selectivity shows little to no improvement. Another issue that lessens its efficacy is more selectivity, which causes lesser permeability [60].

Recent research has shown that zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, are capable of greater thermal and chemical resistance leading to increased stability and may be employed for a range of applications at higher temperatures and harsh circumstances. It is anticipated that adding a highly hydrophobic substance, such ZIF-8, to PDMS would enhance alcohol separation and increase yields. Another benefit is that, in contrast to existing hydrothermal synthesis techniques for preparing zeolites, ZIF-8 particles may be made in a cost-effective, time-saving, and convenient manner at minimal temperature. In contrast to ZIF-8 synthesis, the majority of ZIFs are created at high temperatures at autogenous pressure, which makes the process more difficult and energy-intensive [61].

In order to study the improvement in the separation process as well as the resulting flux, an effort has been made in the submitted paper to use the ultra-hydrophobic ZIF-8 particles infused with DES as fillers in MMMs. The application for testing the flux and selectivity of the ZIF-8 infused with DES and PDMS mixed matrix membranes for pervaporation process was ethanol recovery from aqueous/organic combination.

2.1. Materials

For the particles, composite and membrane synthesis the chemicals were purchased from commercial suppliers. 2-methylimidazole (99%, SIGMA-ALDRICH), Zinc Nitrate Hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99+ %, Sigma-Aldrich), Methanol (MeOH, 99.7%, Sigma-Aldrich), Hexane (95+ %, Sigma-Aldrich), Acetone (99.5%, Bdh), DL Menthol (95+ %, Aldrich), Lauric Acid (99% , Sigma), RTV615A (Techsil), and RTV615B (Techsil).

2.2. ZIF-8 nanoparticles Synthesis

Nanoparticles of ZIF-8 were synthesized according to the literature [62]. In the synthesis of nanoparticles 2.70g of 2-methylimidazole is dissolved in 83.3ml of methanol. Similarly Zinc Nitrate Hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) is dissolved in 83.3ml of methanol. Both solutions were mixed together and resulting mixture is stirred for 24 hours. Then the mixture was left for another 24 hours at room temperature which can be seen in figure 2.1. The particles were centrifuged at 6000 rpm and washed 3 times with methanol. These particles were dried up to 24 hours to get fine white powder. Figure 2.2 shows the synthesized ZIF-8 fine white powder [63].



Figure 2. 1 Synthesis of Zif-8 Nanoparticles Solution



Figure 2. 2 Zif-8 Nanoparticles (White powder)

2.3. Synthesis of Composite (ZIF-8@DES)

The composite is synthesized by Ship in Bottle Technique. The composite is comprised of ZIF-8 nanoparticle infused with deep eutectic solvent which has precursors of DL Menthol and Lauric Acid respectively. ZIF-8 nanoparticles were suspended in Acetone solution and stirred for 1 hour. Then precursors of Deep Eutectic Solvent, DL Menthol and Lauric Acid were added into the Acetone solution simultaneously as shown in figure 2.3. The resulting solution is stirred for 24 hours. After stirring, solution is poured in petri dish and left it for 24 hours to let acetone evaporate at room temperature. After the evaporation off-white colored powder is collected and put it in oven at 80 °C for further drying for 24 hours. The resulting solid was grounded to fine powder which shows yellow tone in color and can be seen in figure 2.4. Results from characterization confirms the synthesis of ZIF infused with DES composite [64].

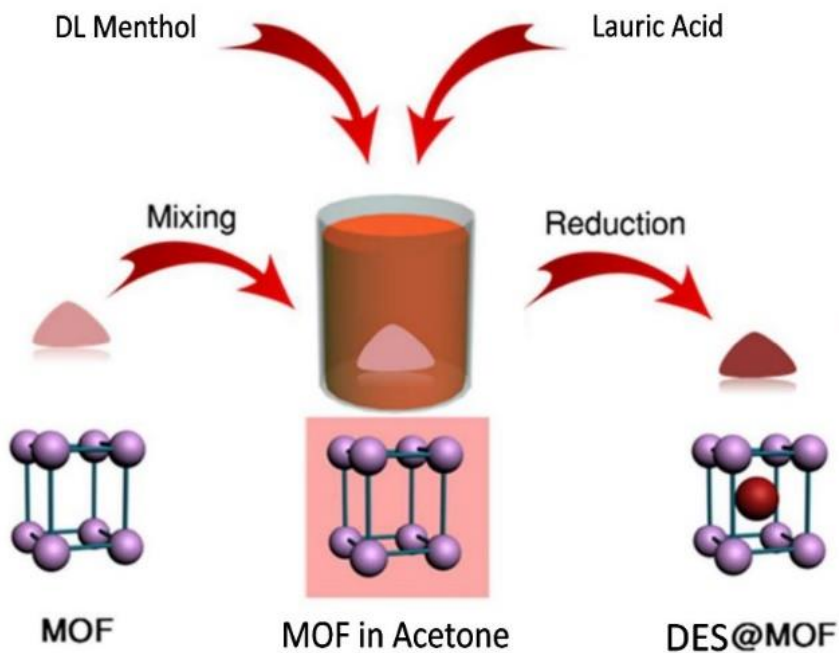


Figure 2. 3 Mechanism of Composite synthesis

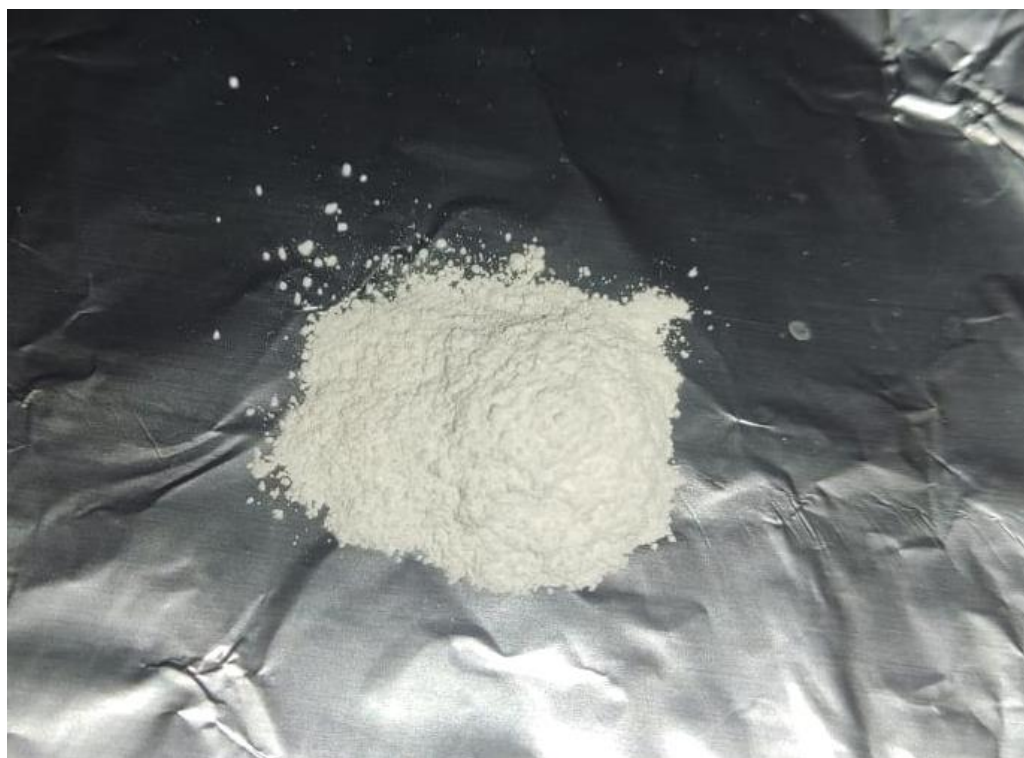


Figure 2. 4 Composite (Zif-8 Nanoparticles + DES) (Yellowish Powder)

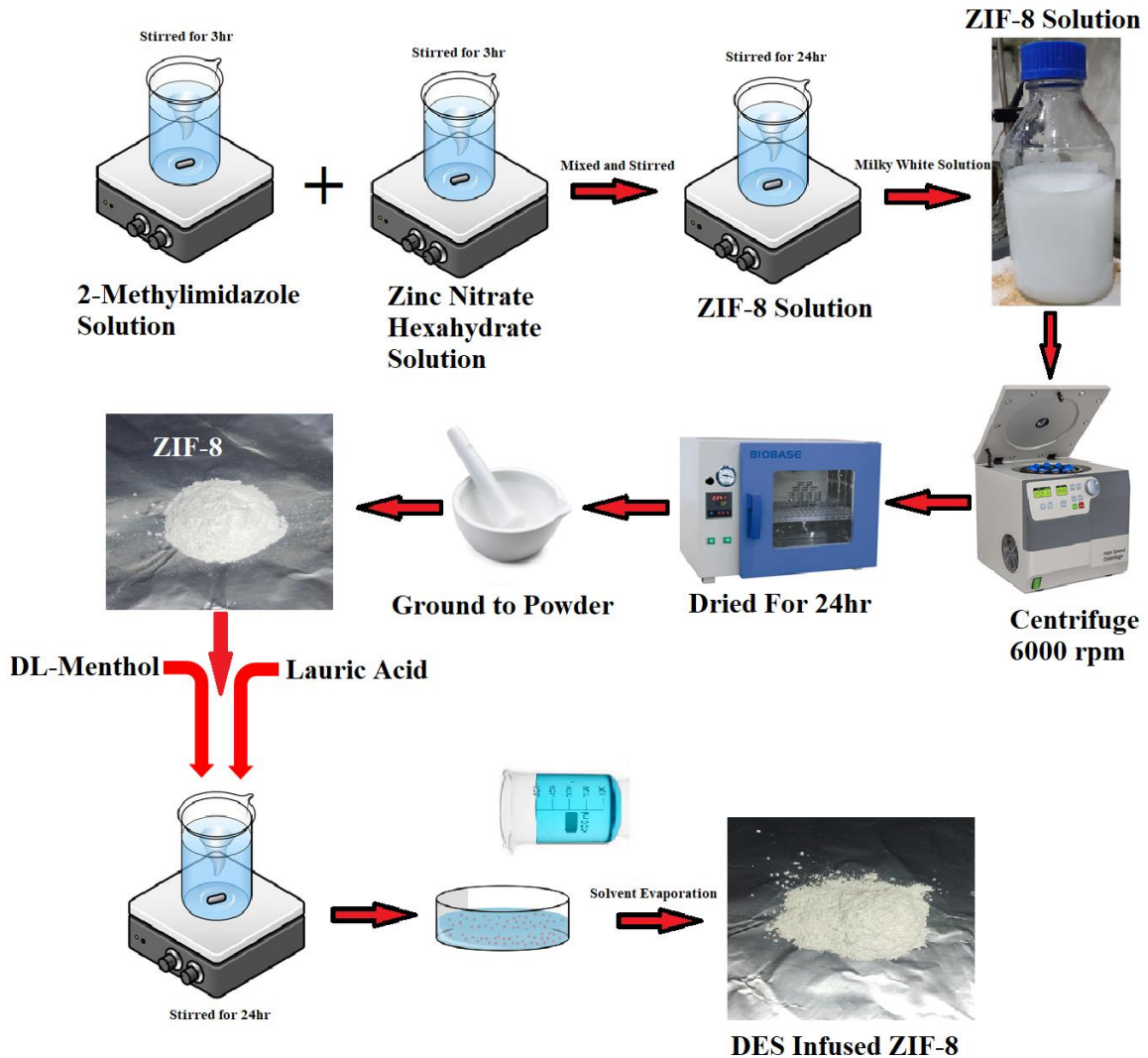


Figure 2. 5 Process flow of DES infused ZIF-8 synthesis

2.4. MMMs Synthesis

The PDMS membranes were prepared from RTV615. The component RTV615A is a vinyl terminated polymer base, and RTV615B is the cross-linker. MMMs were fabricated by in situ interfacial synthesis. Typically, the synthesis started by calculating proper amount of RTV615A (TECHSIL), and RTV615B (TECHSIL) and dissolved in 14.4 ml of Hexane with the ratio of 10:1 and placed in a media bottle with magnetic stirrer and heated at 70°C until the solution becomes viscus. Stirring takes place for 3 hours and then DES infused ZIF-8 composite is added and stirred for 24 hours at 70°C. The resulting solution was cast in Teflon dish and left it at room temperature until solvent evaporates. Figure 2.6 shows the synthesis of MMM. Resulting MMMs were cured at 80 °C for 24 hours. MMMs with ZIF-8 infused DES loading with the loading of 2.5, 5, 7.5, and 10 wt% were fabricated which can be seen in figure 2.7.

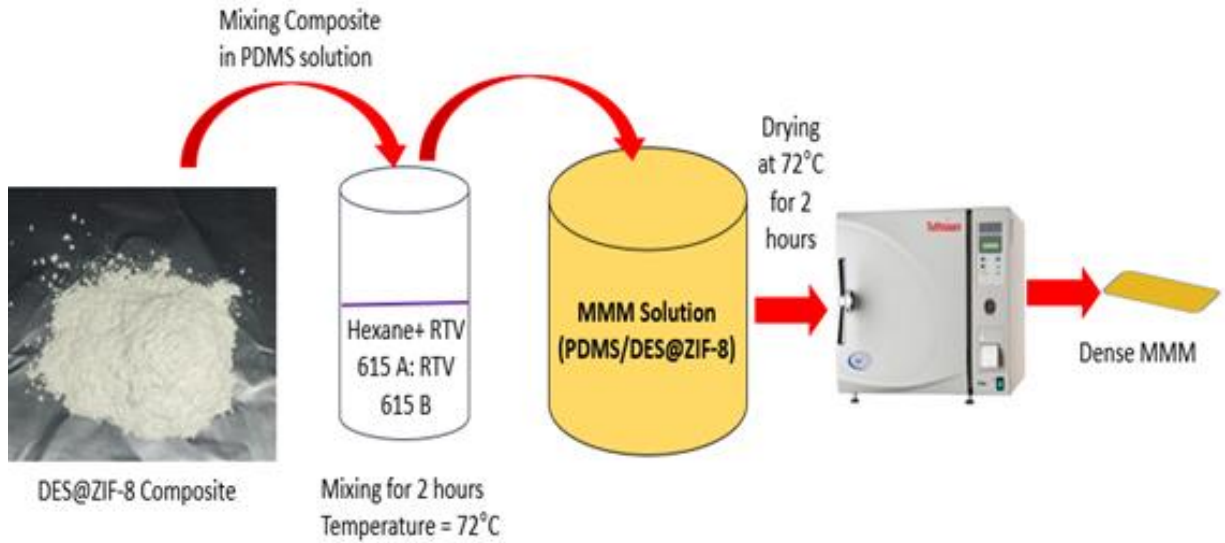


Figure 2. 6 Synthesis of MMM with Composite loading

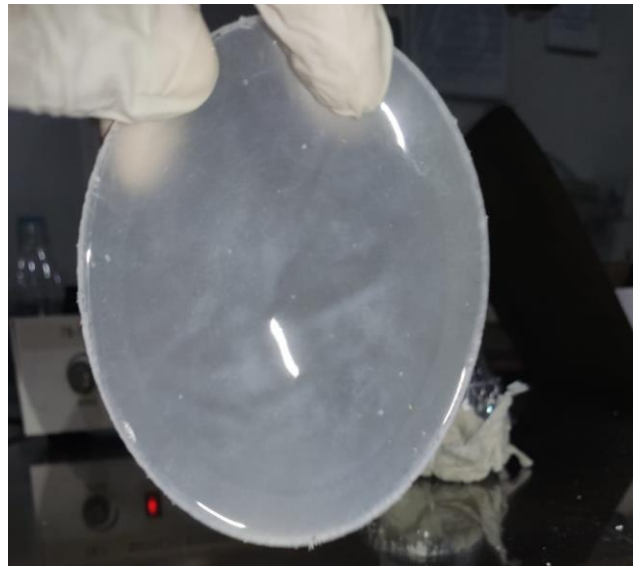


Figure 2. 7 MMM with 2.5% Composite loading

2.5. Experiment

Using a custom-made pervaporation apparatus, the efficiency of separation of the synthesized membranes was evaluated. The membrane was continuously in touch with the chosen feed solution, which included 94/6 weight percent water and ethanol respectively. The membranes were put to the test at the chosen range of 35 to 65C.

Two sections make up the whole system; the first is referred to as the feed section, and the second as the permeate section. It was put a membrane module between the feed and permeate portions. The CF042D membrane module uses a cross flow pattern to function. The membrane's actual surface area was 0.0019 m². Before turning on the whole apparatus, the membranes were kept in touch with the feed solution till they achieved steady state. The feed was then pumped at atmospheric pressure while maintaining a constant volumetric flow rate of 1L/min. A peristaltic pump was used to pump the feed to the membrane module, and the retentate was subsequently recycled back into the feed tank.

To test the variability of selectivity and flow of membranes at various temperature values, feed solution was heated by a heating mental. During the experiment, high vacuum conditions were produced, and a 75 torr vacuum was generated using a vacuum pump. The vapors (permeate) were collected using steel cold traps using ice as a cooling medium, and the flux and separation factor were then determined using equations (iii) and (iv). After every 4 hours, all the samples were taken. For easier understanding, refer to the schematic diagram of this experiment in figure 2.8.

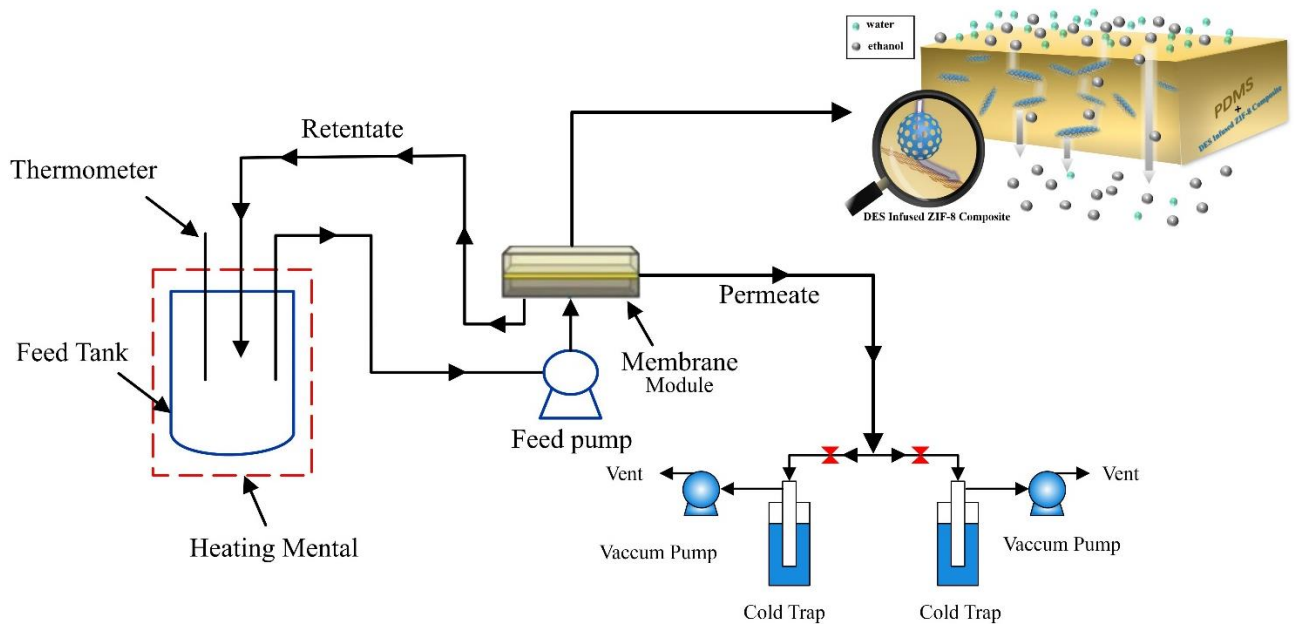


Figure 2. 8 Process flow of Pervaporation System

Chapter 3

Results and Discussions

3. Results and Discussions

3.1.Characterization of prepared ZIF-8 particles

3.1.1. FTIR

Fourier transform infrared spectroscopy, or FTIR for short, is a technique for identifying the functional groups contained in a material. Using this method, an infrared spectrum of a solid, liquid, or gas may be produced. By evaluating the sample based on its capacity to absorb light at various wavelengths, FTIR generates the spectrum. Every functional group absorbs light differently, which accounts for why they exhibit the spectrum at various intensities. This makes comparing the collected data with the data provided in the literature quite straightforward. The FTIR spectrum of ZIF-8 nano-particles is obtained in this study. FTIR was used to pinpoint the functional groups that were present in the spectra. Using a Thermo-Nicolet 6700 P FTIR Spectrometer, the ZIF-8 nano-particle's spectral data were collected [54].

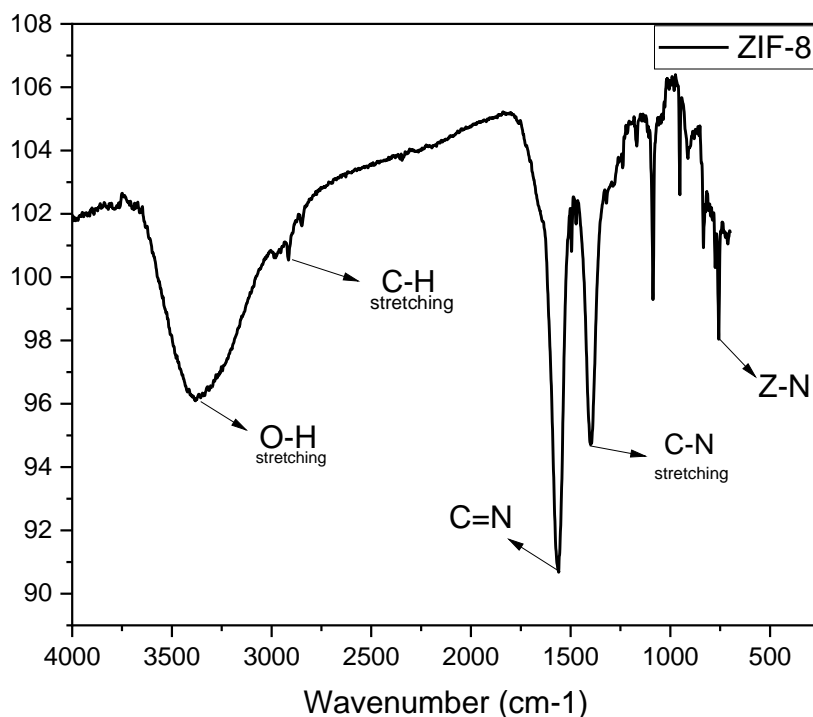


Figure 3. 1 FTIR of ZIF-8

The O-H stretching vibration of water from KBr deliquescence may be responsible for the band at 3455 cm^{-1} . The aromatic and aliphatic C-H asymmetric stretching vibrations, respectively, were linked to the peaks at 3135 and 2929 cm^{-1} , respectively. The stretching vibration of C=N is represented by the peaks at 1585 cm^{-1} . The bending vibration of the imidazole ring is also represented by the twin peaks at 1420 cm^{-1} . The vibration peak of Zn-N is the last peak, located at 721 cm^{-1} .

3.1.2. XRD

The presented sample's crystallinity may be verified using the X-ray diffraction method, or XRD. XRD is used to evaluate how well the synthesized sample performed. It's a crucial approach since the effectiveness of the produced particles is greatly influenced by the findings of XRD. The crystalline structure of a sample affects its prominent features, such as its electrical band structure banded with catalytic surface properties. ZIF-8 nanoparticle peak measurements made with X'Pert PAN Analytical were very comparable to those made in the published literature. XRD is used to determine the crystal phases and lattice properties.

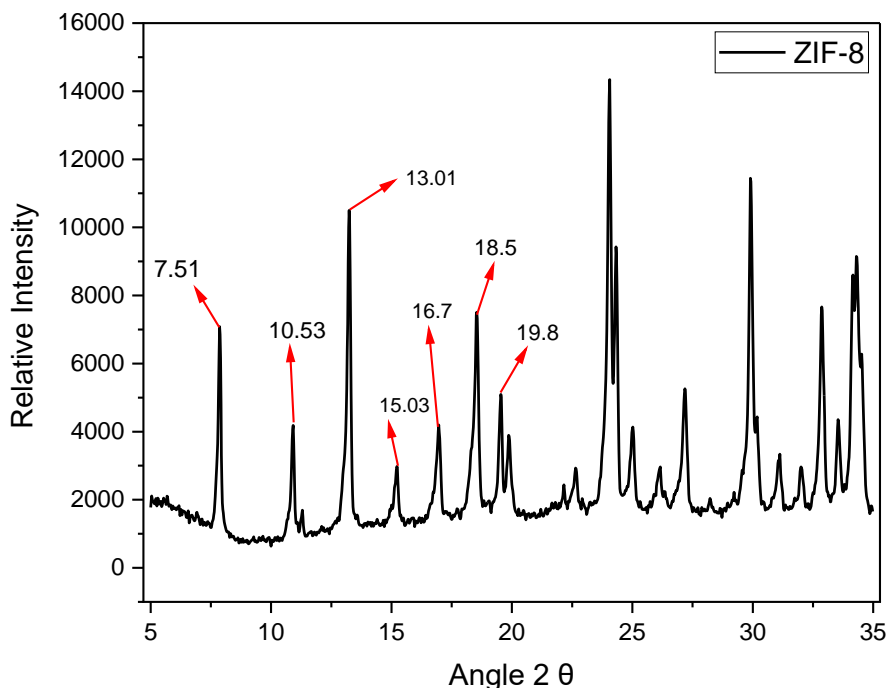


Figure 3. 2 XRD of ZIF-8

The XRD analysis on the prepared ZIF-8 presented in the presence of strong peaks at $2\theta = 7.51, 10.53, 13.01, 15.03, 16.70$ and 19.80° correspond to planes (110), (200), (211),

(220), (310), and (222), respectively, which indicates high crystallinity of the prepared ZIF-8 [65].

3.2. FTIR of DES

A number of intermolecular interactions, based on the chemicals used, result in a eutectic mixture. In deep eutectic solvents, the creation of hydrogen bonds between both the two compounds one of which serves as a donor of hydrogen bond and the other as an acceptor is what leads to the eutectic mixture [66].

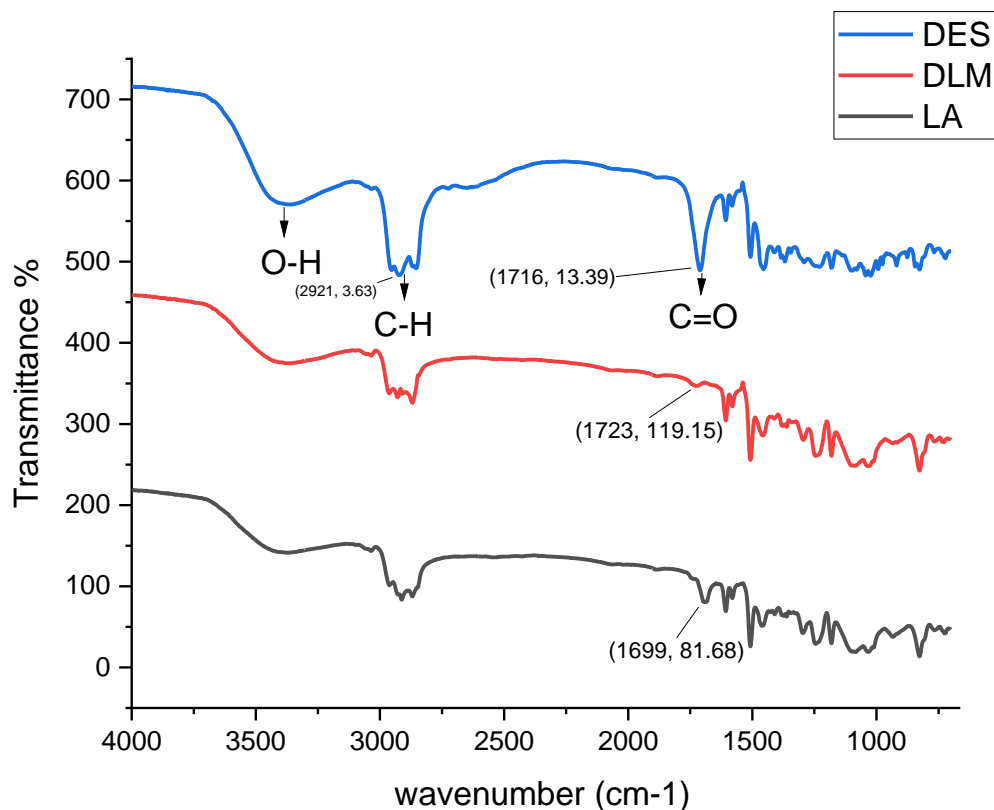


Figure 3. 3 FTIR of DES and its precursors

The carboxylic acid group in the structure of the hydrogen bond donor utilized in the eutectic mixture has a typical band at around 1716 cm^{-1} in the spectra, which may be for a ketone or carbonyl group. On the other hand, just one characteristic band belonging to the hydroxyl group, at around 3300 cm^{-1} , can be detected in the spectra of FTIR of the acceptor of hydrogen bond. The establishment of hydrogen bonds between the precursors which are DL menthol as hydrogen bond acceptor and lauric acid as donors led to the creation of a novel molecule, which was further supported by FTIR studies. The hydrogen bond

intermolecular interaction between the lauric acid and DL-menthol is most visible in the carboxyl group area of the FTIR spectra of the eutectic mixtures. For the eutectic combination of DL-menthol and Lauric acid, the HBD carbonyl band was originally located at low values of wavenumber of 1699 cm^{-1} , but it broadens and changes to the maximum values of 1723 cm^{-1} in the eutectic mixture. This strongly suggests the development of a new hydrogen bond, demonstrating the synthesis of a new molecule. The physical states of the compounds, such as the eutectic combination of DL-menthol and lauric acid, might further support this finding. Initially, both of these compounds are solids, but following DES synthesis, a liquid is produced [67].

3.3. FTIR of prepared DES infused ZIF-8 (Composite)

Fourier transform infrared spectroscopy, or FTIR for short, is a technique for identifying the functional groups contained in a material. Using this method, an infrared spectrum of a solid, liquid, or gas may be produced. By evaluating the sample based on its capacity to absorb light at various wavelengths, FTIR generates the spectrum. Every functional group absorbs light differently, which accounts for why they exhibit the spectrum at various intensities. This makes comparing the collected data with the data provided in the literature quite straightforward. The FTIR spectrum of ZIF-8 infused with DES is obtained in this study. The peaks of both components are presents which shows the successful synthesis of required composite which is based on ZIF infused with DES [68].

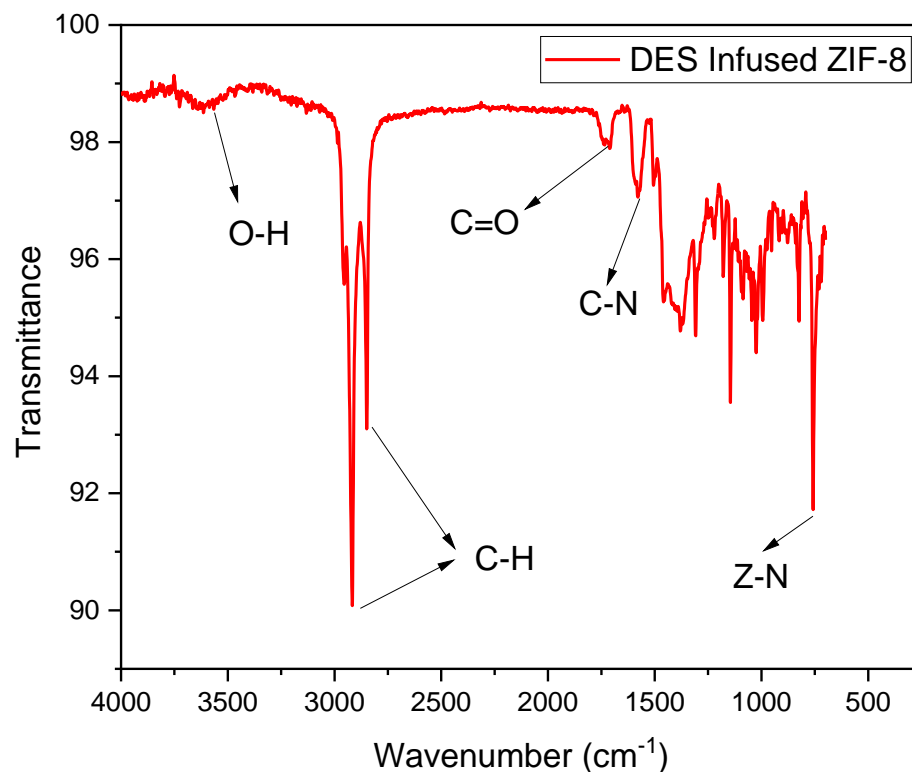


Figure 3. 4 FTIR of DES infused ZIF-8

3.4. FTIR of MMM

When the findings are evaluated with known literature peaks, it is evident that the spectra support the existence of linkages in mixed matrix membranes. The membrane with a 10-weight percent filler loading exhibits an FTIR spectrum with many peaks located at various locations. The C=O bond is seen in the shift at 2150 cm⁻¹. The existence of a C=N bond in the MMM is confirmed by the peak seen between 1400 and 1500 cm⁻¹. Similar to this, the signal at 2800-3000 cm⁻¹ indicates that the membrane has an Ar C-H bond. These peaks confirm the successful synthesis of MMM comprising of ZIF-8 infused DES as a filler [69].

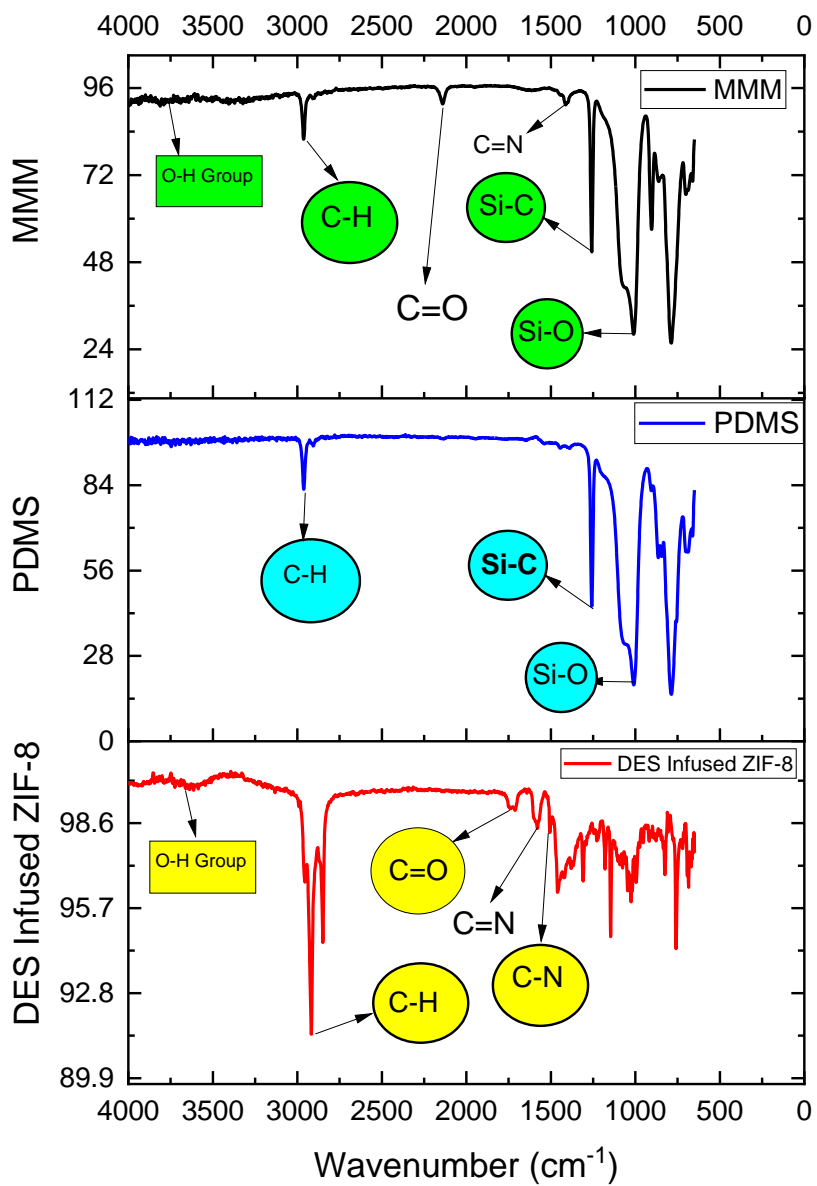


Figure 3. 5 FTIR of MMM

3.5. FTIR of All MMM`

It is evident that the spectra support the existence of linkages in mixed matrix membranes. The membrane with a 2.5, 5, 7.5, and 10-weight percent filler loading exhibits the FTIR spectrums with many peaks located at various locations. The C=O bond is seen in the shift at 2150 cm^{-1} . The existence of a C=N bond in the MMM is confirmed by the peak seen between 1400 and 1500 cm^{-1} . Similar to this, the signal at 2800 - 3000 cm^{-1} indicates that

the membrane has an Ar C-H bond. These peaks confirm the successful synthesis of MMM comprising of ZIF-8 infused DES as a filler. While increasing the filler loading the peak at 2150 cm^{-1} become more prominent which shows the increase in concentration of ZIF-8 infused DES. All of the synthesized membrane showed a similar FTIR as compared to ZIF-8 nanoparticles and ZIF-8 infused DES. This FTIR spectra confirms the presence of bonds presence in synthesized mixed matrix membranes [70].

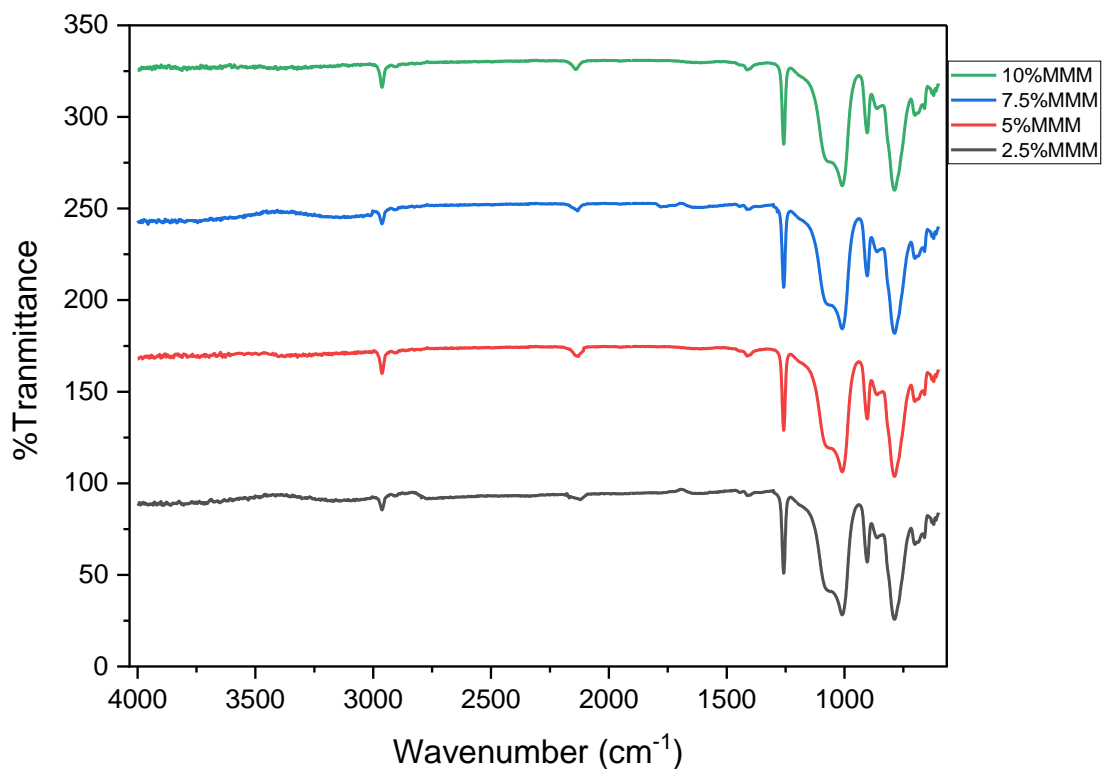


Figure 3. 6 FTIR of MMM with loading %

3.6. Swelling Study of MMM

Solution-diffusion is the guiding concept used in pervaporation. There are three steps to it. Sorption occurs first, followed by diffusion and then desorption. The factors that create the foundation for separation are selective sorption and diffusion. The degree of swelling was utilized to determine the impact of the filler loadings on the PDMS. As the filler loadings were added, the general characteristics of pure PDMS changed. The purest PDMS membrane offers the maximum level of ethanol swelling. For ethanol, the Hildebrand Solubility Parameter is 26.5MPa . As a consequence, pure PDMS membrane gained a high

affinity. The filler loadings ranged from 0 to 10 weight percent. The amount of swelling was measured, and it was determined that pure PDMS exhibited the largest amount of swelling (0.96 mL/g), which reduced to 0.233 mL/g when the filler loading was raised to 10 weight percent. The level of edema was decreased overall. It's because the PDMS matrix's free volume dropped when the composite was absorbed into it, which led to a modest swelling degree. The fillers improved the swelling degree by filling the gaps in the PDMS matrix. Additionally, when filler loading grew, the chain's overall flexibility began to decline at high temperatures [71].

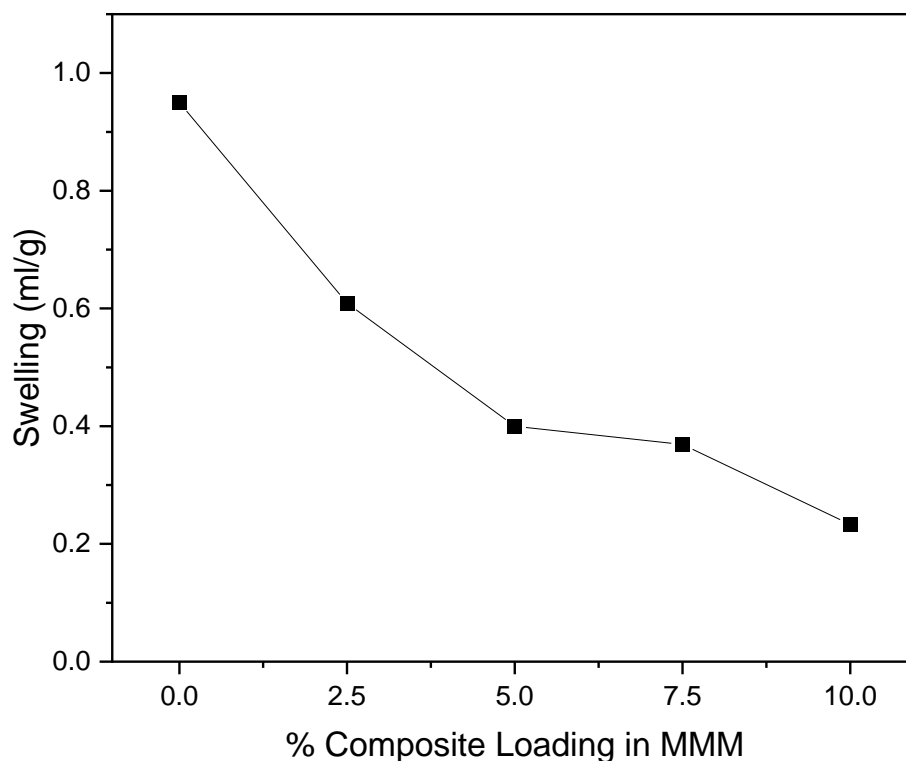


Figure 3. 7 Swelling of membrane with different filler loadings of composite

3.7. Effect of Composite Loading on Mixed Matrix Membranes (MMMs)

The impact of ZIF-8 infused DES composite loading on the functionality of membranes can be seen in fig below. The overall flow dramatically increased when the fillers' loading in the polymer matrix was increased. The polymer matrix gains porosity when fillers are added, which increases the overall flow across the membrane [72].

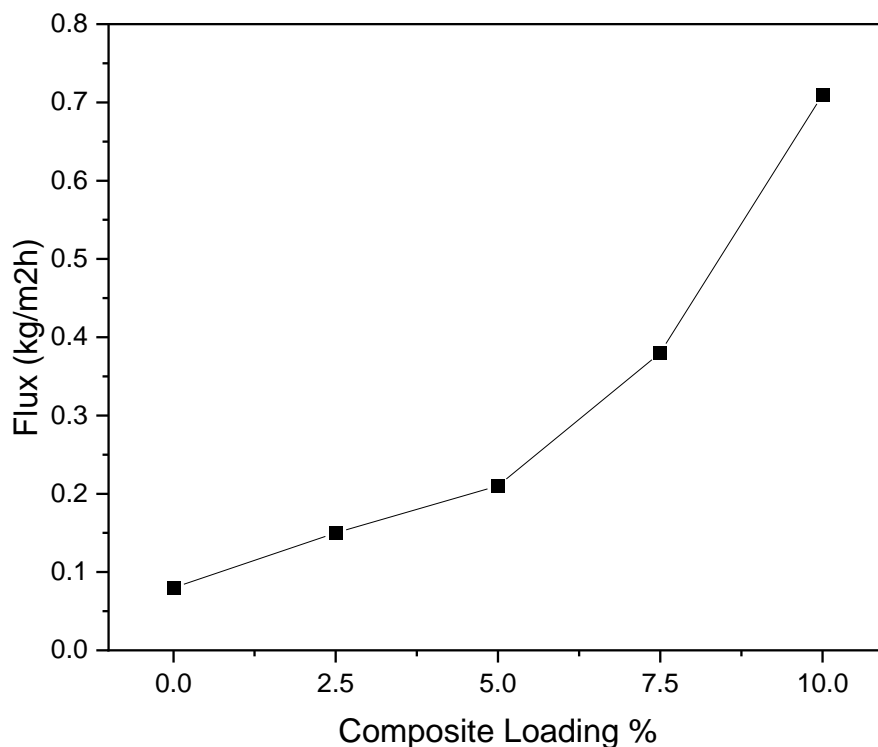


Figure 3. 8 Flux vs MMM with different loadings of composite

3.8. Effect of feed temperature on ZIF-8 Infused Mixed Matrix Membranes (MMMs)

Research was conducted on feed temperature affecting overall flow. From 35°C to 65°C, the impact of temperature was researched. The results demonstrated that when the temperature rose, the overall permeation flux which included both water and ethanol increased as well. Similar behavior was seen at all filler loadings. Water had a higher permeation flux than ethanol because water has a smaller kinetic diameter (0.27 nm) than ethanol (0.43 nm), which allows water to more readily diffuse through the filler's 0.34 nm aperture with an increase in temperature. By raising the temperature, which causes the mobility of polymer chains to increase, the degree of membrane swelling rises. The thermal movement of polymer chains is closely connected to the free volume, according to the free volume hypothesis. Due to the rise in frequency and amplitude of chains, the free volume and activity of penetrating molecules increased as the temperature rose. As a consequence, the overall flow increased [73].

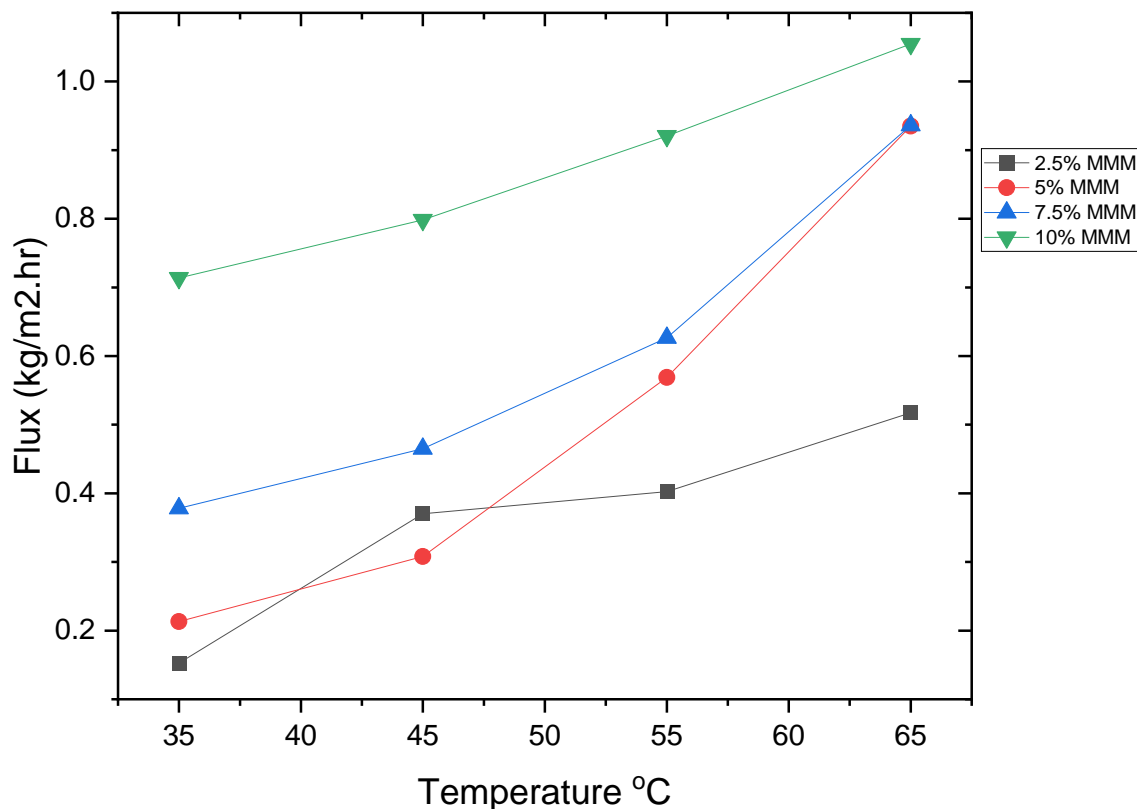


Figure 3. 9 Flux vs MMM with different Temperature °C

3.9. Activation Energy

Activation energies are used to further examine the impact of temperature. Using the Arrhenius Equation, the activation energy of the ethanol stream can be determined. Following is the Arrhenius Equation,

$$J = j_0 \exp\left(\frac{-E_j}{RT}\right) \quad (7)$$

In the equation above J is the flux j_0 is the pre-exponential factor, E_j is the activation energy. R is the deal gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and T is the temperature of liquid in Kelvin [74].

In this respect, several filler loadings were included. The PDMS membrane was taken in its purest form with 0% filler loading. It displayed a 41.5 kJ/mol activation energy. To create mixed matrix membranes, the filler loadings were varied to 2.5, 5, 7.5, and 10 wt%, respectively.

Table 3. 1 Activation Energies of MMM with different %loading of composite

Membrane	Composite Loading (wt%)	Activation Energy E_j (kJ/mol)
Pure PDMS	0	41.5
2.5% MMM	2.5	33.7
5% MMM	5	29.3
7.5% MMM	7.5	24.9
10% MMM	10	21.2

The performance of pervaporation was greatly improved by adding the DES-infused ZIF-8 filler to the PDMS matrix which can be seen in table 3.1. An essential component influencing the performance of the membrane is the physical crosslinking of the filler with the polymer matrix. The performance of the mixed matrix membranes for separation is enhanced by the filler's strong contact with the polymer. In this investigation, the activation energies for mixed matrix membranes with different filler loadings were estimated. The activation energies of various mixed matrix membranes with pure PDMS membrane are shown in Table 3.1 above. 10 wt.% loaded membrane shows 51% lower activation energy as compared to pristine membrane (pure PDMS). The findings of the activation energies demonstrate that they have dropped as the filler loadings have increased. This led to the conclusion that adding additional filler led to the creation of more diffusive voids. This thus offered the permeate additional paths to pass, which results in increasing the fluxes. The figure 3.10 shows the graph of activation energy of each MMM which shows decreasing trend with the increase in filler loading.

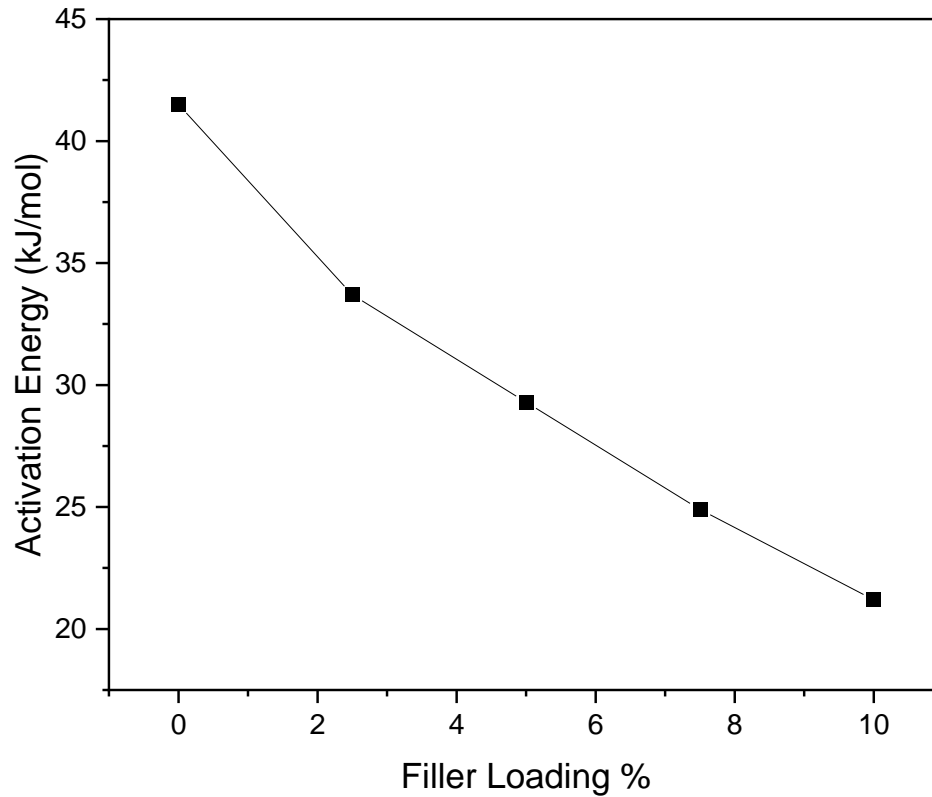


Figure 3. 10 Activation Energy of MMMs

3.10. Research Limitations

Long term stability of MMM is the key point of pervaporation process. If the membranes are stable at required conditions, they provide better results of flux and separation. This research is limited due to the nonavailability of long-term data. Separation results provides the performance of membranes that how much they are efficient in separating species from one another. Due to nonavailability of molar ratios of separated species i.e ethanol and water from feed mix, the results are limited to the membrane performance in accordance with total flux and flux at all temperature for all membranes.

Chapter 4

Conclusion and Future Work

4. Conclusion

For the separation of water/ethanol mixture, hydrophobic PDMS/ZIF-8 mixed matrix membranes (MMM) were synthesized. As-made DES-infused ZIF-8 particles were added to the polymer matrix at various loadings, ranging from 2.5 weight percent to 10 weight percent. The research yields the following conclusions:

- High surface area and pore volume ZIF-8 particles that were produced led to greater separation when added to a polymer matrix.
- The flow has been improved by adding DES-infused ZIF-8 particles to the PDMS membrane.
- As high temperature promotes the diffusion-permeating molecules, the overall flux was seen to increase as the temperature rose from 35°C to 65°C.
- Comparing the clean PDMS to the PDMS/DES infused ZIF-8 mixture, we can see that the swelling rate was reduced.

In conclusion, the pervaporation membrane's performance has improved due to the addition of fillers (DES-infused ZIF-8). The best outcomes were obtained at 65 °C with a composite loading of 10 wt%.

4.1. Practical Implication of Study

It could be possible to separate water and ethanol combinations using PDMS-based DES infused ZIF-8 membranes in industrial-scale pervaporation equipment. Pervaporation will be used in particular to achieve the water/ethanol azeotrope solution. Bioethanol may be produced economically using hybrid systems that combine distillation and pervaporation. A well-constructed model of membrane transport should also be relevant to pervaporation. Insofar as it enables the assessment of the design variables using experimental data acquired under various processing conditions and has significant practical implications, using this model and its parameters, a similar mixed matrix membrane pervaporation process can be designed, scaled up, and made to work better.

4.2. Future Work

For further evaluation of performance, the GCMS characterization data is required. SEM technique will provide information of surface structure of ZIF-8 and DES infused ZIF-8 composite. TGA data is very crucial for the performance of MMMs. The separation

performance of mixed matrix membranes may be improved in a number of ways. To improve the separation, various polymers might be crosslinked. It has been advised to employ several hydrophobic ZIFS to verify the findings. By modifying or crosslinking fillers and polymers, the interaction of the polymer/filler mix may be enhanced. ZIF-67/PDMS membranes should be used to verify the organic/organic separations.

Chapter 5
References

5. References

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